H W M Hyde

# A

# SYSTEMATIC SURVEY

# OF THE

# ORGANIC COLOURING MATTERS

MACMILLAN AND CO., Limited
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# OF THE
# ORGANIC COLOURING MATTERS

BY

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CONSULTING ORGANIC CHEMIST AND CHEMICAL ENGINEER

FOUNDED ON THE GERMAN OF
DRS. G. SCHULTZ AND P. JULIUS

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# PREFACE TO THE 1908 EDITION

In presenting the present edition of this work without further revision, it is felt that some explanation is due to the scientific and technical public. The rapid exhaustion of the edition of 1904, brought about by a sudden demand, has rendered an immediate republication necessary. A full revision of the text could not be undertaken at the present time, and a partial revision would have been unsatisfactory. It has therefore been thought best to reprint the work as it appears in the edition of 1904 without alteration, reserving for a later date the considerable task of submitting the book to the complete revision and extension which the continuous and rapid development of the tinctorial industry will then render necessary.

ARTHUR G. GREEN.

Leeds, 1908.

# PREFACE AND INTRODUCTION TO THE SECOND EDITION

The period which has elapsed since the publication of the First Edition of this work in 1894 has been marked by a great development in the coal-tar colour industry. Many of the older dyestuffs and older methods of manufacture have become obsolete, whilst newer processes have been introduced, new intermediate products discovered, and an enormous array of new colouring-matters have been brought into commerce. A complete revision of the text and a very considerable enlargement of the original work was therefore necessary, but whilst the book has been brought up to date, care has been taken to fully preserve its original scope. It is consequently hoped that it will continue to serve not only as a text-book for the student of chemical technology, but also as a ready work of reference for Colour Manufacturers, Dyers, Calico Printers, Dye Merchants, Paper Stainers, Patent Agents, and many others concerned with the tinctorial arts.

The first section of the book, which deals with the raw and intermediate products of the artificial colour manufacture, and for which the author is solely responsible, has been extended to include the materials and methods of recent introduction. In preparing this section endeavour has been made to render the text as concise as possible, whilst at the same time embodying as full essential details and recent practical knowledge as space would allow. Accordingly only methods of preparation are described which, so far as is known, are in actual manufacturing use, and mention is seldom made of merely laboratory methods (for which the chemical text-books may be consulted) nor of processes which, though formerly employed, have now been abandoned. In like manner only those references have been given which are of most importance technically.

The tables of the organic colouring-matters contained in the second section are chiefly based upon the *Tabellarische Uebersicht der Kunstlichen Organischen Farbstoffen* of Drs. Schultz and Julius, and in the preparation of this section the fourth edition of this work has, with Dr. Schultz's sanction, been largely consulted, though the nomenclature, classification, and formulæ have in many cases been departed from. Of the 454 colouring-matters described in the First Edition, 59, which have now become obsolete, have been removed, whilst 300 new colouring-matters have been added.

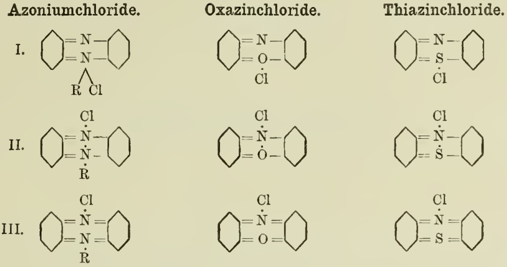
In addition to the 695 artificial colouring-matters which are thus comprised in the tables, it has been thought desirable for the sake of completeness to include an account of those organic colouring-matters of natural origin which are still employed in the arts, more especially as, in view of the artificial production of indigo and the syntheses in the flavone and xanthone groups, a sharp line of demarcation between artificial and natural organic dyestuffs can now no longer be maintained. A total of 711 colouring-matters is thus reached, many of which are types of groups rather than single products, and are represented on the market by several brands of varying but analogous constitution. No claim, however, can be laid to absolute completeness in this list, as there is an increasing number of dyestuffs, mostly of very recent introduction, concerning the preparation and constitution of which but little is known, whilst the manufacturers evince a very natural disinclination to furnish particulars regarding them.

With the advance of our knowledge of the structure of colouring-matters it has become possible to adopt a more systematic classification than was previously the case. The following subdivision has been employed:—

GROUP I. Nitro colouring-matters.
" II. Monoazo colouring-matters.
" III. Disazo colouring-matters.
" IV. Trisazo colouring-matters.
" V. Tetrakisazo colouring-matters.
" VI. Nitroso or quinoneoxime colouring-matters.
" VII. Stilbene colouring-matters.
" VIII. Oxyketone, oxylactone, and oxyquinone colours (excluding anthracene derivatives).
" IX. Diphenylmethane colouring-matters.
" X. Triphenylmethane colouring-matters.
" XI. Xanthene colouring-matters (pyronines, phthaleins, and rhodamines).
" XII. Acridine colouring-matters.
" XIII. Anthracene colouring-matters.
" XIV. Indophenols, indamines, and allies.
" XV. Azines and azonium colouring-matters (eurodines, safranines, indulines, and rosindulines).
" XVI. Oxazine colouring-matters.
" XVII. Thiazine colouring-matters.
" XVIII. Thiazol or thiobenzenyl colouring-matters.
" XIX. Quinoline colouring-matters.
" XX. Sulphide colouring-matters.
" XXI. Indigo and derivatives.
" XXII. Natural colouring-matters (derivatives of pyrone, xanthone, isoquinoline, and others of unknown constitution).

In each group the members are arranged as far as possible in accordance with their structure, commencing with the simplest.

Since the publication of the First Edition, the quinonoid theory of colour originally propounded by Armstrong and Nietzki has found general acceptance. Constitutional formulæ upon a quinone type have therefore been substituted in many groups for those previously employed. Certain groups, *e.g.* the azines, oxazines, thiazines, and acridines, which were formerly considered to have a paraquinonoid constitution, are now generally regarded as orthoquinonoid. This view of their structure was first advanced by the Author in 1892 (see *Proc. Chem. Soc.* 1892, 195; 1896, 226; *Rev. gen. des mat. col.* 1897, 269), and has since been confirmed by the work of Kehrmann and others. The orthoquinonoid structure for these groups of dyestuffs may be represented by three alternative series of formulæ, viz.:—



Formulæ of type I. were advanced by Kehrmann in 1889 (*Ber.* **32**, 2601), those of type II. and III. by the Author. From the point of view of our present knowledge it is scarcely possible to decide between these three possibilities, but for the sake of uniformity with current literature type I. has been adopted, together with the corresponding nomenclature proposed by Kehrmann. In conclusion, I desire to express my thanks to the following Firms for much valuable information, part of which, unfortunately, I have been unable through space limitations to make use of:—

The Berlin Aniline Co.
The British Alizarine Co.
L. Cassella & Co., Frankfort.
The Clayton Aniline Co., Manchester.
Dahl & Co., Barmen.
J. R. Geigy & Co., Basle.
The Mühlheim Colour Works (formerly A. Leonhardt & Co.).
Levinstein Limited, Manchester.
K. Oehler & Co., Offenbach.
Read Holliday & Sons, Limited, Huddersfield.
Société Anonyme des Matières Colorantes de St. Denis.
Société Chimique des Usines du Rhône.
Chemical Works (formerly Weiler-ter-Meer).

My thanks are also due to Messrs. Hermann Heyfelder for allowing me to see the proofsheets of the fourth edition of Drs. Schultz and Julius' tables whilst the latter were still in the press.

London, 1903.

# ABBREVIATIONS

## Names of Firms

| | |
|---|---|
| [*A.*] | Actiengesellschaft für Anilinfabrikation, Berlin (The Berlin Aniline Co.). |
| [*B.*] | Badische Anilin- und Sodafabrik, Ludwigshafen a./Rhein (The Badische Co.). |
| [*B. K.*] | Leipziger Anilinfabrik Beyer & Kegel, Lindenau-Leipzig. |
| [*Bl.*] | The Basle Chemical Co. |
| [*Br. A.*] | The British Alizarine Co., Silvertown, London, E. |
| [*B. S. S.*] | Brooke, Simpson & Spiller, Limited, Atlas Works, Hackney Wick, London, E. |
| [*By.*] | Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld (The Bayer Co.). |
| [*C.*] | Leopold Cassella & Co., Frankfurt a./M. |
| [*C. J.*] | Carl Jäger, Barmen. |
| [*Cl. Co.*] | The Clayton Aniline Co., Limited, Clayton, near Manchester. |
| [*C. R.*] | Claus & Rée, Clayton, near Manchester. |
| [*Cz.*] | Casthelaz & Bruère, Rouen. |
| [*D.*] | Dahl & Co., Barmen. |
| [*D. H.*] | L. Durand, Huguenin & Co., Basle and Hüningen. |
| [*F.*] | A. Fischesser & Co., Lutterbach, Alsace. |
| [*G.*] | J. R. Geigy, Basle. |
| [*H.*] | Read Holliday & Sons, Limited, Huddersfield. |
| [*I.*] | Société pour l'Industrie Chimique (formerly Bindschedler & Busch), Basle. |
| [*Ib.*] | J. B. Ibels, Brussels. |
| [*K.*] | Kalle & Co., Biebrich a./Rhein. |
| [*K. S.*] | Sandoz & Co., Basle (formerly Kern & Sandoz). |
| [*L.*] | Farbwerk Mühlheim (formerly A. Leonhardt & Co., Mühlheim, near Frankfurt). |
| [*Lev.*] | Levinstein Limited, Crumpsall Vale, Manchester. |
| [*L. P.*] | Lucien Picard & Co., St. Fons. See also [*A.*]. |
| [*M.*] | Farbwerke vorm. Meister, Lucius & Brüning, Höchst a./Main (Meister, Lucius & Brüning, Limited). |
| [*M. Ly.*] | Manufacture Lyonnaise des Matières Colorantes, Lyon. See also [*C.*]. |
| [*Mo.*] | Société Chimique des Usines du Rhone (late Gilliard, Monnet & Cartier), 8 Quai de Retz, Lyon. |
| [*N.*] | C. Neuhaus, Elberfeld. |
| [*N. I.*] | Farbwerk Griesheim, Nötzel, Istel & Co., Griesheim a./Main. |

| | |
|---|---|
| [*O.*] | K. Oehler, Offenbach a./Main. |
| [*P.*] | Société Anonyme des Matières Colorantes de St. Denis, Paris. |
| [*P. L.*] | Pick, Lange & Co., Amsterdam. |
| [*R.*] | Chemische Fabriken, Worms (formerly Dr. Paul Remy, Mannheim). |
| [*Sch.*] | The Schöllkopf Aniline and Chemical Co., Buffalo, U.S.A. |
| [*T. M.*] | Chemische Fabriken vorm. Weiler-Ter Meer, Uerdingen a./Rhein, near Crefeld (late J. W. Weiler & Co.; Tilmanns, ter Meer & Co.; and Kuchler & Buff). |
| [*V.*] | Vidal Dyes Syndicate Limited, London. |
| [*W.*] | Williams Bros., Hounslow, Middlesex. |

## REFERENCES

| | |
|---|---|
| **Am. Pat.** | United States Patent. |
| **Ann.** | Liebig's Annalen der Chemie. |
| **Ann. Chim. Phys.** | Annales de Chimie et de Physique. |
| **Ber.** | Berichte der deutschen chemischen Gesellschaft. |
| **Bl.** | Bulletin de la Société Chimique. |
| **Bull. de Mulhouse** | Bulletin de la Société Industrielle de Mulhouse. |
| **Ch. C.** | Chemisches Centralblatt. |
| **Chem. Ind.** | Die chemische Industrie. |
| **Chem. News** | Chemical News. |
| **Chem. Ztg.** | Chemiker Zeitung. |
| **C. R.** | Comptes rendus hebdomadaires des séances de l'académie des sciences. |
| **Ding. pol. J.** | Dingler's polytechnisches Journal. |
| **Eng. Pat.** | English Patent. |
| **Farbztg.** | Lehne's Färber Zeitung. |
| **Fr. Pat.** | French Patent. |
| **Friedländer.** | Fortschritte der Theerfarbenfabrikation. P. Friedländer. I. to V. |
| **Ger. Pat.** | German Patent. |
| **Jahresber.** | Jahresbericht über die Fortschritte der Chemie. |
| **J. Chem. Soc.** | Journal of the Chemical Society. |
| **J. Soc. Chem. Ind.** | Journal of the Society of Chemical Industry. |
| **J. Soc. Dyers.** | Journal of the Society of Dyers and Colorists. |
| **Jour. pr. Chem.** | Journal für praktische Chemie. |
| **Mon. f. Chem.** | Monatshefte für Chemie. |
| **Mon. Scien.** | Le Moniteur Scientifique. |
| **Proc. Chem. Soc.** | Proceedings of the Chemical Society. |
| **Wagner's Jahresber.** | Jahresbericht über die Leistungen der chemischen Technologie. |
| **Zeits. f. angw. Chem.** | Zeitschrift für angewandte Chemie. |
| **Z. Farb. Chem.** | Zeitschrift für Farben- und Textil-Chemie. |

## SECTION I

# RAW PRODUCTS

### COAL TAR

Coal Tar, the primary raw material of the colour industry, is obtained in the manufacture of coal gas, accumulating in the hydraulic mains, condensers, and scrubbers of the gas works. Of recent years, however, a large and constantly increasing quantity has been obtained from the coke-ovens used for making hard coke for metallurgical purposes. In the latter case the gas evolved, instead of being used at once for heating the ovens, is first passed through a system of condensers and scrubbers, by means of which the tar and ammonia are removed and collected. A further variety of coal tar, less rich in benzenoid compounds, is obtained by condensation from blast-furnace gases. Another source of aromatic compounds, though at present scarcely employed, is furnished by the residues of the petroleum industry, which, when submitted to a high temperature, yield a tar rich in aromatic hydrocarbons, but containing very little phenols. The total quantity of coal tar produced in England per annum is given by Beilby as 862,000 tons, consisting of 650,000 tons of gas tar, 62,000 tons of coke-oven tar, and 150,000 tons of blast-furnace tar. In Germany the chief source of benzene and its homologues is now the coke-oven tar, the production of which has greatly increased in recent years. According to Brunck, the world's present production of benzene hydrocarbons is 25,000 to 30,000 tons, the greater part of which is furnished by coke-oven tar. With the inevitable replacement of solid by gaseous fuel for heating and power purposes, there is every prospect in the future of a large increase in the sources of aromatic compounds. Moreover, only about 10% of the total benzene formed in the distillation of coal is contained in the tar; the remaining 90% which occurs in the gas is at present lost for the purposes of the colour industry, but might be readily extracted if the gas were only employed with incandescent burners or as a heating agent.

Coal tar, a black viscid liquid of sp. gr. 1·1 to 1·2, is a very complex mixture, containing, together with finely divided carbon, a great number of bodies (hydrocarbons, phenols, bases, etc.), of which the following are the most important.

I. *Hydrocarbons*

| | Formula. | Melting Point. | Boiling Point. |
|---|---|---|---|
| **Hydrocarbons of the acetylene series** | $C_nH_{2n-2}$ | Fluid | 20° |
| **Hydrocarbons of the ethylene series** | $C_nH_{2n}$ | ... | ... |
| **Hydrocarbons of the methane series** | $C_nH_{2n+2}$ | ... | ... |
| **Cyclopentadiene** | $C_5H_6$ | Fluid | 41° |
| **Benzene** | $C_6H_6$ | 6° | 81° |
| **Toluene** | $C_7H_8$ | Fluid | 111° |
| ***o*-Xylene** | $C_8H_{10}$ | " | 142° |
| ***m*-Xylene** | $C_8H_{10}$ | " | 139° |
| ***p*-Xylene** | $C_8H_{10}$ | 15° | 138° |

### I. *Hydrocarbons* (continued)

| | Formula. | Melting Point. | Boiling Point. |
|---|---|---|---|
| **Styrene** | $C_8H_8$ | Fluid | 146° |
| **Indene** | $C_9H_8$ | ,, | 176°—182° |
| **Mesitylene** | $C_9H_{12}$ | ,, | 163° |
| **Pseudocumene** | $C_9H_{12}$ | ,, | 169° |
| **Naphthalene** | $C_{10}H_8$ | 80° | 218° |
| **Methylnaphthalene** | $C_{11}H_{10}$ | α Fluid ; β 33° | 242° |
| **Dimethylnaphthalene** | $C_{12}H_{12}$ | Fluid | 264° |
| **Diphenyl** | $C_{12}H_{10}$ | 71° | 254° |
| **Acenaphthene** | $C_{12}H_{10}$ | 95° | 277° |
| **Fluorene** | $C_{13}H_{10}$ | 113° | 295° |
| **Phenanthrene** | $C_{14}H_{10}$ | 100° | 340° |
| **Fluoranthrene** | $C_{15}H_{10}$ | 109° | Above 360° |
| **Anthracene** | $C_{14}H_{10}$ | 213° | ,, |
| **Methylanthracene** | $C_{15}H_{12}$ | 210° | ,, |
| **Pyrene** | $C_{16}H_{10}$ | 149° | ,, |
| **Chrysene** | $C_{18}H_{12}$ | 250° | ,, |
| **Picene or Parachrysene** | $C_{22}H_{14}$ | 239° | 520° |

### II. *Other Neutral Bodies*

| | Formula. | Melting Point. | Boiling Point. |
|---|---|---|---|
| **Carbon disulphide** | $CS_2$ | Fluid | 47° |
| **Ethyl alcohol** | $C_2H_5 \cdot OH$ | ,, | 78° |
| **Acetonitrile** | $C_2H_3N$ | ,, | 82° |
| **Thiophene** | $C_4H_4S$ | ,, | 84° |
| **Thiotolene** | $C_5H_6S$ | ,, | 113° |
| **Thioxene** | $C_6H_8S$ | ,, | 137° |
| **Benzonitrile** | $C_7H_5N$ | ,, | 191° |
| **Phenythiocarbimide** | $C_7H_5NS$ | ,, | 220° |
| **Carbazole** | $C_{12}H_9N$ | 238° | 355° |
| **Phenylnaphthylcarbazole** | $C_{16}H_{11}N$ | 330° | Above 440° |
| **Coumarone** | $C_8H_6O$ | Fluid | 170° |
| **Diphenylene oxide** | $C_{12}H_8O$ | 81° | 288° |

### III. *Bases*

| | Formula. | Melting Point. | Boiling Point. |
|---|---|---|---|
| **Pyrrol** | $C_4H_5N$ | Fluid | 126° |
| **Pyridine** | $C_5H_5N$ | ,, | 116° |
| **Picoline** (α, β, and γ) | $C_6H_7N$ | ,, | 134°—144° |
| **Lutidine** (4 isomers) | $C_7H_9N$ | ,, | 142°—157° |
| **Collidine** | $C_8H_{11}N$ | ,, | 179° |
| **Aniline** | $C_6H_7N$ | ,, | 182° |
| **Quinoline** | $C_9H_7N$ | ,, | 239° |
| **Quinaldine** | $C_{10}H_9N$ | ,, | 243° |
| **Acridine** | $C_{13}H_9N$ | 107° | Above 360° |

### IV. *Phenols*

| | Formula. | Melting Point. | Boiling Point. |
|---|---|---|---|
| **Phenol** | $C_6H_6O$ | 42° | 188° |
| *o*-**Cresol** | $C_7H_8O$ | 31° | 188° |
| *p*-**Cresol** | $C_7H_8O$ | 36° | 198° |
| *m*-**Cresol** | $C_7H_8O$ | 4° | 201° |
| α-**Naphthol** | $C_{10}H_8O$ | 94° | 280° |
| β-**Naphthol** | $C_{10}H_8O$ | 123° | 286° |
| **Xylenols and other high boiling phenols** | ... | ... | ... |

The proportions of these constituents vary greatly with the kind of coal employed and with the temperature to which the gas retorts are heated. Usually the aromatic hydrocarbons greatly predominate, and only small quantities of the hydrocarbons of the methane and ethylene series are present; but by employment of cannel coal or a low temperature in the retorts, the quantity of the fatty hydrocarbons is much increased, and the value of the tar consequently diminished. The tar from Newcastle coal is usually richer in naphthalene and anthracene and poorer in benzene and phenol than that from Wigan coal. The proportion of thiophene and its homologues depends upon the quantity of sulphur in the coal, Scotch and German tar usually containing much more than English. Of the many constituents of coal tar the only ones which are at present employed in the colour industry are benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, pyridine, phenol, and cresol. Gas tar contains about 1% of benzene and toluene, 8 to 10% of naphthalene, and ⅓% of anthracene. Coke-oven tar contains about 1% of benzene, 4 to 5% of naphthalene, and ⅔% of anthracene; its specific gravity is less than that of gas tar. In order to isolate the valuable products, the tar is first submitted to a preliminary distillation from large wrought-iron stills, capable of holding from 10 to 40 tons, by which it is separated into the following portions:—

| | | |
|---|---|---|
| A. **First runnings** | up to 110° | 3 to 8% of the tar |
| B. **Light oils** | 110° to 210° | |
| C. **Carbolic oils** | 210° to 240° | 8 to 10% ,, ,, |
| D. **Heavy or creosote oils** | 240° to 270° | 8 to 10% ,, ,, |
| E. **Anthracene oils** | 270° to 400° | 16 to 20% ,, ,, |

whilst a residue of pitch remains behind in the still (about 50%). From the "first runnings" and "light oils" the benzene, toluene, and xylene are obtained; from the "carbolic oils" the phenol, cresol, and naphthalene; and from the "anthracene oils" anthracene. In the further working up of the "first runnings" and "light oils" these products are first submitted to a fractional distillation, by means of which a low boiling portion (containing acetonitrile, fatty hydrocarbons, and carbon disulphide) and a high boiling portion (returned to the "carbolic" or "creosote oils") are removed. The middle portion is then subjected to a series of washings with caustic soda, strong sulphuric acid, and finally water; the caustic soda removes phenols and the sulphuric acid removes bases (pyridine, quinoline, etc.), phenols, hydrocarbons of the acetylene and ethylene series, naphthalene, and thiophene compounds. The product is again submitted to fractional distillation, and from the "crude benzol" thus obtained pure benzene, toluene, and xylene are separated by rectification in a "Savalle" still. The latter is a still of peculiar construction, in which the vapour is caused to pass through a long column divided into a series of chambers by perforated plates, in which the higher boiling portions are condensed and returned to the still. The hydrocarbons distilling after the xylene (*e.g.* cumene, etc.) have at present found no use in the colour industry, but are usually employed as "solvent naphtha." The "crude benzol" from Scotch and German tars contains considerable quantities (often 1%) of thiophene and its homologues, which must be removed, previously to the final rectification in the Savalle still, by agitation with 5% of conc. sulphuric acid; this is not always necessary with benzol from English tar.

Naphthalene is obtained from the "carbolic" and "heavy oils," from which large quantities crystallise out on standing, and is separated by centrifugating and pressing. Further quantities are also obtained from the "carbolic oils" after the phenols have been removed by treatment with caustic soda, and from the so-called "dead oils" obtained in the rectification of the "first runnings" and "light oils." The crude naphthalene is washed with hot aqueous caustic soda to remove phenols, and then agitated with 5 to 10% of conc. sulphuric acid to remove bases, residual phenols, and other impurities, after which it is washed with very dilute alkali and finally distilled or sublimed. The naphthalene thus obtained is nearly chemically pure, and is used for the manufacture of naphthols, naphthylamines, phthalic acid, etc.

For the extraction of phenol and cresol the "carbolic oils" are agitated with a dilute solution of caustic soda, sufficient to dissolve the phenols. The aqueous alkaline liquor is drawn off from the oil, and steam is blown through it to remove small quantities of naphthalene and other hydrocarbons which it still contains. The phenols are then precipitated by neutralisation with sulphuric, hydrochloric, or carbonic acid, separated from the liquor and submitted to a series of fractional distillations. The phenol is thus obtained chemically pure as a white solid, melting at 42°, the cresol as a fluid mixture of the three isomers. The higher phenols are not isolated, but are used for the "creosoting" of timber. Phenol and cresol are largely employed as antiseptic and medicinal agents, and in the colour industry. The last portion of the coal-tar distillation, the so-called "anthracene oil," is a thick, buttery, greenish mass, which contains anthracene, phenanthrene, methylanthracene, diphenyl, acenaphthene, naphthalene, methylnaphthalene, pyrene, chrysene, retene, fluorene, carbazole, acridine, and other bodies. For the extraction of the anthracene, the oil is cooled, and the anthracene which separates out mixed with other hydrocarbons is freed from the oily mother liquor by pressing or centrifugating. The greenish gray mass thus obtained, which only contains from 10 to 12% of pure anthracene, is then submitted to a pressure of 200-300 atmospheres in hydraulic presses heated by steam; by this means a large part of the phenanthrene and other impurities is removed, and the anthracene value of the product is raised to from 25 to 40%. For further purification the crude anthracene is washed with "solvent naphtha" or with light petroleum spirit, in which the anthracene is more sparingly soluble than the accompanying phenanthrene, etc. The anthracene thus purified usually has a value of from 50 to 60%, and is sufficiently pure for the preparation of anthraquinone. Recently pyridine bases or a mixture of these with "solvent naphtha" have been very successfully employed for the washing of anthracene, as by this means the carbazol is more completely removed, and the value of the product in anthracene is raised to about 80% (*cf.* Ger. Pat. 42053). To obtain chemically pure anthracene the commercial product is ground up with a mixture of caustic potash and lime, and submitted to distillation, after which it is again washed with solvents and finally sublimed.

Considering the great number of hydrocarbons, etc., of the aromatic series which coal tar contains, it is remarkable how few are at present employed as raw products in the colour industry. This is largely due to the difficulty of isolating the others (*e.g.* methylnaphthalene) in a state of purity; it is probable, however, that the progress of research will enable many of these bodies to be utilised which are at present valueless.

## **Benzene** (*Benzol*)

$C_6H_6$ *i.e.*

Strongly refractive, colourless, mobile liquid. B.p. 80·5° corr.; m.p. 6°; sp. gr. $\frac{14}{4}$ = ·8839. Solidifies at 0° to a mass of white crystals. Dissolves completely in fuming nitric acid with formation of mono- and dinitrobenzene (distinction from "benzine" or "benzoline," *i.e.* light petroleum).

*Valuation of Commercial "pure benzol."*—The whole should boil within half a degree of the correct boiling point. It should give no crystalline precipitate on standing with a few drops of phenylhydrazine (carbon disulphide). On shaking with conc. sulphuric acid the latter should only be slightly darkened (thiophene or hydrocarbons of the ethylene series). On shaking with sulphuric acid and a fragment of isatin no blue colour should be produced (thiophene). On treatment with nitrosulphuric acid and distillation with steam no unnitrated hydrocarbon should be obtained (hydrocarbons of the paraffin series). It should solidify on cooling below 0°.

"*Crude benzol*" is a mixture in varying proportions of benzene, toluene, etc., and is valued according to the range of its boiling point, being known as "30s." "50s." or "90s.

benzol," according as 30%, 50% or 90% of the whole distils before the thermometer reaches 100° C.

### Toluene (*Toluol*)

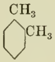
$C_7H_8$ *i.e.* $C_6H_5(CH_3)$ or 

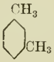
Colourless mobile liquid, which does not solidify at $-20°$. B.p. 111°; sp. gr. $\frac{13}{4} = \cdot 8708$. The commercial "pure toluol" should only be slightly darkened on shaking with conc. sulphuric acid, and should boil between 111° and 112°.

### Xylene (*Xylol*)

$C_8H_{10}$ *i.e.* $C_6H_4(CH_3)_2$

Coal tar xylene is a mixture of the three isomers:—

**Orthoxylene** . .  Liquid. B.p. 142°; m.p. $-28$.

**Metaxylene** . .  Liquid. B.p. 139°; sp. gr. at 19° = ·8668.

**Paraxylene** . .  Solid. B.p. 138°; m.p. 15°; sp. gr. at 19° = ·8621.

According to Levinstein different samples of commercial xylene contain from 2 to 15% of orthoxylene, from 70 to 87% metaxylene, and from 3 to 10% paraxylene, together with from 3 to 10% of hydrocarbons of the paraffin series. Metaxylene, which is technically the most important, can be separated from its isomers by treating the mixture with a limited quantity of sulphuric acid, and hydrolysis of the sulphonic acid formed.

*Valuation of Commercial Xylol.*—The greater part should distil between 135° and 140°. When shaken with sulphuric acid, the latter should only be coloured light brown. For the estimation of the three isomers and of paraffin hydrocarbons, see Levinstein, *J. Soc. Chem. Ind.* **1884**, 77; *Ber.* **17**, 444.

### Naphthalene

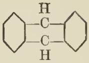
$C_{10}H_8$ *i.e.* 

Colourless crystalline solid. B.p. 218°; m.p. 80°; sp. gr. at 15° = 1·1517. Volatile with steam. Readily sublimes, even volatilising slowly at ordinary temperatures.

*Valuation.*—The commercial product is almost chemically pure. It should melt sharply at 80° and boil correctly within one degree. Allowed to evaporate in the air it should remain white to the last and leave no residue. No red colour should be produced on heating with conc. sulphuric acid. Dissolved in conc. sulphuric acid, diluted with water, filtered, and the filtrate made alkaline, no smell of pyridine bases should be apparent. No phenols should be extracted by boiling with caustic soda.

## Anthracene

$C_{14}H_{10}$ *i.e.*

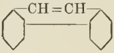


Colourless crystalline plates or tables, which when quite pure have a violet fluorescence. B.p. rather over 360°; m.p. 213°. Somewhat sparingly soluble in solvents (alcohol, benzene, etc.). Converted by oxidising agents into anthraquinone. With picric acid in benzene solution it forms the **picrate** $C_{14}H_{10} \cdot C_6H_2(NO_2)_3OH$, which separates in glistening red needles, melting at 170°.

*Valuation of Commercial Anthracene.*—The commercial product contains from 30 to 90% of pure anthracene, the remainder being phenanthrene, carbazol, chrysene, etc. Its value in pure anthracene is determined by weighing the quantity of anthraquinone which it produces on oxidation. 1 g. of the crude anthracene is boiled with 45 g. of glacial acetic acid, and a solution of 15 g. of chromic acid in 10 c.c. of glacial acetic acid diluted with 10 c.c. of water is slowly run in. After the mixture has been kept boiling for two hours longer it is left till the following day, then diluted with 400 c.c. of cold water and filtered after two hours' standing. The precipitate is washed, first with cold water, then with boiling alkaline water, and finally with boiling water alone, and is transferred to a small porcelain dish and dried at 100°. It is then heated at 100° with 10 g. of slightly fuming sulphuric acid for 10 minutes, left till next day in a damp place, and poured into 200 c.c. of cold water. The precipitated anthraquinone is filtered off, washed with alkaline water, and finally with hot water alone, then washed into a dish, dried, and weighed. The dish is then heated till the anthraquinone has volatilised and is again weighed; the last weight subtracted from the first gives the weight of the anthraquinone, which, multiplied by 85·57, gives the percentage of anthracene in the sample (Luck, *Ber.* **6**, 1347).

## Phenanthrene

$C_{14}H_{10}$ *i.e.*



Colourless crystalline plates. B.p. 340°; m.p. 99°. Easily soluble in alcohol, benzene, and other solvents. Converted by oxidising agents into phenanthraquinone. With picric acid in benzene or alcoholic solution it forms the sparingly soluble **picrate** $C_{14}H_{10} \cdot C_6H_2(NO_2)_3OH$, which separates in golden yellow needles, melting at 145°. It is converted by sulphuric acid into sulphonic acids, and by nitric acid into nitro compounds.

## Phenol (*Carbolic Acid*)

$C_6H_5 \cdot OH$ *i.e.*

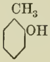
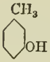
White crystalline solid, consisting of long colourless prisms. B.p. 188° corr.; m.p. 41°; sp. gr. at 40° = 1·05433. Soluble in 15 pts. of water at ordinary temperatures, the solubility increasing rapidly with the temperature, until at 84° it is miscible in all proportions. An aqueous solution of phenol gives a blue coloration with ammonia and bleaching-powder, a violet coloration with ferric chloride, a yellow coloration with hot nitric acid, and a yellowish precipitate of tribromophenol with bromine water. It is estimated by titration with standard bromine water.

*Valuation.*—The commercial product should melt at about 30°, and boil at about 183° to 186°. It should dissolve completely in aqueous caustic soda.

## Cresol (*Cresylic Acid*)

$C_7H_8O$ *i.e.* $C_6H_4(CH_3)\cdot OH$

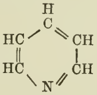
Coal tar cresol is a mixture of the three isomers :—

| | | |
|---|---|---|
| **Orthocresol** . |  | Crystalline solid. B.p. 188°; m.p. 31°. |
| **Metacresol** . |  | Liquid. B.p. 201°; m.p. 4°. |
| **Paracresol** . |  | Prismatic crystals. B.p. 198°; m.p. 36°. |

According to Raschig, the separation of the isomers is effected in the following manner :—The crude cresol is first submitted to a series of fractional distillations through a Savalle column, by means of which the lower-boiling orthocresol is separated from the meta and para. The mixture of the two latter is then sulphonated, and the mixed sulphonic acids are subjected to hydrolysis with superheated steam at 120° to 130°, when metacresol passes over, whilst the paracresol sulphonic acid remains undecomposed until the temperature is raised to 140° to 160°. The mixed sulphonic acids can also be separated by the sparing solubility of the paracresol sulphonic acid, and then separately hydrolysed.

## Pyridine

$C_5H_5N$ *i.e.*

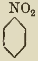


Obtained by fractional distillation of the crude bases extracted from the "light oils" by washing with dilute sulphuric acid. Colourless mobile liquid of penetrating odour. B.p. 116°; sp. gr. at 0° = 0·98. Miscible with water. Forms salts with acids.

# INTERMEDIATE PRODUCTS

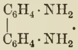
## NITRO COMPOUNDS

### Nitrobenzene (*Nitrobenzol*)

$C_6H_5 \cdot NO_2$ *i.e.* 

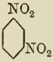
*Preparation.*—A cold mixture of nitric acid (120 pts. of sp. gr. 1·4) and conc. sulphuric acid (180 pts.) is slowly run into benzene (100 pts.), keeping the temperature below 25° until the greater part of the acid has run in, finally allowing it to rise to 50°. The operation is performed in cast-iron jacketed cylinders provided with mechanical agitators and cooled by a stream of water flowing round them ("nitrators"). After standing the nitrobenzene is separated and washed with water. When required quite pure (*e.g.* for perfumery) it is distilled with steam. The yield is 150 to 152 pts. from 100 pts. of benzene thus almost theoretical.

*Properties.*—Light yellow liquid of bitter-almond-like smell. B.p. 207°; m.p. 4°; sp. gr. at $15° = 1·208$.

*Reactions.*—By acid reduction (*e.g.* with iron and hydrochloric acid) it yields aniline $C_6H_5 \cdot NH_2$. By alkaline reduction (*e.g.* zinc dust and caustic soda) it is converted successively into:—**Azoxybenzene** $C_6H_5 \cdot N_2O \cdot C_6H_5$; light yellow needles; m.p. 36°; **Azobenzene** $C_6H_5 \cdot N_2 \cdot C_6H_5$; orange plates; m.p. 68°; b.p. 293°; and **Hydrazobenzene** $C_6H_5 \cdot N_2H_2 \cdot C_6H_5$; colourless tables; m.p. 131°. The latter when warmed with acids undergoes a molecular change, and is converted into **Benzidine**  $\begin{matrix} C_6H_4 \cdot NH_2 \\ | \\ C_6H_4 \cdot NH_2 \end{matrix}$.

*Valuation.*—The commercial product should have the correct specific gravity. It should not contain binitrobenzene (phenylene diamine on reduction), nor unaltered benzene or other hydrocarbons (distillation with steam).

### *m*-Dinitrobenzene (*Binitrobenzol*)

$C_6H_4(NO_2)_2[1:3]$ *i.e.* 

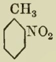
*Preparation.*—By running a mixture of nitric acid (70 pts. of sp. gr. 1·428) and sulphuric acid (100 pts.) into nitrobenzene (100 pts.) contained in a "nitrator," the temperature being slowly raised from 70° at the commencement to 100° at the end. The product is separated from the spent acid and washed with hot water. The yield is nearly theoretical. The commercial product consists chiefly of the meta compound (about 88%), but also contains small quantities of the ortho and para isomers. Pure *m*-dinitrobenzene can be readily obtained by crystallising the commercial product from alcohol.

*Properties.*—Long yellowish white needles. B.p. 297° corr.; m.p. 89°·8. Slightly soluble in boiling water, easily in alcohol. Very slightly volatile with steam.

*Valuation.*—The commercial product should be light in colour and not contain oil. Warm dilute caustic soda should not extract any nitrophenols. On reduction with tin and hydrochloric acid it should give 85-90% of the theoretical quantity of *m*-phenylene diamine, shown by titration with a standard solution of diazobenzene chloride.

### *o*- and *p*-**Nitrotoluene** (*Nitrotoluol*)

$C_6H_4(CH_3)NO_2$

**Orthonitrotoluene** . 

Liquid. B.p. 223°; sp. gr. at 24° = 1·163.

**Paranitrotoluene** . 

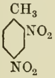
Colourless prisms. B.p. 238°; m.p. 54°.

*Preparation.*—The two isomers are formed simultaneously by nitrating toluene. A mixture of nitric acid (105 pts. of sp. gr. 1·4) and sulphuric acid (175 pts.) is slowly run into toluene (100 pts.) contained in a "nitrator," keeping the temperature below 20°. The product is separated and washed with water. The yield is about 142 pts. from 100 pts. of toluene. It usually consists of about 35% para-, 63% ortho-, and 2% meta-nitrotoluene. It is either employed direct, or the para- and ortho-nitrotoluene are separated by fractional distillation in vacuo through a Savalle column. The distillation is stopped when 40% has distilled, and the distillate on redistillation gives nearly pure orthonitrotoluene. The residue on cooling deposits crystals of paranitrotoluene which are freed from oil by centrifugating.

*Reactions.*—*o*- and *p*-nitrotoluene are converted into *o*- and *p*-toluidine (*q.v.*) by acid reducing agents. By alkaline reduction (*e.g.* zinc dust and caustic soda) *o*-nitrotoluene gives successively **Azoxytoluene** $C_6H_4(CH_3)\cdot N_2O\cdot C_6H_4(CH_3)$, **Azotoluene** $C_6H_4(CH_3)\cdot N_2\cdot C_6H_4(CH_3)$, and **Hydrazotoluene** $C_6H_4(CH_3)\cdot N_2H_2\cdot C_6H_4(CH_3)$, the latter of which is converted into **Tolidine** $\begin{array}{l}C_6H_3(CH_3)\cdot NH_2\\ |\\ C_6H_3(CH_3)\cdot NH_2\end{array}$ when boiled with acids. By fuming, sulphuric *p*-nitrotoluene is readily converted into *p*-**Nitrotoluene-sulphonic acid** $C_6H_3(CH_3)(NO_2)(SO_3H)[1:4:2]$, which is separated as its sparingly soluble sodium salt on adding common salt to the aqueous solution.

*Valuation.*—Crude nitrotoluene should boil between 220° and 240°, and should have the sp. gr. 1·167 at 15°. The percentage of ortho and para isomers it contains is best estimated by the method of Reverdin and de la Harpe (*J. Soc. Chem. Ind.* **1888,** 593).

### *a*- or *m*-**Dinitrotoluene** (*Binitrotoluol*)

$C_6H_3(CH_3)(NO_2)_2[1:2:4]$ *i.e.* 

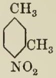
*Preparation.*—By further nitration of nitrotoluene with hot nitrosulphuric acid in the same way as given for dinitrobenzene. From the solid product about 7% of oil is separated by centrifugating, which contains the isomeric dinitrotoluene $C_6H_3(CH_3)(NO_2)_2[1:2:6]$, together with *m*-nitrotoluene, etc.

*Properties.*—Long yellowish needles. M.p. 71°.

*Valuation.*—In the same way as dinitrobenzene.

### *a*-**Nitro-*m*-xylene** (*Nitroxylol*)

$C_6H_3(CH_3)_2NO_2[1:3:4]$ *i.e.*



*Preparation.*—By nitration of *m*-xylene, or together with several other isomers by nitration of crude xylene. A mixture of 90 pts. of nitric acid (sp. gr. 1·4) and 150 pts. of sulphuric acid is run into 100 pts. of xylene, with rapid agitation, keeping the temperature below 17° until most of the acid has run in.

*Properties.*—Light yellow liquid. B.p. 245° corr.; sp. gr. at 17° = 1·126. The commercial product is usually a mixture of isomers containing nitro-*m*-xylene as chief constituent. It is employed without separation for the preparation of xylidine.

### *o*- and *p*-**Chloronitrobenzene**

$C_6H_4Cl(NO_2)[1:2]$ & $[1:4]$

*Preparation.*—A mixture of the two isomers is formed on nitration of chlorobenzene with nitrosulphuric acid. They are separated by alternate fractional distillation in vacuo and fractional crystallisation.

*Properties.*—The ortho isomer forms needles of b.p. 246° and m.p. 32½°. The para isomer forms rhombic plates of b.p. 239° and m.p. 83°. Heated with caustic soda they are converted into the corresponding nitrophenols.

### **Chlorodinitrobenzene**

$C_6H_3Cl(NO_2)[1:2:4]$

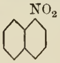
*Preparation.*—By further nitration of chlorobenzene or of *o*- or *p*-chloronitrobenzene.

*Properties.*—Large rhombic crystals. B.p. 315°; m.p. 50°.

*Reactions.*—Condenses with amido derivatives of benzene giving diphenylamine compounds.

### *a*-**Nitronaphthalene**

$C_{10}H_7 \cdot NO_2$ *i.e.*

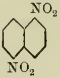


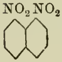
*Preparation.*—Finely ground naphthalene (250 pts.) is slowly sprinkled through a sieve into a mixture of nitric acid (200 pts. of sp. gr. 1·375), conc. sulphuric acid (200 pts.), and spent acid from previous nitrations (600 pts.). The operation is performed in a "nitrator" with rapid agitation, and the temperature is kept at 45° to 50°. When cold the waste acid is separated from the cake of nitronaphthalene, and the latter is washed with hot water. If required quite pure it is melted with $\frac{1}{10}$ of its weight of "solvent naphtha," filtered, and the cake of crystals which is formed on cooling is submitted to hydraulic pressure (Witt, *Chem. Ind.* **10**, 215).

*Properties.*—Long fine yellow needles. B.p. 304°; m.p. 61°; sp. gr. at 4° = 1 331. Readily soluble in alcohol, benzene, etc.

## (1 : 5)- and (1 : 8)-**Dinitronaphthalene**

$C_{10}H_6(NO_2)_2$

**(1 : 5)-Dinitronaphthalene** .  Needles. M.p. 217°. Sparingly soluble in pyridine.

**(1 : 8)-Dinitronaphthalene** .  Thick tables. M.p. 172°. Tolerably soluble in pyridine.

*Preparation.*—The two isomers are formed simultaneously in about the proportion of 1 to 2, by dissolving *a*-nitronaphthalene in 6 parts of sulphuric acid and adding in the cold the calculated quantity of nitric acid mixed with five times its weight of sulphuric acid. The mixture is then warmed to 80°-90° until a clear solution is obtained and allowed to cool. The (1 : 5)-dinitronaphthalene separates out almost completely in a pure state, whilst the (1 : 8)-isomer remains dissolved in the sulphuric acid, and is obtained on adding water (Friedländer, *Ber.* **32**, 3531).

*Reactions.*—By slightly fuming sulphuric acid at 40°-50° they are converted into nitronitrosonaphthols $C_{10}H_5(NO_2)(NO)(OH)[5:1:4]$ and $[8:1:4]$.

## Dinitrodibenzyldisulphonic Acid

$$\begin{array}{l} CH_2 \cdot C_6H_3(SO_3H)NO_2[1:2:4] \\ | \\ CH_2 \cdot C_6H_3(SO_3H)NO_2[1:2:4] \end{array}$$

*Preparation.*—By oxidation of sodium *p*-nitrotoluene sulphonate with sodium hypochlorite (1 mol.) at 40°-50° in presence of a large excess of caustic soda (Green and Wahl, Eng. Pat. $5351^{97}$; *Ber.* **30**, 3097; **31**, 1078; Ris and Simon, *Ber.* **30**, 2618).

*Properties.*—Colourless plates or tables. Tolerably soluble in water. The sodium salt is sparingly soluble. On further oxidation it gives the following compound:—

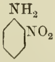
## Dinitrostilbenedisulphonic Acid

$$\begin{array}{l} CH \cdot C_6H_3(SO_3H)NO_2[1:2:4] \\ \| \\ CH \cdot C_6H_3(SO_3H)NO_2[1:2:4] \end{array}$$

*Preparation.*—By oxidation of sodium *p*-nitrotoluene-sulphonate with sodium hypochlorite (2 mols.) at 50°-70° in presence of a limited amount of caustic soda (Green and Wahl, Eng. Pat. $5351^{97}$; *Ber.* **30**, 3097; **31**, 1078; Levinstein, Eng. Pat. $18376^{97}$).

*Properties.*—Colourless or slightly yellow needles. Easily soluble in water. Its sodium salt forms rather sparingly soluble plates. Alkaline reducing agents produce a deep crimson coloration. By a cold solution of potassium permanganate it is oxidised quantitatively to *p*-nitrobenzaldehyde-*o*-sulphonic acid.

## *o*-**Nitraniline**

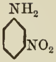
$C_6H_4(NO_2)(NH_2)$ *i.e.* 

*Preparation.*—Obtained as a by-product in the manufacture of paranitraniline (*q.v.*).

*Properties.*—Orange-yellow needles. M.p. $71\frac{1}{2}$°. Tolerably soluble in hot water, sparingly in cold. Its salts are basified on adding water.

### *m*-Nitraniline

$C_6H_4(NO_2)NH_2[1:3]$ *i.e.*



Preparation.—By partial reduction of *m*-dinitrobenzene, either with iron and hydrochloric acid, or with sodium sulphide and sulphur ($= Na_2S_4$) in a small quantity of water. It is also formed together with para- and ortho-nitraniline by nitration of aniline dissolved in a large excess of cold conc. sulphuric acid.

*Properties.*—Long yellow needles or rhombic crystals. B.p. 285°; m.p. 114°. Dissolves in 600 pts. of water at 18°. Is volatile with steam.

### *p*-Nitraniline

$C_6H_4(NO_2)(NH_2)[1:4]$ *i.e.*

*Preparation.*—By slowly adding a mixture of nitric acid (59 pts. of sp. gr. 1·478) and conc. sulphuric acid (100 pts.) to a cooled mixture of acetanilide (100 pts.) dissolved in conc. sulphuric acid (250 pts.). The product is poured into a large bulk of water, and the precipitated paranitracetanilide is filtered off, washed, and saponified by heating with dilute sulphuric acid or caustic soda. The yield is about 75% of the theoretical. The aqueous filtrate from the paranitracetanilide contains the more soluble orthonitracetanilide, which separates on addition of salt (yield about 20%).

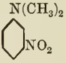
*Properties.*—Yellow needles or prisms. M.p. 147°. Dissolves in 1250 pts. of water at 18°. Very soluble in acetone. Not volatile with steam.

*Reactions.*—On diazotisation with sodium nitrite and hydrochloric acid it is converted into *p*-**nitrodiazobenzene chloride** $C_6H_4(NO_2)\cdot N_2\cdot Cl$, which by combination with betanaphthol on the fibre yields **paranitraniline red** $C_6H_4(NO_2)\cdot N_2\cdot C_{10}H_6\cdot OH$.

*Valuation.*—The commercial product should be nearly chemically pure. It should be a light yellow powder, having the correct melting point, and dissolving without residue in acetone and in hydrochloric acid. On titration with a standard solution of sodium nitrite the theoretical quantity should be required.

### *m*-Nitrodimethylaniline

$C_6H_4(NO_2)\cdot N(CH_3)_2$ *i.e.*

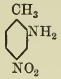


*Preparation.*—By slowly adding a mixture of nitric acid (81 pts. of $86\frac{1}{2}\%$) and conc. sulphuric (100 pts.) to a solution of dimethylaniline (135 pts.) in conc. sulphuric acid (500 pts.), keeping the temperature at 0°-5°. After standing, the product is poured into about 7000 pts. of water, filtered from the precipitated *p*-nitrodimethylaniline, and from the filtrate the *m*-nitrodimethylaniline is separated by neutralisation with sodium carbonate. Yield: about 125 pts.

*Properties.*—Thick red prisms. M.p. 61°. Easily volatile with steam.

*Reactions.*—On reduction it yields the *u*-**Dimethyl**-*m*-**phenylenediamine** $C_6H_4(NH_2)\cdot N(CH_3)_2$. On combination with methyl chloride and reduction of the product, *m*-**Nitrophenyltrimethylammonium chloride** $C_6H_4(NH_2)\cdot N(CH_3)_3Cl[1:3]$ (the base of the Janus colours) is obtained.

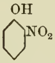
## *p*-Nitro-*o*-toluidine

$C_6H_3(CH_3)(NH_2)(NO_2)[1:2:4]$ *i.e.* 

*Preparation.*—By slowly running a cold mixture of nitric acid (1 mol.) with twice its weight of conc. sulphuric acid into a solution of orthotoluidine (1 mol.) in 10 times its weight of sulphuric acid, cooled to 0° in a freezing mixture. The mixture is poured into water and the base precipitated by neutralisation with sodium carbonate (Nölting and Collin, Ber. **17,** 265). In addition to the *p*-nitro-*o*-toluidine, which constitutes about 75% of the crude product, about 20% of *o*-nitro-*o*-toluidine $C_6H_3(CH_3)(NH_2)(NO_2)[1:2:6]$ and 3 or 4% of *m*-nitro-*o*-toluidine $C_6H_3(CH_3)(NH_2)(NO_2)[1:2:5]$ are also formed (Green and Lawson, *J. Chem. Soc.* **1891**, 1013). The *p*-nitro-*o*-toluidine is obtained pure by crystallisation from water.

*Properties.*—Orange prisms, having an intensely sweet taste. M.p. 107°·5; b.p. about 310°. Dissolves in 100 pts. of boiling water. Slightly volatile with steam.

## *o*-Nitrophenol

$C_6H_4(NO_2)(OH)[1:2]$ *i.e.* 

*Preparation.*—Together with *p*-nitrophenol by nitration of phenol in benzene solution with nitric acid. Separated from the para isomer by distillation with steam.

*Properties.*—Long yellow needles of peculiar smell. B.p. 214°; m.p. 45°. Volatile with steam. Its alkaline salts have a scarlet red colour.

*Derivative.*—By the action of methyl chloride or sodium methyl sulphate upon the sodium salt it is converted into the ether, *o*-**nitroanisol** $C_6H_4(NO_2)(OCH_3)$, a yellow oil of b.p. 275° (*cf.* Paul, *J. Soc. Chem. Ind.* **1897**, 62).

## *p*-Nitrophenol

$C_6H_4(NO_2)(OH)[1:4]$ *i.e.* 

*Preparation.*—Together with *o*-nitrophenol as above, and obtained by crystallisation of the residue after removing the ortho isomer by steam distillation.

*Properties.*—Long colourless needles. M.p. 114°. Not volatile with steam.

## *a*-Dinitrophenol

$C_6H_3(NO_2)_2OH[4:2:1]$

*Preparation.*—Phenol (200 pts.) is heated for 5 hours with conc. sulphuric acid (400 pts.), diluted with water (600 pts.), and a mixture of nitric acid of sp. gr. 1·332 (800 pts.) and water (575 pts.) is slowly added, keeping the temperature below 50°. After standing for a day, the product is heated for 3 days to 100°. On cooling, the dinitrophenol crystallises out in a nearly pure form (Reverdin and de la Harpe, *Chem. Zeit.* **1892,** 45; *cf.* Vidal, French Pat. 315695).

*Properties.*—Yellowish tables. M.p. 114°. Tolerably soluble in hot water, sparingly in cold. Employed in the preparation of "sulphide" blacks.

### Trinitrophenol

(*Picric Acid*)

$C_6H_2(NO_2)_3OH[6:4:2:1]$

*Preparation.*—By nitration of the mixture of phenolsulphonic acids obtained by heating phenol with conc. sulphuric acid (*cf.* Eng. Pat. $4539^{89}$, and French Pat. 315695).

*Properties.*—Pale yellow plates. M.p. 122°. Sparingly soluble in cold water, more easily in hot.

## SULPHONIC ACIDS OF HYDROCARBONS

### Benzenemonosulphonic Acid

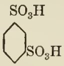
$C_6H_5 \cdot SO_3H$

*Preparation.*—Benzene (2 pts.) is vigorously agitated under gentle heating with fuming sulphuric acid (3 pts.). Any undissolved benzene is removed, and the product, diluted with water, is neutralised with lime, filtered from calcium sulphate, and the calcium salt converted into sodium salt.

*Properties.*—The free acid forms fine deliquescent needles or large tables. M.p. 40° to 42°. Employed for the preparation of phenol by fusion with caustic soda.

### *m*- and *p*-Benzenedisulphonic Acid

$C_6H_4(SO_3H)_2[1:3]$ & $[1:4]$ *i.e.*



and

*Preparation.*—A mixture of these two acids is formed by heating benzene (1 pt.) with fuming sulphuric acid (4 pts.) up to 275° (Bindschedler and Busch, *Mon. Scien.* **1878,** 1169). It is employed without separation for the preparation of resorcinol, as the latter is formed from both isomers on fusion with caustic soda.

*Properties.*—The potassium salt of the meta acid is less soluble than that of the para acid.

### *o*- and *p*-Toluenemonosulphonic Acids

$C_6H_4(CH_3)(SO_3H)[1:2]$ & $[1:4]$

*Preparation.*—A mixture of these two isomers in about equal quantities is formed by sulphonating toluene with conc. sulphuric acid under 100°. A mixture of the corresponding sulphonic chlorides (60% ortho + 40% para) is obtained by the action of sulphuric chlorhydrin (4 pts.) upon toluene (1 pt.) at a temperature not exceeding 5°.

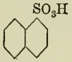
*Properties.*—The chloride of the ortho acid is liquid, that of the para acid a solid of m.p. 69°.

## Naphthalenemonosulphonic Acids

$C_{10}H_7 \cdot SO_3H$

Two isomeric monosulphonic acids are formed by the action of conc. sulphuric acid upon naphthalene. At a low temperature, 80° and under, the product consists chiefly of the *α*-sulphonic acid; at high temperatures, 170° to 200°, the chief product is the *β*-sulphonic acid; at intermediate temperatures mixtures of these two acids are formed. They are employed in large quantities for the preparation of *α*- and *β*-naphthol.

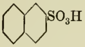
**α-Naphthalenesulphonic acid.**



*Preparation.*—By heating naphthalene (4 pts.) with conc. sulphuric acid (3 pts.) at 80° for 8 or 10 hours (Merz, *Ber.* **3**, 126). Or better by stirring finely-powdered naphthalene (1 pt.) into conc. sulphuric acid (2 pts.) at 40° and keeping at this temperature for several hours (Landshoff and Meyer, Ger. Pat. $50411^{89}$). The melt is dissolved in water, filtered from unsulphonated naphthalene, and the sodium sulphonate precipitated by the addition of salt.

*Properties.*—Deliquescent crystals. M.p. 85° to 90°. On heating it is converted into the *β*-sulphonic acid. Its salts are more soluble than those of the *β*-acid.

**β-Naphthalenesulphonic acid.**



*Preparation.*—By heating naphthalene (1 pt.) with conc. sulphuric acid (1 pt.) for several hours at 180°. The product is dissolved in water, filtered from a little dinaphthylsulphone, and the sodium salt precipitated by the addition of salt.

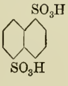
*Properties.*—Non-deliquescent plates.

## Naphthalenedisulphonic Acids

$C_{10}H_6(SO_3H)_2$

The following isomers are of technical importance:—

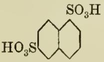
**Naphthalene-disulphonic acid** (1 : 5).
(*Armstrong's δ-acid*)



*Preparation.* — By adding finely-powdered naphthalene (1 pt.) to fuming sulphuric acid of 30% $SO_3$ (4 pts.), keeping the temperature as low as possible. The product is dissolved in 3 or 4 times its weight of water or salt solution, when the free acid or its sodium salt separates out, and any isomers formed simultaneously remain in solution (Armstrong, *Ber.* **15**, 205; Ewer and Pick, Ger. Pat. appl. E. $2619^{89}$).

*Properties.*—Glistening white plates. Its chloride $C_{10}H_6(SO_2Cl)_2$ melts at 183°, and when heated with phosphorus pentachloride yields dichloronaphthalene of m.p. 107°.

**Naphthalene-disulphonic acid** (1 : 6).
(*Ewer and Pick's acid*)



*Preparation.*—By sulphonation of sodium *β*-naphthalenesulphonate (1 pt.) with fuming sulphuric acid of 25% $SO_3$ (2 pts.) at about 100° (Ewer and Pick, Ger. Pat. $45229^{87}$).

*Properties.*—Long white hygroscopic needles. Its sodium salt forms crystalline aggregates ($+ 8H_2O$). Its chloride yields dichloronaphthalene of m.p. 48°.

**Naphthalene-disulphonic acid** (2 : 6).
(*Ebert and Merz's β-acid*)

*Preparation.*—Together with the (2 : 7)-acid by heating naphthalene (1 pt.) with conc. sulphuric acid (5 pts.) at 160° to 180° for 4 hours. When the mixture is heated at 180° for 24 hours, the (2 : 6)-acid is almost the sole product (Ebert and Merz, *Ber.* **9**, 592).

*Properties.*—Plates. Its sodium salt forms needles ($+ H_2O$). The chloride melts at 226°, and by heating with phosphorus pentachloride is converted into dichloronaphthalene of m.p. 135°.

**Naphthalene-disulphonic acid** (2 : 7).
(*Ebert and Merz's α-acid*)

*Preparation.*—Together with a small quantity of the preceding acid by heating naphthalene (1 pt.), or better β-naphthalenesulphonic acid, with conc. sulphuric acid (5 pts.) for a short time at 160° (Ebert and Merz, *Ber.* **9**, 592). It is separated from the (2 : 6)-acid by adding salt to the hot solution of the mixed calcium salts, when the calcium salt of the (2 : 6)-acid is precipitated whilst the calcium salt of the (2 : 7)-acid remains in solution (Landshoff and Meyer, Ger. Pat. 48053$^{88}$).

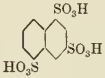
*Properties.*—Deliquescent pointed needles. Its sodium salt forms large needles ($+ 6H_2O$). The chloride melts at 162°, and by heating with phosphorus pentachloride is converted into dichloronaphthalene of m.p. 114°.

## Naphthalenetrisulphonic Acids

$C_{10}H_5(SO_3H)_3$

The following isomeric acids are of technical importance:—

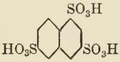
**Naphthalene-trisulphonic acid** (1 : 3 : 5).



*Preparation.*—By further sulphonation of the sodium salt of the 1 : 5 disulphonic acid (2 pts.) dissolved in sulphuric acid 100% (5 pts.), with fuming sulphuric acid 70% $SO_3$ (2½ pts.), at 80° to 90°. The product can be salted out from the concentrated solution.

*Properties.*—Its sodium salt forms easily soluble needles ($+ 4H_2O$). The chloride melts at 149°.

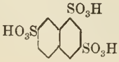
**Naphthalene-trisulphonic acid** (1 : 3 : 6).



*Preparation.*—Sodium naphthalene β-sulphonate (1 pt.) is mixed with fuming sulphuric acid of 40% $SO_3$ (2 pts.). The temperature is kept at 60°, then slowly raised to 125° for an hour, and finally to 160° to 170° for 10 hours (Gurke and Rudolph, Eng. Pat. 15716$^{85}$).

*Properties.*—Its sodium salt ($+ 4H_2O$) is very soluble. The chloride melts at 191°.

**Naphthalene-trisulphonic acid** (1 : 3 : 7).



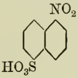
*Preparation.*—By further sulphonation of the sodium salt of the 2 : 6 disulphonic acid with fuming sulphuric acid at 100° (Cassella and Co., Ger. Pat. 75432).

## Nitronaphthalenesulphonic Acids

A number of nitronaphthalene mono- and di-sulphonic acids are employed as between-products in the preparation of naphthylamine- and amidonaphthol-sulphonic acids. They are usually not isolated, the reaction-mixtures being at once reduced.

The following are the most important:—

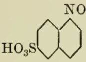
**Nitronaphthalene-sulphonic acid** (1 : 5).
(*a- or Laurent's acid*)



*Preparation.*—By sulphonating nitronaphthalene with a mixture of sulphuric chlorhydrin and sulphuric acid (obtained, for instance, by adding salt or HCl gas to fuming sulphuric acid) at 90°.

*Properties.*—Very soluble pale yellow needles (+ $4H_2O$). The chloride melts at 113°.

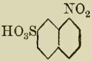
**Nitronaphthalene-sulphonic acid** (1 : 6).
(*Cleve's β-acid*)



*Preparation.*—Together with an equal amount of the following acid by nitration of naphthalene-β-sulphonic acid.

*Properties.*—The acid is soluble in strong hydrochloric acid (separation from the 1 : 7 acid). The chloride melts at 126°.

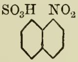
**Nitronaphthalene-sulphonic acid** (1 : 7).
(*Cleve's θ or δ-acid*)



*Preparation.*—See preceding.

*Properties.*—The acid is nearly insoluble in concentrated hydrochloric acid. The chloride melts at 169°.

**Nitronaphthalene-sulphonic acid** (1 : 8).



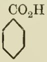
*Preparation.*—As chief product (60% to 70%) together with the 1 : 5 acid (20%) by nitration of naphthalene-*a*-sulphonic acid.

*Properties.*—The chloride melts at 161°.

## CARBOXYLIC ACIDS OF HYDROCARBONS

### Benzoic Acid (*Benzenemonocarboxylic Acid*)

$C_6H_5 \cdot CO_2H$ *i.e.*

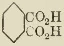


*Preparation.*—The mixture of benzylidenechloride $C_6H_5CHCl_2$ and benzotrichloride $C_6H_5CCl_3$ formed by chlorinating toluene, or the high boiling fractions obtained as a by-product in the preparation of benzylchloride (*q.v.*), are heated with the calculated quantity of milk of lime under a pressure of 4 to 5 atmospheres. The benzaldehyde formed is distilled off with steam and the calcium benzoate remaining is decomposed by hydrochloric acid. The precipitated benzoic acid is filtered off, dried, and sublimed.

*Properties.*—White needles or plates. M.p. 121°; b.p. 249° corr. Soluble in hot water, sparingly in cold (1 pt. in 500 pts. at 10°). Tolerably volatile with steam. Its salts are easily soluble.

*Valuation.*—The commercial product (when made from toluene) usually contains chlorobenzoic acid, which can be estimated by ignition with fusion mixture and precipitation as silver chloride; the quantity should only be small. The benzoic acid should have the right melting point, and dissolve completely in boiling water. It should give correct numbers on titration with normal alkali.

### **Phthalic Acid** (*o-Benzenedicarboxylic Acid*)

$C_6H_4(CO_2H)_2[1:2]$ *i.e.* 

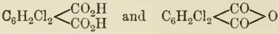
*Preparation.*—By oxidation of naphthalene or naphthalene-sulphonic acids with sulphuric acid in presence of mercury (Eng. Pat. $18221^{96}$). The operation is carried out in practice by quickly distilling a mixture of naphthalene (1 pt.) and slightly fuming sulphuric acid containing 5 to 6% $SO_3$ (13 pts.) from a flat-bottomed iron retort previously coated with mercury. The phthalic acid is separated from the acid distillate, dried, and converted into the anhydride by distillation (*cf.* H. Levinstein, *J. Soc. Dyers*, **1901**, 139).

*Properties.*—Rhombic plates. M.p. 213°. Readily decomposes on heating into phthalic anhydride and water. Not volatile with steam. Very sparingly soluble in water, insoluble in chloroform. Its alkaline salts are easily soluble in water.

*Anhydride* $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O$. Very long white needles or prisms. M.p. 128°; b.p. 284° corr. Slightly soluble in water, readily in alcohol. The commercial product is chemically pure: it should be quite white, have the right melting point, and dissolve in benzene to a clear solution.

*Imide* $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH$ is prepared by passing a stream of ammonia gas through melted phthalic anhydride, the temperature of which is slowly raised in the course of four hours to 140°, and during the next eight hours to 240°. It sublimes in plates. M.p. 238°. Converted by hypochlorites into anthranilic acid.

### **Dichlorophthalic Acid and Anhydride**

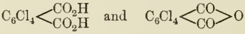


$$C_6H_2Cl_2{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} \quad \text{and} \quad C_6H_2Cl_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O$$

*Preparation.*—By oxidation of dichloronaphthalene tetrachloride $C_{10}H_6Cl_2Cl_4$ with nitric acid (Faust, *Ann.* **160**, 64; Castehaz, Eng. Pat. $447^{79}$).

*Properties.*—The acid forms thick prisms, soluble in hot water. The anhydride melts at 187°.

### **Tetrachlorophthalic Acid and Anhydride**



$$C_6Cl_4{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} \quad \text{and} \quad C_6Cl_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O$$

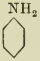
*Preparation.*—(1) By passing a stream of chlorine for several hours through a mixture of phthalic anhydride (1 pt.) and antimony pentachloride (6 pts.) heated to 200°. When the reaction is finished the antimony pentachloride is first distilled off, and then the tetrachlorophthalic anhydride (Gesellsch. f. Chem. Industrie, Ger. Pat. $32564^{85}$; Gnehm, Am. Pat. 322368; *Ann.* **238**, 320). (2) By passing a stream of dry chlorine into a mixture of phthalic anhydride (20 pts.), fuming sulphuric acid of 50 to 60% $SO_3$ (60 pts.), and iodine (1 pt.), keeping the temperature at about 60° at the commencement, and finally raising it to 200°. The product is poured into cold water, keeping the temperature below 50°, and the tetrachlorophthalic anhydride which separates is filtered off, washed, and dried (Juvalta, Ger. Pat. $50177^{89}$).

*Properties.*—The acid forms plates or tables, easily soluble in hot water, sparingly in cold. The anhydride forms long prisms of m.p. 252° corr., insoluble in cold water.

# PRIMARY AMINES AND THEIR SULPHONIC AND CARBOXYLIC ACIDS

## Aniline (*Amidobenzene or Phenylamine*)

$C_6H_5 \cdot NH_2$ *i.e.*



*Preparation.*—By reduction of nitrobenzene with iron and hydrochloric acid. In a large iron still provided with a mechanical agitator and a cohobating condenser, are put 500 pts. of nitrobenzene and 800 pts. of water. The mixture is raised to the boil by blowing in steam, and 16 to 20 pts. of hydrochloric acid are added. The steam is shut off and 500 to 600 pts. of finely ground cast-iron borings ("swarf") are slowly added in the course of several hours. A vigorous reaction takes place, and water nitrobenzene and aniline distil over and are continually returned to the still. When all the iron has been added steam is blown in and the distillate is returned as long as it is yellow. When quite colourless it is collected, and the distillation is continued as long as any aniline comes over. On leaving the distillate to stand, the aniline sinks to the bottom and is drawn off and rectified. The water contains 3% of aniline, and is employed to raise steam for blowing over the aniline in a subsequent operation. The yield is about 70% of the nitrobenzene employed or 106% of the benzene, *i.e.* about 90% of the theoretical yield.

*Properties.*—Colourless refractive oil of peculiar smell. B.p. 182°; m.p. 8°; sp. gr. at 15° = 1·0275. It is soluble in about 32 pts. of water at 15°, and dissolves 5% of water at the same temperature. Readily volatile with steam.

*Valuation.*—Commercial "**pure aniline**" should have the specific gravity 1·0275 at 15°. When distilled in a fractionating flask, with the thermometer in the vapour, 90% of it should boil correctly within half a degree. It should dissolve clear in dilute hydrochloric acid. The presence of a trace of nitrobenzene is shown by the oil having a yellow tint. "**Aniline for red**" is a mixture of aniline, orthotoluidine, and paratoluidine, and is either made by mixing the constituents or by nitration and reduction of a mixture of benzene and toluene ("heavy benzol"); it should boil between 190° and 200° and have the specific gravity 1·007 to 1·009 at 15°. Its average composition is 33% aniline, 43% orthotoluidine, and 24% paratoluidine.

*Derivatives.*—By boiling aniline with an equal weight of glacial acetic acid for 48 hours it is converted into **Acetanilide** $C_6H_5 \cdot NH \cdot CO \cdot CH_3$, a white crystalline solid which boils at 295° and melts at 115°. Aniline heated with chloracetic acid yields **phenylglycine** $C_6H_5 \cdot NH \cdot CH_2 \cdot CO_2H$, a body which has recently become of importance for the preparation of artificial indigo; it forms colourless crystals which melt at 127°. The sulphonic acids of aniline are described as "**Sulphanilic acids,**" the carboxylic acids as "**Amidobenzoic acids**" (*q.v.*).

## *p*-Sulphanilic Acid

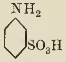
$C_6H_4(NH_2)SO_3H[1:4]$ *i.e.*

*Preparation.*—Acid sulphate of aniline $C_6H_5 \cdot NH_2, H_2SO_4$ obtained by mixing 100 pts. of aniline with 105 pts. of conc. sulphuric acid, is heated on trays in an oven at 180° to 220° until aniline can be no longer detected on boiling a sample with caustic soda (Neville and Winther, *Ber.* **13**, 1940).

*Properties.*—Crystallises from water in large colourless rhombic plates $(+H_2O)$. Sparingly soluble in cold water, more easily in boiling water. By nitrous acid it is converted into *p*-**Diazobenzenesulphonic acid** $C_6H_4<\overset{N=N}{SO_3}>$. Its salts are easily soluble.

### *m*-Sulphanilic Acid

$C_6H_4(NH_2)SO_3H[1:3]$ *i.e.*

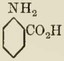


*Preparation.*—By reduction of *m*-nitrobenzenesulphonic acid. Nitrobenzene is mixed with 3 times its weight of fuming sulphuric acid (20% $SO_3$) and then heated for 5 hours at 60° to 70°, adding more anhydrous sulphuric acid until the product is soluble in water. The mixture is then poured into 4 times its weight of water, reduced by adding the requisite quantity of iron, made alkaline with lime, filtered, and the calcium salt converted into sodium salt by sodium carbonate (Limpricht and Bernthsen, *Ann.* **177**, 82).

*Properties.*—Small colourless needles. Tolerably soluble in water. Forms easily soluble salts. By nitrous acid it is converted into *m*-**Diazobenzenesulphonic acid.**

### *o*-Amidobenzoic Acid (*Anthranilic Acid*)

$C_6H_4(NH_2)CO_2H[1:2]$ *i.e.*



*Preparation.*—By the action of sodium hypochlorite upon phthalic-imide. 500 pts. of the latter are dissolved in a cold solution of 144 pts. of chlorine in 640 pts. of caustic soda solution (35% NaOH) and 440 pts. of water. The product is run into water containing sulphurous acid, and acidified with about 600 pts. of hydrochloric acid when the anthranilic acid separates out (Badische Anil. u. Soda Fabrik, Ger. Pat. 55988 of 1890; see Levinstein, *J. Soc. Dyers,* **1901**, 140).

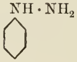
Also by oxidation of acetyl-*o*-toluidine with permanganate in presence of magnesium sulphate and saponification of the product (Eng. Pat. $6475^{97}$).

*Properties.*—Colourless plates. M.p. 145°. Easily soluble in water and alcohol.

*Derivative.*—By the action of chloracetic acid it is converted into **phenylglycine-carboxylic acid** $C_6H_4(CO_2H)\cdot NH\cdot CH_2\cdot CO_2H$, which has recently been employed for the production of artificial indigo.

### Phenylhydrazine

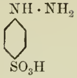
$C_6H_5\cdot NH\cdot NH_2$ *i.e.*



*Preparation.*—A concentrated solution of diazobenzene chloride is run into a saturated solution of sodium sulphite (2 mols.) cooled with ice. The mixture is gently warmed until the diazosulphite redissolves, and is carefully neutralised with hydrochloric acid. Reduction is effected by the sulphurous acid thus disengaged, and is completed on acidifying with acetic acid, and adding a little zinc dust until complete decolorisation. The hydrazine-sulphonate thus obtained is saponified by heating in concentrated solution with hydrochloric acid, the separated hydrazine hydrochloride being basified with caustic soda and distilled in vacuo.

*Properties.*—Colourless crystalline solid. B.p. 233°; m.p. 17°. Soluble in hot water, sparingly in cold. Volatile with steam. Combines readily with aldehydes and ketones forming characteristic hydrazones.

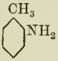
## Phenylhydrazine-*p*-sulphonic Acid

$C_6H_4(NH \cdot NH_2)SO_3H[1:4]$ *i.e.* 

*Preparation.*—By reduction of diazobenzenesulphonic acid $C_6H_4 < {N_2 \atop SO_3} >$ (from *p*-sulphanilic acid) with a warm solution of sodium sulphite, and boiling the product with hydrochloric acid (Fischer, *Ann.* **190**, 74). Also by sulphonation of phenylhydrazine or of phenylhydrazine sodium sulphite with 5 or 6 pts. of conc. sulphuric acid at 100°.

*Properties.*—Colourless needles ($+\frac{1}{2}H_2O$). Sparingly soluble in cold water, easily in hot. Its alkaline salts are easily soluble.

## *o*-Toluidine

$C_6H_4(CH_3)NH_2[1:2]$ *i.e.* 

*Preparation.*—By reduction of *o*-nitrotoluene, or together with *p*-toluidine by reduction of crude nitrotoluene. The reduction is performed in exactly the same way as given for aniline, the yield being about 73% of the nitrotoluene employed. When unseparated nitrotoluene is used, the fluid toluidine obtained is a mixture of about 63% orthotoluidine, 35% paratoluidine, and 2% metatoluidine. This is either employed direct (*e.g.* for "aniline for red") or is separated more or less completely by various methods, *e.g.* freezing out paratoluidine hydrate; fractional neutralisation with oxalic, phosphoric, or sulphuric acids, etc. (Ger. Pats. $37932^{86}$ and $40424^{87}$; Eng. Pat. $3111^{83}$).

*Properties.*—Colourless oily fluid. B.p. 197°; sp. gr. 1·0037 at 15°. Volatile with steam. The acetyl derivative forms long needles of m.p. 107°.

*Valuation.*—The presence of aniline is detected by the production of a violet colour on shaking the ethereal solution with aqueous chloride of lime. For the estimation of paratoluidine in commercial fluid toluidine various methods have been proposed, none of which however can claim to be more than approximately accurate (Rosenstiehl, *Bl.* **17**, 7; Schoop, *Chem. Ztg.* **1887**, 1223; Lunge, *Chem. Ind.* **1885**, 74; Häusermann, *Chem. Ind.* **1887**, 56). Merz and Weith (*Ber.* **2**, 433) proceed as follows:—10 c.c. of the oil, which has been dried over solid caustic potash, is heated with 10 c.c. of acetic anhydride for 2 hours at 140°, the product is mixed with 30 c.c. of acetic acid and poured into 800 c.c. of cold water. After standing for two days the separated paracettoluide is filtered off, washed with dilute acetic acid (10%), dried, and weighed. From this weight the percentage of paratoluidine is calculated, since 100 pts. of paracettoluide correspond to 71·8 pts. of paratoluidine. The method is unsuitable when only small quantities of paratoluidine are present (under 10%). In such cases the following colourimetric method of Schoen gives satisfactory results:—A standard oil is prepared containing 8% of paratoluidine and 92% of orthotoluidine, 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid (35%) in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium bichromate. After standing for 2 hours the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner and compared colourimetrically with the above solution.

Commercial **"pure orthotoluidine"** should give under 1% of paratoluidine when tested as above. **"Fluid toluidine"** should boil within two degrees, and have a specific gravity of 0·9995 to 1·0005. It should dissolve clear in dilute hydrochloric acid.

## *m*-Toluidine

$C_6H_4(CH_3)NH_2[1:3]$

*Preparation.*—By reduction of *m*-nitrobenzylidene chloride $C_6H_4(NO_2)CHCl_2$ (from *m*-nitrobenzaldehyde) with zinc at a low temperature (*Ber.* **13**, 677; **15**, 2011; **18**, 3398).

*Properties.*—Colourless oil. B.p. 197°; sp. gr. at 25° = 0·998. Its acetyl derivative melts at 65°. It combines with diazo compounds with direct production of amidoazo compounds.

## *p*-Toluidine

$C_6H_4(CH_3)NH_2[1:4]$ *i.e.*

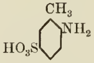
*Preparation.*—By reduction of paranitrotoluene with iron and hydrochloric acid, or by separation from fluid toluidine (*v.* supra).

*Properties.*—Colourless plates of peculiar smell. B.p. 198°; m.p. 45°. Only slightly soluble in cold water; a solution in warm water deposits the crystalline hydrate $C_7H_7NH_2,H_2O$ on cooling. Its acetyl derivative forms needles of m.p. 147°.

*Valuation.*—The commercial product should be a white dry crystalline solid, and should melt and boil correctly. It should not contain oil or water.

## *o*-Toluidine-*m*-sulphonic Acid

$C_6H_3(CH_3)(NH_2)SO_3H[1:2:5]$ *i.e.*



*Preparation.*—By heating acid sulphate of orthotoluidine $C_7H_7NH_2,H_2SO_4$ in an oven at 180° to 200° for several hours.

*Properties.*—Rhombic tables or prisms ($+H_2O$). Sparingly soluble in cold water, easily in hot.

## *p*-Toluidinesulphonic Acids

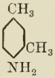
$C_6H_3(CH_3)(NH_2)SO_3H[1:4:2]$ & $[1:4:3]$

*Preparation.*—A mixture of these acids is formed on heating paratoluidine with fuming sulphuric acid or by baking paratoluidine acid sulphate. In the latter case the [1 : 4 : 2] acid is the chief product.

*Properties.*—The [1 : 4 : 2] acid is insoluble in alcohol, sparingly soluble in cold water, and crystallises in rhombohedra. The [1 : 4 : 3] acid is tolerably soluble in cold water, readily in alcohol, and crystallises in needles.

## *m*-Xylidine (*Amido-m-xylene*)

$C_6H_3(CH_3)_2NH_2[1:3:4]$ *i.e.*

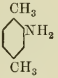


*Preparation.*—By the reduction of nitro-*m*-xylene with iron and hydrochloric acid. The commercial xylidine obtained by nitration and reduction of the unseparated xylenes contains about 50% of this isomer, which can be separated from the mixture more or less completely by neutralising with acetic acid and pressing and basifying the cake of meta-xylidine acetate which is formed. To 121 pts. of crude xylidine 30 pts. of glacial acetic acid are employed (Eng. Pat. $11822^{86}$).

*Properties.*—Colourless oil. B.p. 215° corr.; sp. gr. at 15° = ·9184.

*Valuation.*—Commercial xylidine should distil to the extent of 90% between 210° and 217°. The presence of hydrocarbons is detected by dissolving in hydrochloric acid.

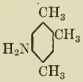
### *p*-**Xylidine** (*Amido-p-xylene*)

$C_6H_3(CH_3)_2NH_2[1:4:2]$ *i.e.* 

*Preparation.*—By nitration and reduction of paraxylene (Nölting and Forel, *Ber.* **18,** 2680). Occurs in commercial xylidine, from which it is obtained as hydrochloride by the addition of hydrochloric acid (1 mol.) to the mother liquors from which the metaxylidine acetate has separated. It can also be obtained in a pure state by means of the well-crystallising benzylidene compound which is formed on adding benzaldehyde to the above mother liquors (Ger. Pat. 71969 of 1893).

*Properties.*—White crystalline solid or oil. B.p. 215°; m.p. 15°; sp. gr. 0·980. It combines with diazo compounds with direct formation of amidoazo derivatives, and is therefore used as a "middle component" of disazo colouring-matters.

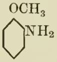
### **ψ-Cumidine**

$C_6H_2(CH_3)_3NH_2[1:2:4:5]$ *i.e.* 

*Preparation.*—By heating crude xylidine (or the residual oils after separation of the meta- and para-xylidines) 10 pts. with methylalcohol (2 pts.) and hydrochloric acid (9 pts.) in an autoclave for 6 hours at about 250°. The pure ψ-cumidine is separated from the product by means of its sparingly soluble crystalline nitrate (Eng. Pat. $3997^{82}$).

*Properties.*—Colourless crystals. B.p. 236°; m.p. 62°.

### *o*-**Anisidine** (*Methyl Ether of o-Amidophenol*)

$C_6H_4(OCH_3)NH_2[1:2]$ *i.e.* 

*Preparation.*—By reduction of the methyl ether of *o*-nitrophenol (Mülhhäuser, *Ann.* **207,** 239).

*Properties.*—Oil. B.p. 226° at 734 mm. Its acetyl derivative melts at 84°.

### *o*-**Phenetidine** (*Ethyl Ether of o-Amidophenol*)

$C_6H_4(OCH_3)NH_2[1:2]$

*Preparation.*—By reduction of the ethyl ether of *o*-nitrophenol (Förster, *Journ. f. Prak. Chem.* [2], **21,** 344).

*Properties.*—Oil. B.p. 229° at 756 mm.

### *m*-Amido-*p*-cresol-methyl-ether

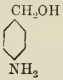
$C_6H_3(CH_3)(NH_2)(OCH_3)[1:3:4]$

*Preparation.*—By etherification and reduction of the *m*-nitro-*p*-cresol obtained by the treatment of *p*-toluidine with nitric and nitrous acids (*Ber.* **22**, 348; **24**, 1960).

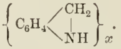
*Properties.*—White crystalline solid. B.p. 235°; m.p. 51·5°. Volatile with steam. Combines with diazo compounds with direct formation of amidoazo derivatives.

### *p*-Amidobenzyl Alcohol

$C_6H_4(NH_2)CH_2OH[1:4]$ *i.e.*



and its anhydride



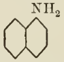
$\left\{ C_6H_4 \begin{matrix} CH_2 \\ | \\ NH \end{matrix} \right\}_x$.

*Preparation.*—The anhydride is obtained by the reaction of formaldehyde (1 mol.) upon a cold solution of aniline (1 mol.) in presence of acid. For instance, a cold solution of 130 pts. of aniline hydrochloride in 600 pts. of water is mixed with 75 pts. of 40% formaldehyde solution and allowed to stand until the whole has become a thick yellow magma. It is then made alkaline and the base filtered off (Kalle and Co., Ger. Pats. 95600 and 96851 of 1895).

*Properties.*—The simple *p*-amidobenzyl alcohol (obtained by reduction of *p*-nitrobenzyl alcohol) melts at 65°; its anhydride is a yellow amorphous powder of very high melting point.

### *a*-Naphthylamine (*a-Amidonaphthalene*)

$C_{10}H_7 \cdot NH_2$ *i.e.*



*Preparation.*—By reduction of *a*-nitronaphthalene with iron and hydrochloric acid. An iron vessel provided with an agitator is charged with 800 pts. of iron borings, a little water, and 40 pts. of hydrochloric acid, and gently warmed: 600 pts. of granulated nitronaphthalene are then slowly added, keeping the temperature at about 70° to 80°. When all has been added the temperature is maintained for 5 or 6 hours by blowing in steam, until the whole of the nitronaphthalene is reduced. The mass is then mixed with milk of lime (from 50 pts. of lime) and emptied out. The mixture is spread out on iron trays, which are placed on shelves in an iron retort. The latter is strongly heated and a current of super heated steam is passed through until no more naphthylamine distils over. The naphthylamine is condensed in a worm surrounded with warm water, separated from water, dried, and rectified from an iron retort. Another method of separation from the iron consists in extracting the mass with solvent naphtha which is subsequently distilled off. The yield is fairly good, though considerably below the theoretical (Witt, *Chem. Ind.* **10**, 215).

*Properties.*—Flat colourless needles or plates. B.p. 300°; m.p. 50°. Nearly insoluble in water. Disagreeable smell.

*Valuation.*—The commercial product forms grayish white or brownish crystalline lumps. It should melt nearly correctly, and only leave a trace of naphthalene, etc., on solution in dilute hydrochloric acid.

*Derivative.*—By reacting with chloracetic acid it gives **a-naphthylglycine** $C_{10}H_7 \cdot NH \cdot CH_2CO_2H$, a crystalline solid of m.p. 198° (*cf.* Ger. Pat. 79861 of 1893).

## *a*-Amido-*β*-naphthol-ethyl-ether (*Naphthylamine Ether*)

$C_{10}H_6(NH_2)(OC_2H_5)[1:2]$

*Preparation.*—By nitration and reduction of the *β*-naphthol ether obtained by heating *β*-naphthol with alcohol and sulphuric acid (Am. Pat. 421640; Paul, *J. Soc. Chem. Ind.* **1897**, 671).

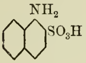
*Properties.*—Colourless needles. M.p. 114°. The corresponding **methyl ether** is obtained in the same manner, and melts at 125°.

## *a*-Naphthylaminemonosulphonic Acids

$C_{10}H_6(NH_2)SO_3H$

All the seven possible monosulphonic acids of *a*-naphthylamine have found technical application:—

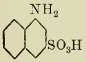
**_a_-Naphthylaminesulphonic acid** (1 : 2).



*Preparation.*—By heating dry powdered sodium naphthionate (1 pt.) with naphthalene (2 or 3 pts.) to the boiling point of the latter for 2 or 3 hours (Landshoff and Meyer, Eng. Pat. 6195$^{90}$; Cleve, *Ber.* **24**, 3472; Erdmann, *Ann.* **275**, 225; Bayer & Co., Ger. Pat. 72833).

*Properties.*—Small glistening needles. Tolerably soluble in water (1 pt. in 225 at 15°). Its sodium salt forms small scales much less soluble than sodium naphthionate (1 pt. in 60 pts. of cold water).

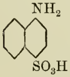
**_a_-Naphthylaminesulphonic acid** (1 : 3).
(*Cleve's γ-acid*)



*Preparation.*—By hydrolysis of the *a*-naphthylaminedisulphonic acid (1 : 3 : 6) by boiling with 75% sulphuric acid (Kalle & Co., Ger. Pat. 64979).

*Properties.*—Small sparingly soluble needles. The sodium salt is easily soluble.

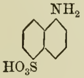
**_a_-Naphthylaminesulphonic acid** (1 : 4).
(*Piria's naphthionic acid*)



*Preparation.*—(1) By baking a mixture of equal mols. of *a*-naphthylamine and sulphuric acid, with which about 3% of crystallised oxalic acid is incorporated, at a temperature of 170° to 180° until the mass becomes dry and brittle.

*Properties.*—Small colourless needles. Very sparingly soluble in water (1 pt. in 4000 at 15°). Its sodium salt forms large colourless crystals ($+ 4H_2O$), easily soluble in water, insoluble in alcohol. Its diazo compound is white.

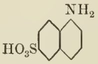
**_a_-Naphthylaminesulphonic acid L.** (1 : 5).
(*Laurent's naphthalidinic acid*)



*Preparation.*—(1) By reduction of the nitronaphthalenesulphonic acid (1 : 5). (2) By adding *a*-naphthylamine hydrochloride to fuming sulphuric acid (20% $SO_3$) in the cold (Witt, *Ber.* **19**, 578).

*Properties.*—Microscopic needles; 1 pt. of the acid is soluble in 950 pts. of water at 15°; in hot water it is tolerably easily soluble. Its sodium salt is soluble in alcohol. Its diazo compound is yellow.

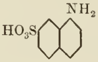
**α-Naphthylaminesulphonic acid** (1 : 6).
(*Cleve's β-acid*)



*Preparation.*—Together with an equal amount of the following acid and a little (1 : 3) acid by nitration and reduction of β-naphthalenesulphonic acid (Cleve, *Bl.* **26**, 444); or together with the (1 : 5) acid by heating α-naphthylamine (1 pt.) with conc. sulphuric acid (5 pts.) for 24 hours at 125° to 130° (Hirsch, *Ber.* **21**, 2371; Erdmann, *Ann.* **275**, 192).

*Properties.*—Plates or needles. 1 pt. dissolves in 1000 pts. of cold water.

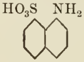
**α-Naphthylaminesulphonic acid** (1 : 7).
(*Cleve's θ-acid*)



*Preparation.*—Together with the (1 : 6) by nitration and reduction of naphthalene-β-sulphonic acid. The mixture of acids obtained in this manner is usually used without separation, chiefly as "middle component" in the preparation of disazo colouring matters.

*Properties.*—1 pt. dissolves in 220 pts. of cold water. Its zinc salt forms yellow glistening needles.

**α-Naphthylaminesulphonic acid S.** (1 : 8).
(*Schöllkopf acid*)



*Preparation.*—By nitration and reduction of α-naphthalenemonosulphonic acid; it is separated from the (1 : 5) acid, which is formed simultaneously, by conversion into the sodium salts, that of the (1 : 8) acid being the least soluble (Schöllkopf Anil. Co., Eng. Pats. $15775^{85}$ and $15782^{85}$; Am. Pat. 333034; H. Erdmann, *Ann.* **247**, 318).

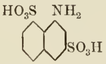
*Properties.*—White needles. 1 pt. dissolves in 4800 pts. of water at 21°, in 240 pts. at 100°. Its diazo compound crystallises in greenish-yellow prisms, which on heating with water are readily converted into the sultone $C_{10}H_6 < \begin{matrix} O \\ SO_2 \end{matrix} > [1:8]$.

## α-Naphthylaminedisulphonic Acids

$C_{10}H_5(NH_2)(SO_3H)_2$

The following are technically important:—

**α-Naphthylamine-disulphonic acid ε** (1 : 3 : 8).

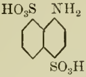


(*Constitution:* Bernthsen, *Ber.* **22**, 3328)

*Preparation.*—(1) Together with the δ-acid by nitration and reduction of the mixture of the (1 : 5) and (1 : 6) naphthalenedisulphonic acids obtained by sulphonating naphthalene with sulphuric anhydride at the ordinary temperature; it is separated from the δ-acid by the greater solubility of its sodium salt (Actienges. f. Anilinfabrikn., Eng. Pats. $4625^{88}$ and $5910^{88}$; Am. Pat. 405938). (2) Nitration and reduction of the (1 : 6) naphthalenedisulphonic acid obtained by sulphonating β-naphthalenemonosulphonic acid with fuming sulphuric acid at 100°, or by sulphonating naphthalene with conc. sulphuric acid at 90° to 120° (Ewer and Pick, Ger. Pat. $52724^{89}$; Bad. Anil. und Soda Fabrik, Ger. Pat. appl. B. 9514; Bernthsen, *Ber.* **22**, 3328).

*Properties.*—Colourless glistening scales. Its acid sodium salt forms rather sparingly soluble long needles. Its diazo compound crystallises in small white needles; by boiling with water it is converted into the naphthosultonesulphonic acid ε.

**α-Naphthylamine-disulphonic acid δ or S.**
(1 : 4 : 8)

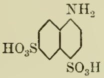


(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 126)

*Preparation.*—(1) By heating α-naphthylaminemonosulphonic acid S (1 pt.) with fuming sulphuric acid of 10% anhydride (3 pts.) at 100° till soluble in water (Schöllkopf Anil. Co., Eng. Pats. $15775^{85}$ and $15782^{85}$; Am. Pat. 333034). (2) Together with the preceding acid (*q.v.*) by nitration and reduction of the mixture of (1 : 5) and (1 : 6) disulphonic acids of naphthalene, obtained by sulphonating naphthalene with fuming sulphuric acid at the ordinary temperature.

*Properties.*—The acid sodium salt crystallises in long prisms, the neutral salt in long needles or clear yellow compact crystals ($+ 2H_2O$). The diazo compound on boiling with water yields α-naphthosultonesulphonic acid δ (Bernthsen, *Ber.* **23**, 3090).

**α-Naphthylamine-disulphonic acid** (1 : 4 : 6).
(*Dahl's acid II.*)

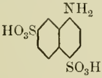


(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 126)

*Preparation.*—Together with the following acid by heating 1 pt. of α-naphthylamine with 4 to 5 pts. of fuming sulphuric acid (25% $SO_3$) at 120°; or by further sulphonation of naphthionic acid by the action of 3½ pts. of fuming sulphuric acid (25% $SO_3$) upon 1 pt. of naphthionic acid at a temperature below 30° for several days. The mixed acids are converted into calcium salts, and extracted with boiling 85% alcohol, when the calcium salt of the acid II. dissolves, whilst that of acid III. remains insoluble (Dahl and Co., Ger. Pat. $41957^{86}$; Erdmann, *Ann.* **275**, 218).

*Properties.*—Needles. Easily soluble in hot water, less in cold. Its salts are very soluble. The diazo compound forms small silky yellow needles, which give a yellow colouring matter on warming with dilute nitric acid.

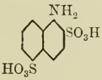
**α-Naphthylamine-disulphonic acid** (1 : 4 : 7).
(*Dahl's acid III.*)



*Preparation.*—Together with a smaller quantity of acid II. by sulphonating α-naphthylamine or naphthionic acid with fuming sulphuric acid (see above).

*Properties.*—Small needles. Sparingly soluble in cold water, easily in hot (1 pt. in 20). The diazo compound is converted into "Naphthol yellow S" on boiling with dilute nitric acid.

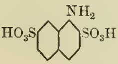
**α-Naphthylamine-disulphonic acid** (1 : 2 : 5).
(*Landshoff & Meyer's acid*)



*Preparation.*—By sulphonating α-naphthylaminesulphonic acid (1 : 2) with fuming sulphuric acid (Landshoff and Meyer, Eng. Pat. $6195^{90}$).

*Properties.*—Not readily soluble. Its diazo compound forms brilliant yellow needles.

**α-Naphthylamine-disulphonic acid** (1 : 2 : 7).
(*Kalle's acid*)



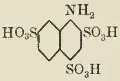
*Preparation.*—By heating the salts of α-naphthylaminetrisulphonic acid (1 : 2 : 4 : 7) with water under pressure at 230° (Kalle and Co., Ger. Pat. $62634^{91}$).

*Properties.*—Fine needles. Its barium salt is very sparingly soluble even in hot water. The diazo compound forms easily soluble needles.

## α-Naphthylaminetrisulphonic Acids

$C_{10}H_4(NH_2)(SO_3H)_3$

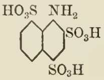
**α-Naphthylaminetrisulphonic acid** (1:2:4:7).



*Preparation.*—By heating naphthionic acid (1 pt.) with fuming sulphuric acid of 40% anhydride (3 to 4 pts.) for 10 hours at 120° (Meister, Lucius, and Bruning, Ger. Pat. $22545^{82}$).

*Properties.*—Its diazo compound is converted into "Naphthol yellow S" on warming with dilute nitric acid.

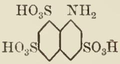
**α-Naphthylaminetrisulphonic acid** (1:2:4:8). (*Naphthsultam-disulphonic acid S*)



*Preparation.*—By further sulphonation of α-naphthylamine-8-monosulphonic or 4:8-disulphonic acid with fuming sulphuric acid at 100° (Bayer and Co., Eng. Pat. $4979^{93}$; Dressel and Kothe, *Ber.* **27**, 2139).

*Properties.*—Does not combine with diazo compounds, and is not diazotisable.

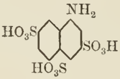
**α-Naphthylaminetrisulphonic acid** (1:3:6:8).



*Preparation.*—By nitration and reduction of the naphthalenetrisulphonic acid obtained by direct sulphonation of naphthalene (Koch, Eng. Pat. $9258^{90}$).

*Properties.*—Its diazo compound is colourless.

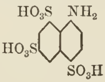
**α-Naphthylaminetrisulphonic acid** (1:3:5:7).



*Preparation.*—By nitration and reduction of the naphthalenetrisulphonic acid formed by further sulphonation of the (2:6) naphthalenedisulphonic acid (Cassella and Co., Eng. Pat. $6972^{91}$).

*Properties.*—Its acid sodium salt and its diazo compound are sparingly soluble.

**α-Naphthylaminetrisulphonic acid** (1:4:6:8).



*Preparation.*—By nitration and reduction of naphthalenetrisulphonic acid (1:3:5) (Eng. Pat. $515^{94}$).

*Properties.*—In alkaline solution it has an intense green fluorescence. Its acid sodium salt forms easily soluble needles.

## β-Naphthylamine (*β-amidonaphthalene*)

$C_{10}H_7 \cdot NH_2$ *i.e.* 

*Preparation.*—By heating β-naphthol (10 pts.) with strong aqueous ammonia ($7\frac{1}{2}$ pts.) in an autoclave at 200°. When cold the melt is powdered, and after extracting unaltered β-naphthol with aqueous caustic soda, is distilled in vacuo (Bad. Anil. und Soda Fabrik, Ger. Pat. $14612^{80}$).

*Properties.*—White pearly plates. B.p. 294°; m.p. 112°. Odourless. Soluble in hot water, sparingly in cold. Tolerably volatile with steam.

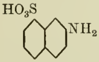
*Valuation.*—The commercial product forms pinkish-white crystalline lumps, almost odourless. It should melt correctly, and only leave a small residue on solution in dilute hydrochloric acid.

## β-Naphthylaminemonosulphonic Acids

$C_{10}H_6(NH_2)SO_3H$

The following four isomers are employed technically, either separately or more or less mixed with one another:—

**β-Naphthylamine-*α*-sulphonic acid** (2 : 8).
(*Badische acid*)

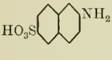


(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1888**, 105; **1889**, 53; Witt, *B.* **21**, 3490)

*Preparation.*—(1) Together with the γ (about 40%), β (about 5%), and δ acid (about 5%) by heating β-naphthylamine (1 pt.) with conc. sulphuric acid (3 to $3\frac{1}{2}$ pts.) for 5 or 6 hours at 100° to 105° (Bad. Anil. und Soda Fabrik, Ger. Pat. $20760^{81}$). (2) Together with the γ-acid (about 70% γ and 30% *α*) by warming β-naphthylamine (1 pt.) with fuming sulphuric acid of 20% $SO_3$ (3 pts.) at 85° for a short time (Dahl and Co., Eng. Pats. $7712^{84}$ and $7713^{84}$). (3) Together with the γ-acid (55% γ and 45% *α*) by treating β-naphthylamine (1 pt.) with conc. sulphuric acid (3 pts.) at the ordinary temperature (15° to 20°) for several days (Dahl and Co.). The *α*-acid is separated from its isomers by extracting the mixed sodium salts with boiling 90% alcohol, in which the sodium salts of the β-, γ-, and δ-acids are readily soluble, but not the *α*-sodium salt.

*Properties.*—Prisms. Very sparingly soluble in water. Its sodium and ammonium salts crystallise in large soluble prisms. Its diazo compound is a sparingly soluble greenish yellow precipitate.

**β-Naphthylamine-β-sulphonic acid** (2 : 6).
(*Brönner's acid*)

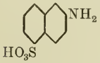


(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 51; **1890**, 130)

*Preparation.*—(1) By heating β-naphthol-β-sulphonic acid S with aqueous ammonia in an autoclave at 180° for several hours (Brönner, Eng. Pat. $3724^{82}$; Am. Pat. 332829). (2) By baking the acid sulphate of β-naphthylamine at 200° to 210° (Liebmann, *Mon. Scien.* **1885**, 1043). (3) Together with about an equal quantity of the δ-acid by heating β-naphthylamine sulphate (1 pt.) with conc. sulphuric acid (3 pts.) at 150° to 160° (Bayer and Duisberg, *Ber.* **20**, 1426; Schultz, *Ber.* **20**, 3158).

*Properties.*—Prismatic needles or silky plates. Its ammonium salt forms very large thin plates with violet fluorescence.

**β-Naphthylamine-γ-sulphonic acid** (2 : 5).
(*Dahl's acid*)



(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 48; **1890**, 128)

*Preparation.*—Together with the *α*-acid (see above) by sulphonating β-naphthylamine at low temperatures. Separated by the solubility of the sodium salt in boiling alcohol of 90%, which leaves the sodium salt of the *α*-acid undissolved (Dahl and Co., Eng. Pats. $7712^{84}$ and $7713^{84}$; Green, *Chem. Soc.* **1889**, 35).

*Properties.*—Long white needles. Sparingly soluble in water. Its diazo compound is a microcrystalline greenish yellow powder.

**β-Naphthylamine-δ-sulphonic acid** (2 : 7).
(*Bayer's acid*)
(*Cassella's acid F*)

(*Constitution:* Weinberg, *Ber.* **20**, 2910)

*Preparation.*—(1) By heating β-naphtholsulphonic acid F (*q.v.*) with 2 pts. of aqueous ammonia (20%) in an autoclave at 250° for six hours (Cassella, Eng. Pat. $12908^{86}$; Am. Pat. 362560; Weinberg, *Ber.* **20**, 2907). (2) Together with the β-acid by heating β-naphthylamine sulphate (1 pt.) with conc. sulphuric acid (3 pts.) at 150° to 160° (Bayer and Co., Eng. Pat. $5646^{86}$). The two acids can only be separated with great difficulty.

*Properties.*—Long fine needles. More soluble in warm water than the β-acid (separation). The calcium salt forms plates (+ $6H_2O$) with blue fluorescence. The diazo compound is an orange-red crystalline powder.

## β-Naphthylaminedisulphonic Acids

$C_{10}H_5(NH_2)(SO_3H)_2$

The following isomers have at present found technical application:—

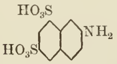
**β-Naphthylamine-disulphonic acid R** or *a*.
(2 : 3 : 6)
(*Amido-R-salt*)

(*Constitution:* Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 12 and 128)

*Preparation.*—By heating β-naphtholdisulphonic acid R with aqueous ammonia in an autoclave at 200° to 250° (Duisberg and Pfitzinger, *Ber.* **22**, 396).

*Properties.*—Its diazo compound forms sparingly soluble small yellow needles. The acid combines with diazo compounds.

**β-Naphthylamine-disulphonic acid G** or γ
(2 : 6 : 8)
(*Amido-G-salt*)



(*Constitution:* A. and W.)

*Preparation.*—(1) By heating β-naphthylaminesulphate (1 pt.) with fuming sulphuric acid of 25% $SO_3$ (3 pts.) at 110° to 140° (Gans and Co., Eng. Pat. $816^{84}$). (2) By heating β-naphtholdisulphonic acid G with aqueous ammonia under pressure. (3) By long action of fuming sulphuric acid of 20% $SO_3$ upon the *a*-monosulphonic acid at ordinary temperatures (Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 128).

*Properties.*—Both the acid and its salts are easily soluble in water. It does not combine with diazo compounds.

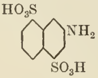
**β-Naphthylamine-disulphonic acid δ** or **F**.
(2 : 3 : 7)

(*Constitution:* A. and W.)

*Preparation.*—By heating the β-naphtholdisulphonic acid δ with aqueous ammonia for 12 hours at 200° (Cassella and Co., Ger. Pat. $46711^{88}$).

*Properties.*—Sparingly soluble in cold water, readily in hot.

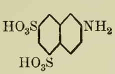
**β-Naphthylamine-disulphonic acid C.**
(2 : 4 : 8)



*Preparation.*—Naphthalenedisulphonic acid (1 : 5) is nitrated in sulphuric acid solution, the mixture poured into salt and water, and the precipitated sodium salt is reduced (Cassella, Ger. Pat. appl. C. 3542).

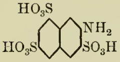
*Properties.*—Concentric prisms. The alkaline solution has a deep blue fluorescence. Its diazo compound forms small yellowish needles, rather sparingly soluble.

**β-Naphthylamine-disulphonic II. of A. and W.**
(2 : 5 : 7)



*Preparation.*—By further sulphonation of β-naphthylaminesulphonic acid γ (Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 128), or of β-naphthylaminesulphonic acid δ (Ger. Pat. 79243; *Ber.* **27**, 1194).

**β-Naphthylamine-trisulphonic acid.**
(2:3:6:8)



*Preparation.*—By heating β-naphtholtrisulphonic acid (2 : 3 : 6 : 8) with aqueous ammonia under pressure at 200° to 250°. Also by further sulphonation of the G-disulphonic acid with fuming sulphuric acid at 120° to 130° (Dressel and Kothe, *Ber.* **27**, 2152).

*Properties.*—Its acid potassium salt forms rather sparingly soluble glistening needles ($+ 1\frac{1}{2}H_2O$).

## SECONDARY AND TERTIARY AMINES AND THEIR DERIVATIVES

### Monomethylaniline

$C_6H_5{\cdot}NH(CH_3)$ *i.e.*

*Preparation.*—By heating aniline hydrochloride or a mixture of aniline and hydrochloric acid with rather more than 1 mol. of methyl alcohol at 180° in an autoclave. The product is basified and fractionated. The commercial product contains 90 to 95% of pure monomethylaniline.

*Properties.*—Colourless oil. B.p. 192°; sp. gr. at 15° = ·976. The salts are uncrystallisable and easily soluble. By nitrous acid it is converted into the oily **nitrosamine** $C_6H_5{\cdot}N(CH_3)(NO)$, which by the action of alcoholic hydrochloric acid undergoes isomeric change into the *p*-**Nitrosomethylaniline** $C_6H_4(NO){\cdot}NHCH_3$.

### Dimethylaniline

$C_6H_5 \cdot N(CH_3)_2$

*Preparation.*—By heating a mixture of aniline (75 pts.), aniline hydrochloride (25 pts.), and methyl alcohol (free from acetone) (75 pts.) in a cast-iron autoclave at 230° to 270°. The product is rectified. The yield is about 120 pts. from the above proportions (Schoop. *Chem. Ztg.* **1887**, 253; *J. Soc. Chem. Ind.* **1887**, 436).

*Properties.*—Colourless oil. B.p. 192°; sp. gr. at 15° = ·96. Solidifies at + ·5° to a crystalline solid.

*Valuation.*—The commercial product is usually nearly pure. It should have the correct specific gravity and distil completely between 190° and 192°. Dissolved in a little ether and mixed with a drop or two of conc. sulphuric acid it should give no precipitate of aniline sulphate. The presence of monomethylaniline is detected and roughly estimated by mixing 5 c.c. of the oil with 5 c.c. of acetic anhydride and observing the rise of temperature: each degree rise indicates about $\frac{1}{2}$% of monomethylaniline. A more accurate method is to distil off the dimethylaniline and excess of acetic anhydride and weigh the residue of methylacetanilide. A good sample should not contain more than $\frac{1}{2}$ to 1% of monomethylaniline.

*Derivatives.*—By fuming sulphuric acid it is converted into the *m*-**sulphonic acid** $C_6H_4N(CH_3)_2{\cdot}SO_3H[1:3]$. By the action of nitrous acid on a cold solution of the hydrochloride, *p*-**Nitrosodimethylaniline** $C_6H_4(NO){\cdot}N(CH_3)_2[1:4]$ is formed, which crystallises in large green plates of m.p. 92°, volatile with steam. The nitroso compound is reduced by zinc dust and hydrochloric acid to *p*-**Amidodimethylaniline** (dimethyl-*p*-phenylenediamine) $C_6H_4(NH_2){\cdot}N(CH_3)_2[1:4]$, a base which forms long white needles of m.p. 41° and b.p. 257°, and is easily soluble in water.

### *m*-Nitrodimethylaniline

$C_6H_4(NO_2)\cdot N(CH_3)_2[1:3]$

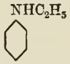
*Preparation.*—Together with the para isomer by nitration of dimethylaniline (135 pts.) dissolved in 100% sulphuric acid (500 pts.) with a mixture of nitric acid of 87% (81 pts.) and 100% sulphuric acid (200 pts.) at 0° to 5°. The product is poured into 5000 pts. of water, filtered from the precipitated para isomer, and the filtrate neutralised with caustic soda. The yield is 135 pts. of meta and 32 pts. of para.

*Properties.*—Large orange-red crystals. M.p. 61°. Easily volatile with steam. On reduction it gives the **Dimethyl-*m*-phenylene diamine**, which boils at 268° to 270°.

*Derivatives.*—By combination with methyl iodide it yields the nitroammonium base which on reduction with zinc and hydrochloric acid gives *m*-**Amidophenyltrimethylammonium chloride.** This compound is employed as "first component" in the preparation of the basic-azo or Janus colours. It forms a characteristic zinc double chloride which crystallises in thick colourless prisms (Eng. Pat. $14494^{95}$).

### Monoethylaniline

$C_6H_5\cdot NH(C_2H_5)$ *i.e.*



*Preparation.*—By heating aniline and aniline hydrochloride or a mixture of aniline and hydrochloric acid with rather more than 1 mol. of ethyl alcohol at 200°.

*Properties.*—Colourless oil. B.p. 204°; sp. gr. at 18° = ·954. Its salts are very soluble in water. The hydrochloride crystallises in needles.

### Diethylaniline

$C_6H_5\cdot N(C_2H_5)_2$

*Preparation.*—By heating aniline hydrochloride and aniline with rather more than 2 mols. of ethyl alcohol (see dimethylaniline). The product contains a considerable quantity of monoethylaniline. It is obtained more readily and in nearly theoretical yield by heating aniline hydrobromide with $2\frac{1}{5}$ mols. of ethyl alcohol at 145° to 150° (Staedel, Ger. Pat. $21241^{82}$).

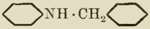
*Properties.*—Colourless oil. B.p. 214°; sp. gr. at 18° = ·939.

*Valuation.*—See dimethylaniline. It should distil to the extent of 90% between 212° and 214°.

*Derivatives.*—By nitrous acid it is converted into *p*-nitrosodiethylaniline, which forms large green prisms of m.p. 84°, sparingly soluble in water. By reduction with zinc dust and hydrochloric acid the nitroso compound yields *p*-**Amidodiethylaniline** $C_6H_4(NH_2)\cdot N(C_2H_5)_2[1:4]$.

### Benzylaniline

$C_6H_5\cdot NH\cdot CH_2\cdot C_6H_5$ *i.e.*



*Preparation.*—By heating aniline with benzyl chloride at 160° (Fleischer, *Ann.* **138**, 225).

*Properties.*—Prisms. B.p. 310°; m.p. 33°.

### Methylbenzylaniline

$C_6H_5\cdot N(CH_3)\cdot CH_2\cdot C_6H_5$

*Preparation.*—By heating equal mols. of monomethylaniline, benzyl chloride, and aqueous caustic soda at 100° (Nölting, *Jahresber.* **1883**, 702).

*Properties.*—Oil. B.p. 308°.

*Sulphonic acid.*—By fuming sulphuric acid at 50° to 60° it is converted into the easily soluble **sulphonic acid** $C_6H_5\cdot N(CH_3)\cdot CH_2\cdot C_6H_4\cdot SO_3H$.

### Ethylbenzylaniline

$C_6H_5\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_5$

Prepared in the same way as the methylbenzylaniline. Oil. B.p. 286° uncorr. at 710 mm.; sp. gr. at 18° = 1·034. By fuming sulphuric acid at 50° to 60° it is converted into the easily soluble **sulphonic acid** $C_6H_5\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_4(SO_3H)$, which is used for the preparation of "Acid green," "Thiocarmine R," "Formyl violet," etc. By nitrous acid it is converted into a **nitroso compound** which forms steel-blue crystals of m.p. 62°.

### Methyl-*o*-toluidine

*Preparation.*—By heating *o*-toluidine (75 pts.) with methyl alcohol (40 pts.) and hydrochloric acid (70 pts.) for a day at 200° to 220°.

*Properties.*—Colourless oil. B.p. 208°; sp. gr. at 15° = 0·973.

### Ethyl-*o*-toluidine

Prepared like the preceding. Oil. B.p. 214°; sp. gr. at 15° = 0·9534.

### Diphenylamine

$(C_6H_5)_2NH$ *i.e.*

*Preparation.*—By heating equal mols. of aniline and aniline hydrochloride in an autoclave for several hours at 220°. The product is boiled with dilute hydrochloric acid to remove unaltered aniline, and the diphenylamine which remains insoluble is distilled. The yield is 60 to 70% of the aniline.

*Properties.*—Monoclinic plates. B.p. 310°; m.p. 54°. Gives a deep blue colour on adding a drop or two of nitric acid to its solution in conc. hydrochloric or sulphuric acid. Is a very weak base, its salts being decomposed by water.

*Valuation.*—The commercial product is a yellow crystalline solid of pleasant smell. It should melt tolerably correctly and contain no oil.

*Derivatives.*—Various derivatives of diphenylamine are employed in the preparation of sulphide colours. They are prepared by the action of dinitrochlorobenzene (1 : 3 : 4), dinitrodichlorobenzene (1 : 3 : 4 : 6), and nitrochlorobenzenesulphonic acid (1 : 4 : 3) upon *p*-phenylenediamine, *p*-amidophenol, and amidosalicylic acid. The most important is the **Dinitrooxydiphenylamine** $[4:3:1]C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4(OH)[1:4]$ obtained from dinitrochlorobenzene (1 : 3 : 4) and *p*-amidophenol.

## Methyldiphenylamine

$(C_6H_5)_2NCH_3$

*Preparation.*—By heating diphenylamine (100 pts.), hydrochloric acid (68 pts.), and methyl alcohol (24 pts.) for 10 hours at 250° in an autoclave (Girard, *Bl.* **23**, 2).

*Properties.*—Oil. B.p. 293°; sp. gr. $\frac{20}{4} = 1{\cdot}0476$.

## Dimethyl-α-naphthylamine

$\alpha C_{10}H_7 \cdot N(CH_3)_2$

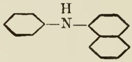
Prepared by heating α-naphthylamine hydrochloride with methyl alcohol at 180°. Oily liquid. B.p. 273° uncorr. (Friedländer and Welmans, *Ber.* **21**, 3123).

## Dimethyl-β-naphthylamine

$\beta C_{10}H_7 \cdot N(CH_3)_2$

Is formed by the action of dimethylamine on β-naphthol. Crystalline solid. B.p. 305°; m.p. 46°.

## Phenyl-α-naphthylamine

$\alpha C_{10}H_7 \cdot NH \cdot C_6H_5$ *i.e.* 

*Preparation.*—By heating α-naphthol with aniline or aniline hydrochloride at a high temperature.

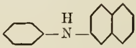
*Properties.*—Colourless plates or needles. B.p. 335° at 238 mm.; m.p. 62°. Is employed for the preparation of "Victoria blue."

## Methylphenyl-α-naphthylamine

$\alpha C_{10}H_7 \cdot N(CH_3)C_6H_5$

Prepared by heating phenyl-α-naphthylamine with methyl alcohol and hydrochloric acid. Its solutions show a blue fluorescence.

## Phenyl-β-naphthylamine

$\beta C_{10}H_7 \cdot NH \cdot C_6H_5$ *i.e.* 

*Preparation.*—By heating β-naphthol (6 pts.) with aniline hydrochloride (5 pts.) for 7 or 8 hours at 170° to 190°. Also by heating β-naphthol (7 pts.) with aniline (5 pts.) for 10 hours at 200° to 210°. The operation is performed in an open vessel (Ger. Pat. $14612^{80}$). The product is boiled with dilute hydrochloric acid to remove unaltered aniline and with caustic soda to remove unaltered naphthol, and the phenyl-β-naphthylamine is dried and distilled.

*Properties.*—Colourless needles or trimetric crystals. B.p. 395°; m.p. 108°. Sparingly soluble in cold solvents, easily in hot, with a blue fluorescence.

## *p*-Tolyl-*α*-naphthylamine

$\alpha C_{10}H_7 \cdot NH \cdot C_6H_4(CH_3)[1:4]$

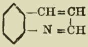
Prepared from *α*-naphthol and paratoluidine in the same way as phenyl-*α*-naphthylamine (Friedländer, *Ber.* **16**, 2084). Short colourless prisms which melt at 79°.

## *p*-Tolyl-*β*-naphthylamine

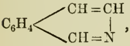
$\beta C_{10}H_7 \cdot NH \cdot C_6H_4(CH_3)[1:4]$

Prepared from *β*-naphthol and paratoluidine in the same way as phenyl-*β*-naphthylamine (Friedländer, *Ber.* **16**, 2078). Colourless plates of m.p. 103°. Sparingly soluble in alcohol.

## Quinoline

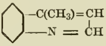
$C_9H_7N$ *i.e.* 

*Preparation.*—By heating a mixture of aniline (216 pts.), nitrobenzene (144 pts.), glycerine (600 pts.), and sulphuric acid (600 pts.), for a day at about 125°, then at 180° to 200° till the reaction is complete. The mixture is diluted with water, and the excess of nitrobenzene is boiled off; it is then made alkaline with soda, and the quinoline is distilled off and freed from aniline by treatment in acid solution with potassium bichromate or sodium nitrite. The yield is about 70% of the theoretical (Skraup, *Mon. f. Chem.* **1**, 317; Königs, *Ber.* **13**, 911).

For the preparation of colouring matters it is usually obtained from the basic portion of coal tar oils, and contains, in addition to quinoline, **quinaldine** and **isoquinoline**  $C_6H_4\left\langle\begin{matrix} CH=CH \\ | \\ CH=N \end{matrix}\right.$, to the presence of which the formation of some of the derived colours is due.

*Properties.*—Colourless oil. B.p. 238°; sp. gr. at 20° = 1·0947. It forms easily soluble salts. The picrate crystallises in yellow needles of m.p. 203°.

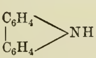
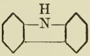
## Quinaldine (*Methylquinoline*)

$C_{10}H_9N$ *i.e.* 

*Preparation.*—By boiling a mixture of aniline (100 pts.), paraldehyde (150 pts.), conc. hydrochloric acid (200 pts.), and aluminium or zinc chloride (5 pts.) for 4 or 5 hours (Eng. Pat. $956^{83}$). Also by melting with zinc chloride the condensation product obtained by the action of paraldehyde (5 pts.) upon a cold solution of aniline hydrochloride (8 pts.) in water (16 pts.) (Eng. Pat. $4207^{83}$). The base is distilled off with steam after making alkaline. The latter method gives the best yield.

*Properties.*—Colourless oil. B.p. 246°. Chiefly used for the preparation of "Quinoline yellow."

## Carbazole

$C_{12}H_9N$ *i.e.*  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>NH$ or 

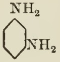
*Preparation.*—(1) Occurs in crude anthracene, from which it is extracted by boiling with strong aqueous caustic potash until all the water has evaporated. The layer of anthracene is removed, and the caustic potash is dissolved in water by which the carbazol potassium $C_{12}H_8NK$ which it contains is decomposed and the carbazol separates. It is purified by crystallisation from alcohol or toluene. (2) By boiling thiodiphenylamine $C_6H_4{<}\substack{S\\NH}{>}C_6H_4$ (obtained by heating diphenylamine with sulphur) with copper powder (Goske, *Ber.* **20**, 233).

*Properties.*—Colourless plates or tables. B.p. 351° corr.; m.p. 238°. Sublimes readily. Its sulphuric acid solution gives a blue colour with a trace of nitric or nitrous acid. The picrate forms red needles of m.p. 182°, slightly soluble in cold alcohol or benzene.

## DIAMINES AND THEIR SULPHONIC ACIDS

### *m*-Phenylene diamine (*m-Diamidobenzene*)

$C_6H_4(NH_2)_2[1:3]$ *i.e.*



*Preparation.*—By reduction of *m*-dinitrobenzene with iron and hydrochloric acid. The operation is performed in a large iron "reducer" (see Aniline), which is charged with 200 pts. of dinitrobenzene and 200 pts. of water. The mixture is raised to the boil by blowing in steam, 16 pts of hydrochloric acid are put in, and then 420 to 450 pts. of ground cast-iron borings are slowly added, keeping up a vigorous reaction. When the reduction is complete, sodium carbonate is added until slightly alkaline, the mass is boiled up with 800 to 1000 pts. of water, and the solution of the phenylene diamine filtered from the iron sludge, which is again extracted with water. This solution is either used direct (*e.g.* for Bismarck brown or Chrysoidine), or is neutralised with hydrochloric acid and evaporated. On adding strong caustic soda solution to the concentrated solution of the hydrochloride the base separates as an oil, which rises to the surface and solidifies on cooling. It is purified by distillation.

*Properties.*—Colourless crystalline solid which quickly becomes coloured in the air. B.p. 287°; m.p. 83°. Easily soluble in water. With sodium nitrite and acetic acid it gives a brown colour, even in very dilute solution.

*Derivatives.*—The **Nitro-*m*-phenylene diamine** $C_6H_3(NH_2)_2NO_2[1:3:4]$ is obtained by nitration and saponification of the diacetyl derivative or by heating *p*-nitranilinesulphonic acid with aqueous ammonia under pressure at 180° (Fr. Pat. $314468^{1901}$).

The ***m*-Phenylene diamine disulphonic acid** is prepared by heating the diamine hydrochloride with fuming sulphuric acid of 40% $SO_3$ (5 pts.) at 100° to 120° for several hours. Colourless crystalline powder (Eng. Pat. $14678^{93}$).

### *p*-Phenylene diamine (*p-Diamidobenzene*)

$C_6H_4(NH_2)_2[1:4]$ *i.e.*

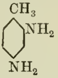
*Preparation.*—By reduction of *p*-nitraniline or amidoazobenzene with iron and hydrochloric acid.

*Properties.*—Colourless crystals. B.p. 267°; m.p. 140°. Easily soluble in water. By oxidising agents it is converted into quinone. When oxidised in presence of aniline or *o*-toluidine it yields blue indamines, which on boiling are converted into safranines.

*Derivatives.*—The **acetyl derivative** $C_6H_4(NH_2)NH{\cdot}CO{\cdot}CH_3$ is formed by careful reduction of *p*-nitracetanilide, and crystallises from water in needles of m.p. 191°.

### *m*-Tolylene diamine (*Diamidotoluene*)

$C_6H_3(CH_3)(NH_2)_2[1:2:4]$ *i.e.*



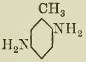
*Preparation.*—By reduction of *m*-dinitrotoluene with iron and hydrochloric acid in the same way as *m*-phenylene diamine (*q.v.*). The base crystallises from the strong aqueous solution in large prismatic crystals.

*Properties.*—Rhombic prisms. B.p. 280°; m.p. 99°. Easily soluble in hot water. With nitrous acid it reacts like *m*-phenylene diamine.

*Sulphonic acid.*—Fuming sulphuric acid in excess converts it into the monosulphonic acid $C_6H_2(CH_3)(NH_2)_2SO_3H$.

### *p*-Tolylene diamine

$C_6H_3(CH_3)(NH_2)_2[1:2:5]$ *i.e.*



*Preparation.*—By reduction of amidoazotoluene (from *o*-toluidine) with zinc dust and hydrochloric acid (Nietzki, *Ber.* **10**, 1158).

*Properties.*—Colourless tables. B.p. 274°; m.p. 64°. Easily soluble in water. Oxidised in presence of aniline or orthotoluidine it gives blue indamines, which on boiling are converted into safranines.

### Dimethyl-*p*-phenylene diamine

$C_6H_4(NH_2)\ N(CH_3)_2[1:4]$

*Preparation.*—A solution of sodium nitrite (7 pts.) in water (20 pts.) is slowly run into a solution of dimethylaniline (10 pts.) in hydrochloric acid (50 pts.) and water (60 pts.) mixed with chopped ice (40 pts.). The nitrosodimethylaniline obtained is reduced by slowly adding zinc dust to the mixture until the yellow colour of the solution has completely disappeared. It is then filtered, and the filtrate after concentration is mixed with caustic soda and extracted with benzene.

*Properties.*—Long needles. B.p. 257°; m.p. 41°. Very soluble in water.

*Thiosulphonic acid* $C_6H_3(NH_2)(S{\cdot}SO_3H)N(CH_3)_2[1:2:4]$.—Obtained by oxidation of the diamine in presence of sodium thiosulphate with sodium bichromate and acetic acid. It forms sparingly soluble white crystals.

### Diphenyl-*m*-phenylene diamine

$C_6H_4(NHC_6H_5)_2[1:3]$

*Preparation.*—By heating resorcin with aniline in presence of calcium chloride and a little zinc chloride at 210° (Calm, *Ber.* **16**, 2795).

*Properties.*—Flat needles. M.p. 95°. Insoluble in water, sparingly soluble in cold alcohol.

### Di-*p*-tolyl-*m*-phenylene diamine

$C_6H_4(NHC_7H_7)_2[1:3]$

Prepared in the same way from resorcin and *p*-toluidine. Long needles. M.p. 137°. (Hatschek and Zega, *Jour. pr. Chem.* [2] **33**, 218.)

### *β*-Dinaphthyl-*m*-phenylene diamine

$C_6H_4(NHC_{10}H_7\beta)_2[1:3]$

*Preparation.*—By heating *m*-phenylene diamine (108 pts.) with *β*-naphthol (320 pts.) at 260° to 300° for several hours. The melt is extracted with hot caustic soda, then ground and extracted with alcohol. The residual dinaphthylphenylene diamine is nearly pure.

*Properties.*—Needles. M.p. 191°. Nearly insoluble in most solvents.

### Diphenyl-(2 : 7)-naphthylene diamine

$C_{10}H_6(NHC_6H_5)[2:7]$ *i.e.*

*Preparation.*—By heating (2 : 7)-dioxynaphthalene (16 pts.) with aniline (37 pts.) and aniline hydrochloride (13 pts.) at 140° to 180° (Durand and Huguenin, Eng. Pat. 14283$^{86}$; Ger. Pat. 40886$^{86}$).

*Properties.*—Silvery plates. M.p. 164°. Sparingly soluble in alcohol.

### Di-*p*-tolyl-(2 : 7)-naphthylene diamine

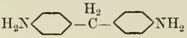
$C_{10}H_6(NHC_7H_7)_2[2:7]$

*Preparation.*—By heating (2 : 7)-dioxynaphthalene with *p*-toluidine and *p*-toluidine hydrochloride (Durand and Huguenin, *loc. cit.*).

*Properties.*—Fine needles. M.p. 237°. Nearly soluble in alcohol.

### *pp*-Diamidodiphenylmethane

$[4:1]NH_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NH_2[1:4]$ *i.e.*



*Preparation.*—By heating formaldehydeanilide $C_6H_5 \cdot N:CH_2$ (obtained by combination of formaldehyde with aniline) with aniline hydrochloride and aniline at 100° (Meister, Lucius, and Brüning, Eng. Pat. 20678$^{89}$; Ger. Pats. 53937$^{89}$ and 55565$^{89}$).

*Properties.*—Silvery plates (from water) or large crystals (from benzene). M.p. 86°. The sulphate is tolerably soluble in water, sparingly in alcohol.

### *pp*-Diamidoditolylmethane

$[4:1]NH_2 \cdot C_7H_6 \cdot CH_2 \cdot C_7H_6 \cdot NH_2[1:4]$

*Preparation.*—From formaldehyde and *o*-toluidine in the same way as the preceding (Meister, Lucius, and Brüning).

*Properties.*—Glistening plates. M.p. 149°. Its sulphate is easily soluble.

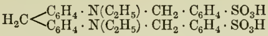
### *pp*-Tetramethyldiamidodiphenylmethane

$[4:1](CH_3)_2N \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot N(CH_3)_2[1:4]$

*Preparation.*—By heating dimethylaniline (254 pts.) with hydrochloric acid of sp. gr. 1·19 (254 pts.) and formaldehyde of 40% (75 pts.) for 12 hours at 100° (*Ber.* **35**, 358).

*Properties.*—Glistening plates. M.p. 90°; b.p. 390°.

### *pp*-Diethyldibenzyldiamidodiphenylmethanedisulphonic Acid



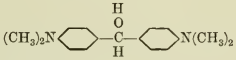
$$H_2C<\genfrac{}{}{0pt}{}{C_6H_4\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3H}{C_6H_4\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3H}$$

*Preparation.*—By heating ethylbenzylanilinesulphonic acid with an aqueous solution of formaldehyde (Cassella and Co., Eng. Pat. 857[91]; Geigy and Co., Ger. Pat. 59811[90]).

*Properties.*—By oxidation with potassium bichromate or lead peroxide it is converted into the corresponding **carbinol** $(OH)HC\{C_6H_4\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3H\}_2$.

### *pp*-Tetramethyldiamidodiphenylcarbinol (*tetramethyldiamidobenzhydrol*)

$[4:1](CH_3)_2N\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot N(CH_3)_2[1:4]$ *i.e.*



*Preparation.*—A solution of tetramethyldiamidodiphenylmethane (20 pts.) in water (50 pts.) and hydrochloric acid (2 mols.) is diluted with 1600 pts. of water, mixed with acetic acid glac. (9·4 pts.) and oxidised at 0° under rapid agitation with a thin paste of lead peroxide (containing 18·8 pts.). The lead is removed by adding Glauber salt (26 pts.) and the base precipitated from the filtrate by caustic soda (Möhlau and Heinze, *Ber.* **35**, 359).

*Properties.*—Colourless triclinic prisms. M.p. 96°. Forms colourless solutions in benzene and ether, blue in alcohol and acetic acid.

### *p*-Amido-benzyl-dimethylamine

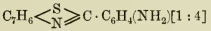
$$C_6H_4(NH_2)\cdot CH_2\cdot N(CH_3)_2[1:4]$$

*Preparation.*—By the reaction of dimethylamine upon *p*-nitrobenzyl chloride (or the crude nitration product of benzyl chloride) and reduction.

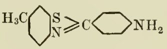
*Properties.*—Thick colourless oil. B.p. a little above 300°. Soluble in water. Employed for the preparation of basic azo dyestuffs (Cassella and Co., Eng. Pat. 22572[92]; *Ber.* **28**, 1140).

## PRIMARY AMINES AND DIAMINES USED IN THE PREPARATION OF SUBSTANTIVE COTTON COLOURS

### Dehydrothio-*p*-toluidine (*Amidobenzenyl-o-amidothiocresol*)



$C_7H_6<\genfrac{}{}{0pt}{}{S}{N}\geqslant C\cdot C_6H_4(NH_2)[1:4]$ *i.e.*



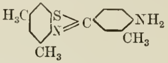
*Preparation.*—Together with primuline base, by heating paratoluidine (2 mols.) with sulphur (4 atoms) at 180° to 250° till the evolution of hydric sulphide has ceased. It is separated from the primuline base by extraction with solvents or by distillation in vacuo (Green, *J. Chem. Soc.* **1889**, 228).

*Properties.*—Long yellowish iridescent needles. M.p. 191° uncorr.; b.p. 434° uncorr. at 766 mm. Very slightly soluble in water, moderately in alcohol. Its solutions have a violet-blue fluorescence. Its salts are decomposed by water. When heated with sulphur it yields **Primuline base** $C_6H_3(CH_3)<\genfrac{}{}{0pt}{}{S}{N}\geqslant C\cdot C_6H_3<\genfrac{}{}{0pt}{}{S}{N}\geqslant C\cdot C_6H_3<\genfrac{}{}{0pt}{}{S}{N}\geqslant C\cdot C_6H_4\cdot NH_2$ with evolution of hydric sulphide. Its diazo compound is easily soluble.

*Sulphonic acid* $C_6H_3(CH_3)<^{S}_{N}\geqslant C\cdot C_6H_3(NH_2)SO_3H$. Prepared by sulphonating the base with fuming sulphuric acid at 40° to 50°. It crystallises in yellow needles ($+H_2O$) or orange leaflets ($+2H_2O$), insoluble in water. The ammonium salt forms sparingly soluble white plates ($+H_2O$). The copper salt is a brownish red insoluble precipitate.

## **Dehydrothioxylidine** (*Amidotoluenyl-o-amidothioxylenol*)

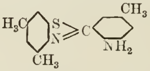
$C_6H_2(CH_3)_2<^{S}_{N}\geqslant C\cdot C_6H_3(CH_3)NH_2$ *i.e.*



*Preparation.*—By heating metaxylidine (2 mols. or more) with sulphur (4 atoms) at 185° to 190° as long as hydric sulphide is evolved. The product is distilled in vacuo and separated from the isodehydrothioxylidine, formed simultaneously, by extraction with hydrochloric acid of 30% in which the latter base is insoluble (*Ber.* **20**, 582; *J. Soc. Chem. Ind.* **1897**, 730; **1902**, 469).

*Properties.*—Yellowish white prisms. M.p. 107°; b.p. 283° at 14 mm. Very soluble in hot alcohol, sparingly in cold, insoluble in water. Its salts are decomposed by water. The diazo compound is easily soluble. By fuming sulphuric acid at 50° it is converted into the **sulphonic acid**, a sparingly soluble yellow precipitate, the salts of which are colourless.

## **Isodehydrothioxylidine**



Prepared as above. Yellow needles. M.p. 121°

## **Benzidine** (*Di-p-amidodiphenyl*)

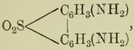
$$\begin{array}{l}C_6H_4(NH_2)[1:4]\\ |\\ C_6H_4(NH_2)[1:4]\end{array}\quad i.e.$$

*Preparation.*—Nitrobenzene is reduced with zinc dust and caustic soda in an iron vessel provided with a rapid agitator. After distilling off any aniline which is formed with steam, the product is run out, and the zinc hydrate is removed by treatment with cold dilute hydrochloric acid. The hydrazobenzene $C_6H_5\cdot NH\cdot NH\cdot C_6H_5$ which is left insoluble is converted into benzidine by boiling with hydrochloric acid, the solution is filtered, and the benzidine precipitated as sulphate by the addition of sulphuric acid or sodium sulphate. The base is obtained by decomposing the sulphate with caustic soda, and distilling in vacuo. For the preparation of cotton azo colours the sulphate is usually diazotised direct, without drying.

*Properties.*—Large colourless silky plates. M.p. 122°; b.p. above 360°. Somewhat soluble in hot water, very slightly in cold. Dilute solutions give dark blue precipitates on the addition of potassium bichromate or potassium ferricyanide.

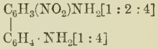
*Derivatives.*—By nitrous acid it is converted into salts of **Tetrazodiphenyl** $\begin{array}{l}C_6H_4\text{-}N:N\cdot OH\\ |\\ C_6H_4\text{-}N:N\cdot OH\end{array}$, which combine with the sulphonic acids of phenols and amines to form azo colours, dyeing cotton from an alkaline bath without a mordant.

By the action of sulphuric acid, ordinary or fuming, under different conditions it is converted into **Benzidine-mono-** or **di-sulphonic acid** or into **Benzidinesulphone**



, and its **mono-** and **di-sulphonic acid** (Griess and Duisberg, *Ber.* **22**, 2459).

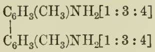
By nitration in sulphuric acid solution it yields *o*-**Nitrobenzidine**



$\begin{array}{l} C_6H_3(NO_2)NH_2[1:2:4] \\ | \\ C_6H_4 \cdot NH_2[1:4] \end{array}$

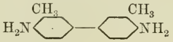
(Eng. Pat. $13475^{92}$).

## **Tolidine** (*Di-p-amidoditolyl*)



$\begin{array}{l} C_6H_3(CH_3)NH_2[1:3:4] \\ | \\ C_6H_3(CH_3)NH_2[1:3:4] \end{array}$

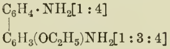
*i.e.*



*Preparation.*—By reduction of *o*-nitrotoluene with zinc dust and caustic soda, and conversion of the hydrazotoluene $C_6H_4(CH_3) \cdot NH \cdot NH \cdot C_6H_4(CH_3)$ into tolidine by boiling with hydrochloric acid (see Benzidine).

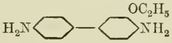
*Properties.*—Glistening plates. M.p. 128°. Sparingly soluble in water, easily in alcohol. Its sulphate is sparingly soluble, though more soluble than benzidine sulphate.

## **Ethoxybenzidine** (*Di-p-amidoethoxydiphenyl*)



$\begin{array}{l} C_6H_4 \cdot NH_2[1:4] \\ | \\ C_6H_3(OC_2H_5)NH_2[1:3:4] \end{array}$

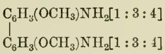
*i.e.*



*Preparation.*—Benzeneazophenetolsulphonic acid $C_6H_5 \cdot N_2 \cdot C_6H_3(OC_2H_5)SO_3H[1:2:5]$, obtained by combining diazobenzene chloride with phenol-*p*-sulphonic acid and etherifying the product by heating with ethyl bromide, is reduced in aqueous solution with stannous chloride and hydrochloric acid, or with zinc dust and caustic soda followed by hydrochloric acid. The ethoxybenzidinemonosulphonic acid thus obtained is heated in an autoclave with water at 170° (Cassella and Co., Eng. Pat. $14464^{87}$; Am. Pat. 380067; Weinberg, *Ber.* **20**, 3171).

*Properties.*—Glistening flat needles. M.p. 135°. Sparingly soluble in water, easily in alcohol. The sulphate forms colourless prisms, sparingly soluble in water, easily in hydrochloric acid.

## **Dianisidine** (*Di-p-amidodimethoxydiphenyl*)



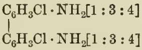
$\begin{array}{l} C_6H_3(OCH_3)NH_2[1:3:4] \\ | \\ C_6H_3(OCH_3)NH_2[1:3:4] \end{array}$

*i.e.*

*Preparation.*—The methyl ether of *o*-nitrophenol $C_6H_4(NO_2)OCH_3$ is reduced by zinc dust and caustic soda to the hydrazo compound $C_6H_4(OCH_3)NH \cdot NHC_6H_4(OCH_3)$, which is then boiled with hydrochloric acid (see Paul, *J. Soc. Chem. Ind.* **1897**, 63).

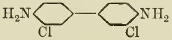
*Properties.*—White plates. M.p. 137°.

## **Dichlorobenzidine**



$\begin{array}{l} C_6H_3Cl \cdot NH_2[1:3:4] \\ | \\ C_6H_3Cl \cdot NH_2[1:3:4] \end{array}$

*i.e.*



Prepared by chlorination of diacetylbenzidine and saponification of the product (Levinstein, Eng. Pat. $25725^{96}$). Crystalline solid. M.p. 133°.

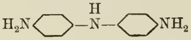
### **Diamidodiphenic Acid** (*Benzidinedicarboxylic Acid*)

$$\begin{array}{l} C_6H_3(CO_2H)NH_2[1:3:4] \\ | \\ C_6H_3(CO_2H)NH_2[1:3:4] \end{array}$$ *i.e.*

Prepared by reducing *o*-nitrobenzoic acid (20 pts.) at 100° with zinc dust (20 pts.) and caustic soda lye of 30% (21 pts.) and filtering the product into a mixture of hydrochloric acid (33 pts.) and water (20 pts.), which is then boiled. On cooling, the hydrochloride separates (*Ber.* **7**, 1612; **25**, 2797). Also from *m*-nitrobenzaldehyde by boiling with caustic soda, reducing with zinc dust, and acidifying (Ger. Pat. 69541).

### *pp*-**Diamidodiphenylamine**

$HN(C_6H_4 \cdot NH_2)_2[1:4]$ *i.e.*



*Preparation.*—By reducing with zinc dust and hydrochloric acid, the blue indamine obtained by oxidation of equal mols. of the hydrochlorides of aniline and *p*-phenylenediamine in aqueous solution at 0° by means of potassium bichromate (Nietzki, *Ber.* **16**, 474).

*Properties.*—Plates. M.p. 158°. Its sulphate forms thin needles, sparingly soluble in water.

### **Diamidoazoxytoluene** (*Azoxytoluidine*)

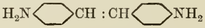
$[1:2:4]C_6H_3(CH_3)(NH_2) \cdot N_2O \cdot C_6H_3(NH_2)(CH_3)[4:2:1]$

*Preparation.*—By alkaline reduction of *p*-nitro-*o*-toluidine (Limpricht and Graeff, *Ber.* **18**, 1404), preferably by means of an alkaline solution of sodium stannite (Green and Lawson, *J. Chem. Soc.* **1891**, 1015).

*Properties.*—Yellow needles or orange prisms. M.p. 168° uncorr. Insoluble in water. Its salts are moderately soluble in water, sparingly in presence of hydrochloric acid. The hydrochloride forms small colourless needles.

### *p*-**Diamidostilbene** (*Diamidodiphenylethylene*)

$[4:1]C_6H_4(NH_2) \cdot CH:CH \cdot C_6H_4(NH_2)[1:4]$ *i.e.*



*Preparation.*—By reduction of dinitrostilbene obtained by adding aqueous caustic soda to a warm alcoholic solution of *p*-nitrobenzyl chloride $C_6H_4(NO_2)CH_2Cl$ (Actienges. f. Anilinfabrikn., Eng. Pat. $7284^{86}$).

*Properties.*—Colourless needles or plates. M.p. 227°. Its sulphate and hydrochloride are sparingly soluble.

### **Diamidostilbenedisulphonic Acid**

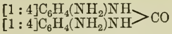
$[4:2:1]C_6H_3(NH_2)(SO_3H) \cdot CH:CH \cdot C_6H_3(SO_3H)(NH_2)[1:2:4]$

*Preparation.*—*p*-Nitrotoluenesulphonic acid $C_6H_3(CH_3)(SO_3H)(NO_2)[1:2:4]$, obtained by sulphonating *p*-nitrotoluene with fuming sulphuric acid, is boiled with aqueous caustic soda, and the yellow condensation-product which is formed is reduced by adding zinc dust and boiling till permanently decolorised, then filtered and acidified (Leonhardt and Co., Eng. Pat. $4387^{86}$; Am. Pat. 360553; Bender and Schultz, *Ber.* **19**, 3235).

Also by reduction of dinitrostilbenedisulphonic acid with ferrous hydrate and ammonia (Green and Wahl, Eng. Pat. $5351^{97}$; *Ber.* **30**, 3100).

*Properties.*—Yellowish microscopic needles. Nearly insoluble in water. Its salts are easily soluble.

### *pp*-Diamidodiphenylurea

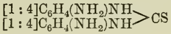


$$\begin{matrix}[1:4]C_6H_4(NH_2)NH \\ [1:4]C_6H_4(NH_2)NH\end{matrix}\!\!>\!CO$$

*Preparation.*—By reduction of tetranitrodiphenylurea (Fleischer and Nemes, *Ber.* **10**, 1296).

*Properties.*—Plates. Soluble in hot water, sparingly in cold.

### *pp*-Diamidodiphenylthiourea



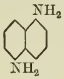
$$\begin{matrix}[1:4]C_6H_4(NH_2)NH \\ [1:4]C_6H_4(NH_2)NH\end{matrix}\!\!>\!CS$$

*Preparation.*—By boiling an alcoholic solution of *p*-phenylenediamine (432 pts.) with carbon disulphide (76 pts.). On cooling, the base separates out (Ger. Pat. 58204).

*Properties.*—Crystalline solid. M.p. 195°.

### 1:5-Diamidonaphthalene (*Naphthylenediamine*)

$C_{10}H_6(NH_2)_2$ *i.e.*

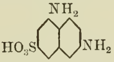


*Preparation.*—(1) By reduction of *a*-dinitronaphthalene of m.p. 216° (Zinin, *Ann.* **52**, 361; **85**, 329; Aguar, *Ber.* **7**, 306). (2) By heating (1 : 5) dioxynaphthalene with aqueous ammonia at 150° to 300° (Ewer and Pick, *Ann.* **247**, 361).

*Properties.*—Colourless prisms. M.p. 190°. Soluble in hot water, nearly insoluble in cold. Sublimes. Ferric chloride gives a bluish violet precipitate. The sulphate is almost insoluble in dilute sulphuric acid.

### 1:3-Diamidonaphthalenesulphonic Acid

$C_{10}H_5(NH_2)_2SO_3H[1:3:6]$ *i.e.*

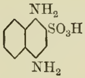


*Preparation.*— By heating the *a*-naphthylamine- or *a*-naphthol-disulphonic acid (1 : 3 : 6) with aqueous ammonia under pressure at 160° to 180° (Kalle and Co., Eng. Pat. $9103^{95}$; Am. Pat. 587757).

*Properties.*—Small needles. Rather sparingly soluble in water.

### 1:4-Diamidonaphthalenesulphonic Acid

$C_{10}H_5(NH_2)_2SO_3H[1:4:2]$ *i.e.*



*Preparation.*—From *a*-naphthylaminesulphonic acid (1 : 2) by combination with diazobenzene and reduction (Levinstein, Eng. Pat. $2946^{96}$).

*Properties.*—Sparingly soluble in water. In alkaline solution it is oxidised by the air to a yellow crystalline substance having a magnificent greenish yellow fluorescence.

*Acetyl Derivative.*—See Eng. Pat. $17064^{96}$ (Levinstein).

### (1:4)-Diamidonaphthalenesulphonic Acid

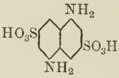
$C_{10}H_5(NH_2)_2SO_3H$ [1 : 4 : 6 or 7]

*Preparation.*—From *a*-naphthylaminesulphonic acid (1 : 6) or (1 : 7) by combination with diazobenzene and reduction (Levinstein, Eng. Pat. $12119^{98}$; Am. Pat. 700574).

*Properties.*—Silvery needles. Sparingly soluble in water. Its acetyl compound, formed by boiling with 60% acetic acid and sodium acetate, is diazotisable without decomposition.

### 1:5-Diamidonaphthalenedisulphonic Acid

$C_{10}H_4(NH_2)_2(SO_3H)_2$[1 : 5 : 3 : 7] *i.e.*

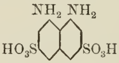


*Preparation.*—By dinitration and reduction of (2 : 6)-naphthalenedisulphonic acid (Cassella and Co., Eng. Pat. $15346^{90}$).

*Properties.*—The acid is nearly insoluble in water. The sodium salt dissolves in 21 pts. of water at 15°. It gives a sparingly soluble light yellow tetrazo-compound. It combines with diazo compounds.

### 1:8-Diamidonaphthalenedisulphonic Acid

$C_{10}H_4(NH_2)_2(SO_3H)_2$[1 : 8 : 3 : 6] *i.e.*



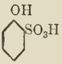
*Preparation.*—By dinitration and reduction of (2 : 7)-naphthalenedisulphonic acid (Cassella and Co., Eng. Pat. $15346^{90}$).

*Properties.*—Long thin needles; easily soluble in hot water. Its sodium salt forms long pointed needles, soluble in 55 pts. of water at 15°. It does not yield a tetrazo compound, but combines with diazo compounds. Heating with dilute sulphuric acid at 120° converts it into amidonaphtholdisulphonic acid ("acid H").

## PHENOLS AND THEIR SULPHONIC AND CARBOXYLIC ACIDS

### *o*- and *p*-Phenolsulphonic Acids $C_6H_4(OH)SO_3H$

*i.e.*



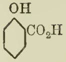
and

*Preparation.*—The two isomers are formed by the action of conc. sulphuric acid upon phenol (equal mols.). At ordinary temperatures the *o*-sulphonic acid is chiefly formed; at 100° to 110° the product is almost exclusively the *p*-sulphonic acid.

*Properties.*—The para acid forms a syrup. The salts of the ortho acid are more soluble than those of the para.

## **Salicylic Acid** (*Phenol-o-carboxylic Acid or o-Oxybenzoic Acid*)

$C_6H_4(OH)CO_2H$ *i.e.*



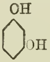
*Preparation.*—Dry sodium phenol (from phenol and caustic soda) is submitted to the action of dry carbonic acid at the ordinary temperature as long as the gas is absorbed. The product, which is sodium phenyl carbonate $C_6H_5\ O\cdot CO_2Na$, is heated in a closed vessel at 120° to 130° for several hours, when it undergoes isomeric change and is converted quantitatively into sodium salicylate. The latter is dissolved in water, and the salicylic acid is precipitated by the addition of a mineral acid (Schmitt, Eng. Pat. $10167^{84}$; Am. Pat. 334290).

*Properties.*—Fine white needles. M.p. 156°. Is volatile with steam. Sparingly soluble in cold water (1 pt. in 1800 pts.), easily in hot water. Ferric chloride gives a violet coloration. Its salts are easily soluble. It combines with diazo compounds.

*Valuation.*—It should dissolve in pure sulphuric acid to a colourless solution (not yellow). It should melt correctly and leave no residue on ignition. Higher homologues are detected and estimated by titration with standard caustic soda or baryta, or by distillation with lime and examination of the phenol obtained (Ewell and Prescott, *Analyst*, **13**, 208, 237).

## **Resorcinol** (*m-Dioxybenzene*)

$C_6H_4(OH)_2[1:3]$ *i.e.*



*Preparation.*—Benzene is converted into the disulphonic acid $C_6H_4(SO_3H)_2$ by heating it with fuming sulphuric acid or with conc. sulphuric and sodium sulphate. The product is limed and converted into the sodium salt, and the latter is fused with twice its weight of caustic soda at 270° for several hours. The melt is dissolved in water, neutralised with hydrochloric acid, and the resorcin extracted by shaking the liquor with ether. The crude resorcin left after distilling off the ether is purified by crystallisation from benzene or by distillation in vacuo (Mühlhäuser, *Ding. pol. J.* **263**, 154; *J. Soc. Chem. Ind.* 1887, 284).

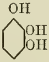
*Properties.*—Colourless rhombic crystals. M.p. 118°; b.p. 277°. Very soluble in water and alcohol, insoluble in chloroform and carbon disulphide. Sweet taste. Gives a dark violet colour with ferric chloride. Heated with dibasic acids, such as phthalic, succinic, or tartaric acid, it gives yellow colours with brilliant green fluorescence.

*Estimation.*—By treatment with standard bromine water, and titration of the excess of bromine with potassium iodide and sodium thiosulphate.

*Valuation.*—The commercial product is usually nearly chemically pure. It should be light in colour, dissolve completely in ether, and have nearly the correct melting point. Water is estimated by drying over sulphuric acid.

## **Pyrogallol** (*Pyrogallic Acid or c-Trioxybenzene*)

$C_6H_3(OH)_3[1:2:3]$ *i.e.*



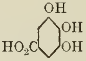
*Preparation.*—(1) By heating gallic acid with 3 times its weight of water in an autoclave at 200° to 210° (De Luynes and Esperandieu, *Ann.* (1866) **138**, 60). (2) By heating gallic acid dissolved in 3 times its weight of glycerine in an open vessel at 190° to 200°.

as long as carbonic acid is evolved (Thorpe, *Ber.* **14**, 1001). The yield by either method is theoretical.

*Properties.*—White needles or thin plates. M.p. 132° uncorr.; b.p. 210°. Easily soluble in water (1 in $2\frac{1}{4}$ at 13°). Its alkaline solution rapidly absorbs oxygen from the air and becomes dark in colour.

## **Gallic Acid** (*Trioxybenzoic Acid*)

$C_6H_2(OH)_3CO_2H$ [1 : 2 : 3 : 5] *i.e.*



*Preparation.*—Finely powdered gall-nuts (preferably Chinese galls) are moistened with water and allowed to ferment in a warm place with addition of some beer yeast. The product is extracted with boiling water and filtered, the gallic acid crystallising from the filtrate on cooling.

*Properties.*—Silky needles ($+H_2O$). Melts with decomposition at 220° to 240°. 1 pt. dissolves in 130 pts. of cold water, in 3 pts. of boiling water. Ferric chloride gives a blue-black coloration. It is not precipitated by solutions of gelatine (distinction from tannic acid).

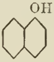
*Ethylether.*—By heating gallic acid with alcohol and hydrochloric acid. Prisms ($+2\frac{1}{2}H_2O$). M.p. (anhydrous) 158°.

*Amide* (Gallamic acid).—Prepared by boiling tannin (2 pts.) with a strong solution of acid ammonium sulphite (1 to 2 pts.) and aqueous ammonia (4 to 6 pts.) until excess of ammonia is driven off. On cooling, the amide crystallises out. Large plates ($+1\frac{1}{2}H_2O$). Sparingly soluble in cold water. M.p. (anhydrous) 243°.

*Anilide* (Gallanilic acid).—Prepared by heating tannin with aniline at 150°. Plates ($+2H_2O$). M.p. 207°. Easily soluble in boiling water.

## *a*-**Naphthol** (*a-Oxynaphthalene*)

$C_{10}H_7 \cdot OH$ *i.e.*



*Preparation.*—(1) By fusing sodium *a*-naphthalene sulphonate (1 pt.) with caustic soda (2 or 3 pts.) and a little water at 270° to 300° in an iron pot provided with a mechanical stirrer. The sodium naphtholate which rises to the surface is separated from the lower layer of caustic soda and sodium sulphite, dissolved in water, and decomposed with hydrochloric, or better with carbonic acid. The precipitated naphthol is dried and distilled.

(2) By heating *a*-naphthylamine sulphate or hydrochloride (1 pt.) with water (5 pts.) at 200° in an autoclave for 3 or 4 hours (Meister, Lucius, and Brüning, Eng. Pat. $14301^{92}$). The product is purer than that from the previous method.

*Properties.*—Colourless glistening needles. M.p. 94°; b.p. 280°. Slightly soluble in hot water, nearly insoluble in cold. Volatile with steam. Dissolves readily in caustic alkalies. With chloride of lime it gives a dark violet colour.

*Valuation.*—The commercial product forms white crystalline lumps. It usually contains 5 or 10% of *β*-naphthol, which can be estimated approximately by taking the melting point and comparing with that of standard mixtures of pure *a*- and *β*-naphthol. It should dissolve in caustic soda with very little residue.

## α-Naphtholcarboxylic Acid (*α-Oxy-β-naphthoic Acid*)

$C_{10}H_6(OH)CO_2H[1:2]$

*Preparation.*—From sodium α-naphtholate and carbonic acid in the same way as salicylic acid (Schmitt and Burkard, *Ber.* **20**, 2699; Ger. Pat. $31240^{84}$; Am. Pat. 350468).

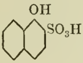
*Properties.*—Needles. M.p. 186°. Sparingly soluble in water. Its salts are sparingly soluble. Blue coloration with ferric chloride.

## α-Naphtholmonosulphonic Acids

$C_{10}H_6(OH)SO_3H$

Of the various isomeric sulphonic acids of α-naphthol the (1 : 4)-acid is by far the most important (cf. Friedländer and Faussig, *Ber.* **30**, 1456; *J. Soc. Chem. Ind.* **1897**, 728).

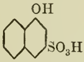
**α-Naphtholsulphonic acid** (1 : 2).
*(Schäffer's or Baum's acid)*



*Preparation.*—By heating α-naphthol (1 pt.) with conc. sulphuric acid (1 pt.) for $\frac{1}{2}$ hour at 90°, dissolving in water (5 pts.), and neutralising with soda. On cooling, the sodium salt crystallises out in silky plates.

*Properties.*—Long soluble needles. M.p. 101°. Ferric chloride gives a blue colour, becoming green on heating. By nitric acid it is converted into dinitronaphthol.

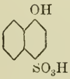
**α-Naphtholsulphonic acid** (1 : 3).
*(Armstrong and Wynne's acid)*



*Preparation.*—By boiling the diazo compound of α-naphthylamine sulphonic acid (1 : 3) (*Ber.* **28**, 1951; **30**, 1456).

*Properties.*—It yields *o*-azo dyestuffs with diazo compounds.

**α-Naphtholsulphonic acid NW.** (1 : 4).
*(Nevile and Winther's acid)*

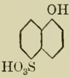


(*Constitution:* Witt and Kaufmann, *Ber.* **24**, 3157)

*Preparation.*—(1) By boiling diazotised naphthionic acid with dilute sulphuric acid (Nevile and Winther, *Ber.* **13**, 1949). (2) By heating sodium naphthionate (1 pt.) with 50% aqueous caustic soda (1 pt.) in an autoclave for 10 hours at 240° to 260° (Actienges. f. Anilinfabrikn., Ger. Pat. 46307).

*Properties.*—Very soluble transparent tables. M.p. 170°. Ferric chloride gives a blue coloration, becoming red on heating. Nitrous acid gives a yellow crystalline nitroso compound. With nitric acid it yields dinitronaphthol. Its salts are very soluble.

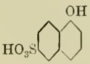
**α-Naphtholsulphonic acid L.** (1 : 5).
*(Cleve's acid)*



*Preparation.*—(1) By boiling the diazo compound of Laurent's α-naphthylaminesulphonic acid with dilute sulphuric acid (Cleve, *Bl.* **24**, 512). (2) By fusing naphthalenedisulphonic acid (1 : 5) with caustic soda at 160° to 190° (Ewer and Pick, Ger. Pat. $41934^{87}$).

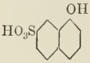
*Properties.*—Deliquescent crystalline solid. The sodium salt forms transparent prismatic needles.

**α-Naphtholsulphonic acid** (1 : 6).



*Preparation.*—By heating naphthalenedisulphonic acid (1 : 6) with aqueous caustic soda under pressure. Also by decomposition of the diazo compound of Cleve's α-naphthylaminesulphonic acid (1 : 6) by boiling with dilute sulphuric acid.

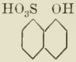
**α-Naphtholsulphonic acid** (1 : 7).
(*Liebmann and Studer's acid*)



*Preparation.*—By hydrolysis of the disulphonic acid of α-naphthol-β-carboxylic acid by heating with dilute sulphuric acid (*Ber.* **30**, 1456).

*Properties.*—It gives a crystalline nitroso derivative which on nitration yields naphthol-yellow S. Its azo derivatives are not fast to alkalies.

**α-Naphtholsulphonic acid** δ or **S.** (1 : 8).
(*Schöllkopf acid*)



*Preparation.*—By boiling the diazo compound of α-naphthylaminesulphonic acid S with dilute sulphuric acid, and heating the sultone with aqueous alcohol (Schöllkopf Anil. Co., Eng. Pat. $15775^{85}$; Am. Pat. 333034; Erdmann, *Ann.* **247**, 343).

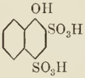
*Properties.*—Very soluble crystalline solid. M.p. 107°. Ferric chloride gives a dark green colour, becoming first yellow and then red. On dehydration it is converted into the insoluble **sultone** $C_{10}H_6<\genfrac{}{}{0pt}{}{SO_2}{O}$, which crystallises in prisms of m.p. 154° and b.p. about 360° (Schultz, *Ber.* **20**, 3162).

### α-Naphtholdisulphonic Acids

$C_{10}H_5(OH)(SO_3H)_2$

The following isomers have more or less technical importance :—

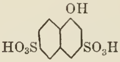
**α-Naphtholdisulphonic acid** (1 : 2 : 4).



*Preparation.*—By sulphonating α-naphthol (1 pt.) with conc. sulphuric acid (3 pts.) for a short time at about 70°.

*Properties.*—By nitric acid it is converted into dinitronaphthol (Martius yellow). It does not combine with diazo compounds or form a nitroso compound.

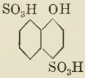
**α-Naphtholdisulphonic acid GR.** (1 : 3 : 6).



*Preparation.*—(1) From (1 : 3 : 6)-naphthalenetrisulphonic acid by heating with caustic soda at 170° to 180° under pressure (Eng. Pat. $15716^{85}$). (2) From the 1 : 3 : 6-naphthylaminedisulphonic acid by heating with water at 180° (Cassella).

*Properties.*—The sodium salt is easily soluble. Ferric chloride gives a blue coloration.

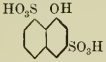
**α-Naphtholdisulphonic acid** δ or **S.** (1 : 4 : 8).



*Preparation.*—(1) By boiling the diazo compound of α-naphthylaminedisulphonic acid δ with water. (2) By sulphonating naphthosultone $C_{10}H_6<\genfrac{}{}{0pt}{}{SO_2}{O}$ with 3 pts. of conc. sulphuric acid at 100° (Schöllkopf Anil. Co., Eng. Pats. $15775^{85}$ and $15782^{85}$; Bernthsen, *Ber.* **23**, 3090).

*Properties.*—The sodium salt forms very soluble plates; the barium salt is sparingly soluble. Ferric chloride gives a blue coloration. It combines with diazo compounds. On dehydration it yields the **sultonesulphonic** acid $C_{10}H_5(SO_3H)<\genfrac{}{}{0pt}{}{SO_2}{O}$.

**α-Naphtholdisulphonic acid ε. (1 : 3 : 8).**

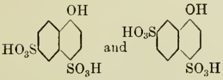


*Preparation.*—By boiling the diazo compound of α-naphthylaminedisulphonic acid ε with dilute sulphuric acid; on cooling, the sultonesulphonic acid crystallises out and is converted into salts of the disulphonic acid by dissolving in alkalies (Actienges. f. Anilinfabrikn., Eng. Pats. 4625[88] and 5910[88]; Ewer and Pick, Ger. Pat. 52724[89]).

*Properties.*—The sodium salt forms very soluble long colourless prisms ( + $6H_2O$). Ferric chloride gives a deep blue colour.

*Sultonesulphonic acid* (ζ acid) $C_{10}H_5(SO_3H){<}\genfrac{}{}{0pt}{}{SO_2}{O}$.—Formed by dehydration of the disulphonic acid. Silky needles. M.p. 241°. Easily soluble in water. Converted by ammonia into the amide acid $C_{10}H_5(SO_3H)(SO_2NH_2)OH$. The sodium salt forms long colourless needles ( + $3H_2O$), sparingly soluble in cold water. No coloration with ferric chloride (Bernthsen, *Ber.* **22**, 3330).

**α-Naphthol-disulphonic acids (1 : 4 : 6) and (1 : 4 : 7).**
*(Dahl's acids)*



*Preparation.*—Obtained from Dahl's α-naphthylaminedisulphonic acids II. and III. respectively, by boiling the diazo compounds with water (Dahl and Co., Ger. Pat. 41957[86]). Also from α-naphthol carbonate by tetrasulphonation with fuming acid in the cold, and partial hydrolysis (Meister, Lucius, and Brüning, Eng. Pat. 14134[94]).

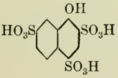
*Properties.*—By nitric acid they are converted into dinitronaphtholsulphonic acids, that from the latter being identical with "Naphthol yellow S" (Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 17).

## α-Naphtholtrisulphonic Acids

$C_{10}H_4(OH)(SO_3H)_3$

The following acids are of technical importance:—

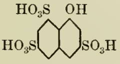
**α-Naphtholtrisulphonic acid (1 : 2 : 4 : 7).**



*Preparation.*—By the action of fuming sulphuric acid of 50% $SO_3$ (4 pts.) upon α-naphthol (1 pt.) at 40° to 50° for 6 hours (Bad. Anil. and Soda Fabrik, Eng. Pat. 5305[79]).

*Properties.*—It does not combine with diazo compounds or form a nitroso compound. By nitric acid it is converted into dinitronaphtholsulphonic acid ("Naphthol yellow S").

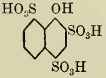
**α-Naphtholtrisulphonic acid (1 : 3 : 6 : 8).**



*Preparation.*—From the corresponding α-naphthylaminesulphonic acid (*q.v.*) by boiling its diazo compound with water (Koch, Eng. Pat. 9258[90]).

*Properties.*—By dehydration it yields a naphthosultonedisulphonic acid.

**α-Naphtholtrisulphonic acid (1 : 2 : 4 : 8).**

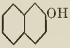


*Preparation.*—By further sulphonation of naphthosultone, or of α-naphtholmono- or di-sulphonic acid S with fuming sulphuric acid of 25% $SO_3$ (Bayer and Co., Eng. Pat. 3397[90]).

*Properties.*—Does not combine with diazo compounds. Converted by nitric acid into a dinitronaphtholsulphonic acid.

## β-Naphthol (*β-Oxynaphthalene*)

$C_{10}H_7 \cdot OH$ *i.e.*



*Preparation.*—By fusing sodium β-naphthalene sulphonate (1 pt.) with caustic soda (2 pts.) in the same way as α-naphthol (*q.v.*). The product is distilled in vacuo.

*Properties.*—Colourless plates or rhombic tables. M.p. 123°; b.p. 286°. Sparingly soluble in water, easily in alcohol, ether, etc. Not volatile with steam. Dissolves readily in caustic alkalies. Ferric chloride or chloride of lime gives no coloration.

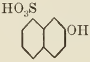
*Valuation.*—The commercial product is nearly chemically pure. It forms yellowish white crystalline lumps which have very little odour. It should have nearly the right melting point (120° to 121° C.) and dissolve in caustic soda to a colourless solution, leaving very little residue. The presence of α-naphthol is detected by dissolving in alcohol, diluting with water and adding a few drops of ferric chloride; the formation of a violet blue colour indicates the presence of α-naphthol (usually ·1% to ·5%).

## β-Naphtholmonosulphonic Acids

$C_{10}H_6(OH)SO_3H$

The following three isomers are employed for the preparation of colours:—

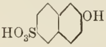
**β-Naphtholsulphonic acid**
α or **B.** (2 : 8).
(*Bayer's acid*)



*Preparation.*—Together with some β-acid by dissolving finely powdered β-naphthol (1 pt.) in conc. sulphuric acid (2 pts.) at 50° to 60° (Bayer and Co., Eng. Pat. $1225^{81}$ and $2030^{81}$; Am. Pat. 256381); or by the action of conc. sulphuric acid in the cold upon β-naphthol for several days (Leonhardt and Co., Ger. Pat. $33857^{84}$). The α-acid is separated from the β-acid, which is formed simultaneously, by precipitating the latter as sodium salt by adding sodium chloride; or more completely by adding to the dilute alkaline solution the requisite quantity of a diazo chloride, which combines first with the β-acid.

*Properties.*—Its sodium salt $C_{10}H_6(ONa)SO_3Na$ is soluble in hot 90% alcohol, and very soluble in water.

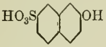
**β-Naphtholsulphonic acid**
β or **S.** (2 . 6).
(*Schäffer's acid*)



*Preparation.*—By heating β-naphthol (1 pt.) with conc. sulphuric acid (1 to 2 pts.) at 100°; on dissolving the melt in water and adding salt, the sodium salt of the β-acid crystallises out, whilst isomeric acids, formed simultaneously, remain in solution (Schäffer, *Ann.* **152**, 296; Armstrong and Graham, *J. Chem. Soc.* **39**, 136; Eng. Pat. $7098^{84}$).

*Properties.*—Very soluble small colourless plates. M.p. 125°. The sodium salt forms long colourless needles or plates ($+ 2H_2O$), moderately soluble in water, insoluble in alcohol. Nitrous acid forms nitrosonaphtholsulphonic acid, the iron salts of which are deep green colouring matters.

**β-Naphtholsulphonic acid**
δ or **F.** (2 : 7).
(*Cassella's acid*)



*Preparation.*—By fusing naphthalenedisulphonic acid (2 : 7) with caustic soda at 200° to 250°, or by heating it in an autoclave with aqueous caustic soda (Cassella and Co., Ger. Pat. $42112^{86}$; Eng. Pat. $12908^{86}$; Weinberg, *Ber.* **20,** 2906).

*Properties.*—Needles. M.p. 89°. Very soluble in water and alcohol. Ferric chloride gives a dark blue coloration. The sodium salt is easily soluble, the barium salt sparingly soluble.

## β-Naphtholdisulphonic Acids

$C_{10}H_5(OH)(SO_3H)_2$

The following are of technical importance:—

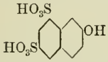
**β-Naphtholdisulphonic acid**
*a* or **R.** (2 : 3 : 6).

(*Constitution :* Armstrong and Wynne, *Proc. Chem. Soc.* **1890,** 12)

*Preparation.*—By heating β-naphthol (1 pt.) with conc. sulphuric acid (3 pts.) at 100° to 110° for several hours. On dissolving the melt in water, and adding salt, the nearly pure sodium salt of the R-acid ("R-salt") crystallises out, whilst the "G-salt," which is formed simultaneously, remains in solution (Meister, Lucius, and Brüning, Eng. Pat. $1715^{78}$; Griess, *Ber.* **13,** 1956; Beyer and Kegel, Eng. Pat. $7097^{84}$).

*Properties.*—Deliquescent silky needles. Very soluble in water. The alkaline solution has a bluish green fluorescence. Its sodium salt is insoluble in alcohol. It combines with diazo compounds much more readily than the G-acid.

**β-Naphtholdisulphonic acid**
β, γ, or **G.** (2 : 6 : 8).



(*Constitution :* Armstrong and Wynne, *Proc. Chem. Soc.* **1890,** 12)

*Preparation.*—By dissolving β-naphthol (1 pt.) in conc. sulphuric acid (4 pts.) and keeping at 60° for 48 hours, or at 20° for 8 to 10 days. The product consists mainly of the G-acid, together with 10% to 15% of the monosulphonic acid S, which latter is removed by salting out or treating the alkaline solution with the necessary quantity of diazobenzene chloride to combine with it, and filtering from the orange produced (Meister, Lucius, and Brüning, Eng. Pat. $816^{84}$; Am. Pat. 331059).

*Properties.*—Its sodium salt forms colourless plates or prisms, soluble in 90% alcohol. The salts are more soluble in water than those of the R-acid.

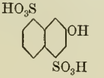
**β-Naphtholdisulphonic acid**
δ or **F.** (2 : 3 : 7).

(*Constitution :* Armstrong and Wynne, *Proc. Chem. Soc.* **1890,** 127)

*Preparation.*—By heating β-naphtholmonosulphonic acid δ with conc. sulphuric acid (2 pts.) at 120° for 12 hours (Cassella and Co., Ger. Pat. $44070^{87}$; Eng. Pat. $8265^{87}$; Weinberg, *Ber.* **20,** 2912).

*Properties.*—Its salts have a green fluorescence; the barium salt forms small prisms ($+ 2\frac{1}{2}H_2O$), sparingly soluble in boiling water. The sodium salt is easily soluble in water, sparingly in alcohol.

**β-Naphtholdisulphonic acid C.** (2 : 4 : 8).



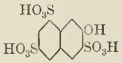
*Preparation.*—From the corresponding β-naphthylaminedisulphonic acid C by boiling the diazo compound with water (Cassella and Co., Ger. Pat. appl. C. $3542^{90}$).

*Properties.*—Its alkaline solution has a pure blue fluorescence.

### β-Naphtholtrisulphonic Acid

$C_{10}H_4(OH)(SO_3H)_3$

Probably (2 : 3 : 6 : 8)



*Preparation.*—By heating β-naphthol (1 pt.) with fuming sulphuric acid of 20% $SO_3$ (4 to 5 pts.) at 140° to 160°, or by heating β-naphthol with a large excess of sulphuric acid for a long time (R. Meldola, Eng. Pat. $1864^{79}$; Meister, Lucius, and Brüning, Eng. Pat. $2544^{82}$; Levinstein, *Ber.* **16**, 726). The first product of the reaction appears to be the **sultone-disulphonic acid** $C_{10}H_4(SO_3H)_2{<}\begin{smallmatrix}SO_2\\ |\\ O\end{smallmatrix}$, which gives salts of the trisulphonic acid on boiling with alkalies (Nietzki, *Chem. Ztg.*, March 1891).

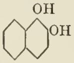
*Properties.*—Its alkaline solution has a pure green fluorescence. It only combines very slowly with diazoxylene, but with diazoazo compounds it combines readily. The sultone does not combine with diazo compounds at all.

### Dioxynaphthalenes

$C_{10}H_6(OH)_2$

Of the ten possible dioxynaphthalenes, which are now all known, only a few have yet received much technical application; some are only employed in the form of their sulphonic acids.

**Dioxynaphthalene** (1 : 2).
(*β-hydronaphthoquinone*)

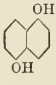


*Preparation.*—By reduction of β-naphthoquinone with sulphurous acid.

*Properties.*—Silvery plates. M.p. 60°.

*Sulphonic acids.*—The disulphonic acids are obtained by boiling the acid sodium salts of the amido-β-naphtholdisulphonic acids formed by reduction of the azo colours derived from β-naphtholdisulphonic acid R and G (Witt, Ger. Pat. $49857^{89}$; *Ber.* **21**, 3468).

**Dioxynaphthalene** (1 : 5).

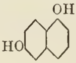


*Preparation.*—By fusing (1 : 5)-naphthalenedisulphonic or α-naphtholsulphonic acid L with caustic soda (Armstrong, *Ber.* **15**, 200; Bernthsen and Semper, *Ber.* **20**, 938; Ewer and Pick, Ger. Pat. $41934^{87}$).

*Properties.*—Long needles. M.p. 260°. Sparingly soluble in water.

*Sulphonic acids.*—Mono- and di-sulphonic acids are obtained by heating the (1 : 5)-dioxynaphthalene with sulphuric acid (Ewer and Pick, Ger. Pat. $41934^{87}$).

**Dioxynaphthalene** (1 : 6).

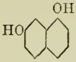


*Preparation.*—From the (1 : 6)-naphthalenedisulphonic acid by soda fusion (Ewer and Pick, Ger. Pat. $45229^{87}$).

*Properties.*—Plates. M.p. 136°.

*Sulphonic acid* (probably 1 : 6 : 4).—Obtained by fusing α-naphthylaminedisulphonic acid II. of Dahl with caustic soda. Small plates; moderately soluble in water (Dahl and Co., Eng. Pat. $735^{90}$).

**Dioxynaphthalene** (1 : 7).

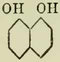


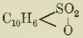
*Preparation.*—From the (1 : 7)-naphthalenedisulphonic acid or from β-naphthol-α-sulphonic acid by fusion with caustic soda (Armstrong and Graham, *J. Chem. Soc.* **1881**, 133; Bayer and Co., Eng. Pat. $14230^{89}$).

*Properties.*—Fine needles. M.p. 158°.

*Sulphonic acid* (1 : 7 : 3).—Obtained by fusing β-naphthol-disulphonic acid G with caustic soda. Its sodium salt forms long thick needles (Bayer and Co., Ger. Pat. $53567^{89}$; Meister, Lucius, and Brüning, Eng. Pat. $9642^{89}$).

**Dioxynaphthalene** (1 : 8).



*Preparation.*—From naphthosultone  $C_{10}H_6{<}\begin{smallmatrix}SO_2\\ |\\ O\end{smallmatrix}$ by fusion with caustic soda (Erdmann, *Ann.* **247**, 358).

*Properties.*—Needles or plates. M.p. 138°.

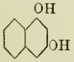
*Monosulphonic acid* (1 : 8 : 4).—Obtained from α-naphthol-disulphonic acid δ or S by caustic soda fusion (Bayer and Co., Ger. Pat. $54116^{89}$; Eng. Pat. $13665^{89}$). Also by heating diamidonaphthalenesulphonic acid (1 : 8 : 4) with milk of lime at about 230° under pressure (Cassella).

*Monosulphonic acid* (1 : 8 : 3).—Obtained from α-naphthol-disulphonic acid ε by caustic soda fusion (Bayer and Co., Eng. Pat. $18577^{89}$).

*Disulphonic acid* (1 : 8 : 3 : 6) (*Chromotropic acid* or *Chromogen I.*) — Obtained from Koch's α-naphtholtrisulphonic acid (1 : 3 : 6 : 8) by soda fusion (Koch, Eng. Pat. $9258^{90}$; Bayer and Co., Eng. Pat. $13443^{90}$). Also from α-naphthylamine-trisulphonic acid (1 : 8 : 3 : 6) or amidonaphtholdisulphonic acid H by heating with caustic soda solution at 280° (Cassella and Co., Eng. Pat. $11522^{92}$), or from diamidonaphthalenedisulphonic acid (1 : 8 : 3 : 6) by heating under pressure with dilute mineral acids. Flat colourless needles.

*Disulphonic acid* (1 : 8 : 2 : 4).—Obtained by soda fusion from the α-naphtholtrisulphonic acid (1 : 2 : 4 : 8) (Eng. Pat. $3397^{90}$).

**Dioxynaphthalene** (1 : 3).
(*Naphthoresorcin*)



*Preparation.*—By heating the disulphonic acid (see below) with dilute acids at 230° under pressure (Bayer and Co., Ger. Pat. $90096^{95}$).

*Properties.*—Transparent plates. Easily soluble in water. M.p. 124°. With phthalic anhydride gives a fluorescent dyestuff (Friedländer and Rüdt, *Ber.* **29**, 1610).

*Disulphonic acid* (1 : 3 : 5 : 7).—Prepared (together with a less soluble isomer) by the action of caustic soda under pressure at 200° upon the naphthalene tetrasulphonic acid obtained by further sulphonation of the naphthalenedisulphonic acid (2 : 6) with fuming sulphuric acid of 25% (3 pts.) first at 90° and then at 260° (Bayer and Co., Eng. Pat. $25074^{93}$).

**Dioxynaphthalene** (2 : 3).

*Preparation.* — By heating the sodium salt of dioxynaphthalenesulphonic acid R (*v.* infra) by itself, or by heating the acid with dilute sulphuric acid at 200°. Or direct from β-naphtholdisulphonic acid R (1 pt.) by fusion with caustic soda (4 pts.) at 300° to 320° for 3 or 4 hours (Bad. Anil. and Soda Fabrik, Eng. Pat. $15803^{90}$).

*Properties.*—Colourless crystals. M.p. 160°.

*Sulphonic acids* are obtained by soda fusion from the β-naphtholdisulphonic acids R and F and from β-naphtholtrisulphonic acid (Bayer and Co., Ger. Pat. $53567^{89}$; Meister, Lucius, and Brüning, Eng. Pat. $9642^{89}$). The sodium salt of the dioxynaphthalenemonosulphonic acid R forms glistening plates, very sparingly soluble in salt solution.

**Dioxynaphthalene** (2 : 6).

*Preparation.*—From the (2 : 6)-naphthalenedisulphonic acid or from β-naphthol-β-sulphonic acid by fusion with caustic soda (Darmstädter and Wichelhaus, *Ann.* **152,** 306; Emmert, *Ann.* **241,** 369).

*Properties.*—Plates. M.p. 216°.

**Dioxynaphthalene** (2 : 7).

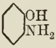
*Preparation.*—From the (2 : 7)-naphthalenedisulphonic acid or from β-naphtholsulphonic acid F by fusion with caustic soda (Ebert and Merz, *Ber.* **9,** 609; Weber, *Ber.* **14,** 2206).

*Properties.*—Long needles (from water) or plates (by sublimation). M.p. 186°.

## AMIDOPHENOLS AND THEIR DERIVATIVES

### *o*-Amidophenol

$C_6H_4(NH_2)(OH)[1:2]$ *i.e.*



*Preparation.*—By reduction of *o*-nitrophenol, mixed with aqueous ammonia, by means of a stream of sulphuretted hydrogen (see Paul, *J. Soc. Chem. Ind.* **1897,** 63).

*Properties.*—Crystalline solid. M.p. 170°.

*Derivatives.*—The following derivatives are employed as first components in the preparation of mordant azo colouring-matters:—

**Picramic acid** $C_6H_2(NO_2)_2(NH_2)(OH)[6:4:2:1]$, obtained by partial reduction of picric acid, forms red needles of m.p. 168° to 170°.

*p*-**Nitro**-*o*-**amidophenol** $C_6H_3(NO_2)(NH_2)(OH)[4:2:1]$, obtained by partial reduction of dinitrophenol (4 : 2 : 1) (Stückenberg, *Ann.* **205,** 75; Eng. Pat. $26262^{98}$).

*o*-**Nitro**-*o*-**amidophenol**-*p*-**sulphonic acid** $C_6H_2(NO_2)(SO_3H)(NH_2)(OH)[6:4:2:1]$, obtained by nitration and partial reduction of phenol-*p*-sulphonic acid (Eng. Pat. $14251^{98}$).

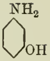
*o*-**Chloro**-*o*-**amidophenol**-*p*-**sulphonic acid** $C_6H_2Cl(SO_3H)(NH_2)(OH)[6:4:2:1]$, obtained from the preceding compound by Sandmeyer reaction and reduction (Eng. Pat. $25650^{98}$).

*p*-**Chloro**-*o*-**amidophenol**-*o*-**sulphonic acid** $C_6H_2Cl(SO_3H)(NH_2)(OH)[4:6:2:1]$, obtained by the action of sodium sulphite upon *p*-chloro-*o*-nitrophenol.

**Diamidophenolsulphonic acids** $C_6H_2(NH_2)_2(SO_3H)(OH)[6:2:4:1]$ and $[4:2:6:1]$, obtained by nitration and complete reduction of the phenol-*o*- and *p*-sulphonic acids.

## *m*-Amidophenol

$C_6H_4(OH)NH_2[1:3]$ *i.e.*



*Preparation.*—(1) By fusing *m*-sulphanilic acid (1 pt.) with caustic soda (2 pts.) and a little water at 280° to 290°. The melt is made neutral, and the solution extracted with ether (Gesellsch. f. Chem. Industrie, Ger. Pat. $44792^{88}$; Am. Pat. 403678). (2) By heating resorcinol (10 pts.) with aqueous ammonia of 10% $NH_3$ (20 pts.) and ammonium chloride (6 pts.) for 12 hours at about 200° in an autoclave (Leonhardt and Co., Eng. Pat. $8156^{89}$).

*Properties.*—White prismatic needles. M.p. 121°. Easily soluble in hot water, moderately in cold.

## Dimethyl-*m*-amidophenol (*m-Oxydimethylaniline*)

$C_6H_4(OH) \cdot N(CH_3)_2[1:3]$

*Preparation.*—(1) By soda fusion (see above) of dimethyl-*m*-sulphanilic acid, obtained by sulphonating dimethylaniline with fuming sulphuric acid (Gesellsch. f. Chem. Industrie, Ger. Pat. $44792^{88}$). (2) By heating resorcinol with aqueous dimethylamine and dimethylamine hydrochloride at about 200° in an autoclave (Leonhardt and Co., Eng. Pat. $8156^{89}$).

*Properties.*—Crystals. M.p. 87°; b.p. 265° to 268°. Nearly insoluble in water. By nitrous acid it is converted into a **nitroso compound** $C_6H_3(NO)(OH) \cdot N(CH_3)_2$, the hydrochloride of which forms yellow crystals.

## Monoethyl-*m*-amidophenol (*m-Oxymonoethylaniline*)

$C_6H_4(OH) \cdot NH(C_2H_5)[1:3]$

*Preparation.*—By soda fusion from monoethyl-*m*-sulphanilic acid, obtained by sulphonating monoethylaniline with fuming sulphuric acid (see above).

*Properties.*—Colourless crystals. M.p. 62°; b.p. 176° at 12 mm. B.

## Diethyl-*m*-amidophenol (*m-Oxydiethylaniline*)

$C_6H_4(OH) \cdot N(C_2H_5)_2[1:3]$

Prepared by soda fusion of diethyl-*m*-sulphanilic acid, obtained by sulphonating diethylaniline with fuming sulphuric acid (see above). Crystalline solid or oil. M.p. 14°; b.p. 275° to 280°. Nearly insoluble in water. Gives a nitroso compound.

## Phenyl-*m*-amidophenol (*m-Oxydiphenylamine*)

$C_6H_4(OH) \cdot NH \cdot C_6H_5[1:3]$

*Preparation.*—By heating resorcinol with aniline and zinc chloride at 280° to 290° (Calm, *Ber.* **16**, 2786); or by heating *m*-amidophenol (10 pts.) with aniline hydrochloride (12 pts.) in an autoclave at 210° to 215° (Bad. Anil. und Soda Fabrik, Ger. Pat. $46869^{88}$).

*Properties.*—Glistening plates. M.p. 82°; b.p. 340°. Moderately soluble in boiling water.

### *o*- and *p*-**Tolyl**-*m*-**amidophenol**

$C_6H_4(OH) \cdot NH \cdot C_7H_7[1:3]$

Obtained in the same way from resorcinol or *m*-amidophenol and *o*- or *p*-toluidine. The *o*-compound is a liquid of b.p. 370° to 375° corr.; the *p*-compound forms glistening needles or prisms of m.p. 91° and b.p. 350° corr.

### Dimethyl-*m*-amido-*p*-cresol

$C_6H_3(CH_3)(OH) \cdot N(CH_3)_2[1:4:2]$

*Preparation.*—From dimethyl-*o*-toluidine by sulphonation with fuming sulphuric acid in the cold and caustic soda fusion of the sulphonic acid (see Möhlau, Klimmer, and Kahl, *Zeit. Farb. Chem.* **1902**, 316).

*Properties.*—Crystalline powder. M.p. 46°; b.p. 253°. Its nitroso compound forms reddish brown needles of m.p. 102°.

### Diethyl-*m*-amido-*p*-cresol

$C_6H_3(CH_3)(OH) \cdot N(C_2H_5)_2[1:4:2]$

*Preparation.*—From diethyl-*o*-toluidine in the same manner as above (*l.c.*).

*Properties.*—Crystalline. M.p. 49°; b.p. 259°. Serves for the preparation of Capri Blue.

### *p*-Amidophenol

$C_6H_4(NH_2)(OH)[1:4]$ *i.e.*

*Preparation.*—(1) By reduction of *p*-nitrophenol with iron. (2) By the action of ammonia on *p*-chloronitrobenzene. (3) By electrolytic reduction of nitrobenzene in sulphuric acid solution.

*Properties.*—Plates. M.p. 184°. Very oxidisable. Largely used for the preparation of "sulphide" blacks.

*Derivatives.*—The following derivatives are employed in the preparation of mordant azo colouring-matters ("chrome colours"):—

**Amidosalicylic acid** $C_6H_3(NH_2)(CO_2H)(OH)[4:2:1]$, prepared by nitration and reduction of salicylic acid; forms very sparingly soluble glistening needles (Hübner, *Ann.* **195**, 18).

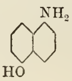
*o*-**Nitro**-*p*-**amidophenol** $C_6H_3(NO_2)(NH_2)(OH)[2:1:4]$ (Hübner, *Ann.* **210**, 381; Eng. Pat. $26262^{98}$).

*o*-**Nitro**-*p*-**amidophenol**-*o*-**sulphonic acid** $C_6H_2(SO_3H)(NO_2)(NH_2)(OH)[6:2:4:1]$, obtained by nitration of *p*-amidophenol sulphonic acid (Eng. Pat. $14253^{98}$). It is nearly insoluble in cold water, and forms an easily soluble diazo salt.

### Amidonaphthols (*Oxynaphthylamines*)

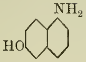
The following amidonaphthols are employed in the preparation of azo colours, chiefly in the form of their sulphonic acids:—

**Amidonaphthol** (1:5).



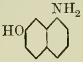
*Preparation.*—From α-naphthylaminesulphonic acid L by heating with caustic soda (Actienges. f. Anilinfabrikn., Ger. Pat. $49448^{89}$).

**Amidonaphthol** (1 : 6).



*Disulphonic acid* (1 : 6 : 3 : 7).—By further sulphonation of the 1 : 6 : 3 amidonaphthol monosulphonic acid, obtained from the *a*-naphthylaminedisulphonic acid (1 : 3 : 6) by soda fusion (Cassella and Co., Ger. Pat. $82676^{94}$ and $84952^{94}$).

**Amidonaphthol** *δ* (1 : 7).



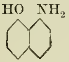
*Preparation.*—From *a*-naphthylaminesulphonic acid (1 : 7) by soda fusion at about 260° (Cassella and Co., Ger. Pat. 69458).

*Properties.*—Flat colourless prisms. M.p. 206°. Soluble in hot water.

*Sulphonic acid* (1 : 7 : 3) ("B acid").—Obtained from (2 : 6) naphthalenedisulphonic acid by nitration, reduction, and fusion with caustic soda (Cassella and Co., Ger. Pat. $38352^{90}$). It forms sparingly soluble glistening needles and gives an insoluble yellow diazo compound.

*Sulphonic acid* (1 : 7 : 4).—Obtained by sulphonation of the 1 : 7-amidonaphthol (Cassella and Co., Ger. Pat. $75066^{91}$).

**Amidonaphthol** (1 : 8).



*Preparation.*—From *a*-naphthylaminemonosulphonic acid S by fusion with caustic soda (Bad. Anil. und Soda Fabrik, Eng. Pat. $9676^{90}$; Ger. Pat. $55404^{89}$). Also by heating the 1 : 8 : 4-sulphonic acid with dilute mineral acids under pressure at about 140° (Ger. Pat. 73381).

*Properties.*—Long colourless needles. M.p. 97°. The sulphate is nearly insoluble in water.

*Sulphonic acid* (1 : 8 : 3).—Obtained from *a*-naphthylaminedisulphonic acid *ε* by fusion with caustic soda (Bayer and Co., Eng. Pat. $13443^{90}$). Forms sparingly soluble white needles.

*Sulphonic acid* (1 : 8 : 4) ("S acid"). — Obtained from *a*-naphthylaminedisulphonic acid S by soda fusion (Bad. Anil. und Soda Fabrik, Eng. Pat. $7713^{91}$). Also by heating the diamidonaphthalenesulphonic acid (1 : 8 : 4) with aqueous sodium bisulphite in presence of acetone (Eng. Pat. $16921^{00}$). It forms very sparingly soluble crystals.

*Disulphonic acid* (1 : 8 : 3 : 6) ("H acid").—Obtained from Koch's *a*-naphthylaminetrisulphonic acid (1 : 3 : 6 : 8) by fusion with soda (Bayer and Co., Eng. Pat. $13443^{90}$). Also from the diamidonaphthalenedisulphonic acid (1 : 8 : 3 : 6), obtained by di-nitration and reduction of (2 : 7)-naphthalenedisulphonic acid, by heating with dilute sulphuric acid at 110° to 120° (Cassella and Co., Eng. Pat. $1742^{91}$). It forms fine sparingly soluble needles.

*Disulphonic acid* (1 : 8 : 3 : 5) ("B acid").—Obtained by sulphonation of the 1 : 8 : 3-monosulphonic acid.

*Disulphonic acid* (1 : 8 : 4 : 6) ("K acid").—Obtained from the *a*-naphthylaminetrisulphonic acid (1 : 4 : 6 : 8) by soda fusion (Kalle and Co., Eng. Pats. $17141^{93}$ and $515^{94}$; Am. Pat. 563382).

*Disulphonic acid* (1 : 8 : 2 : 4) ("2S acid").—Obtained by soda fusion from the *a*-naphthylaminetrisulphonic acid (1 : 2 : 4 : 8) (Bayer and Co., Eng. Pat. $4979^{93}$).

**Amidonaphthol** (2 : 3).

*Sulphonic acid* (2 : 3 : 6) (" R acid ").—Obtained from β-naphthylaminedisulphonic acid R by fusion with caustic soda (Meister, Lucius, and Brüning, Eng. Pat. 15176$^{89}$; cf. Friedländer, *Ber.* **27**, 761). Very sparingly soluble in water (1 in 4000 at 15°).

*Sulphonic acid* (probably 2 : 3 : 7).—Obtained by heating dioxynaphthalenesulphonic acid R (2 : 3 : 6) with ammonia under pressure (Actienges. f. Anilinfabrikn., Ger. Pat. 62964$^{90}$). Sparingly soluble in water (1 in 1160 at 15°). Its sodium salt forms glistening plates.

**Amidonaphthol** (2 : 5).

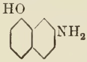
*Sulphonic acid* (2 : 5 : 7).—Obtained by soda fusion of β-naphthylamine disulphonic acid (2 : 5 : 7) (Ger. Pat. app. B 14154; Eng. Pat. 2614$^{93}$).

**Amidonaphthol** (2 : 7).

*Preparation.*—From β-naphthylamine-δ-sulphonic acid by fusion with caustic soda (Gesellsch. f. Chem. Industrie, Ger. Pat. 47816$^{88}$).

*Properties.*—Needles. M.p. above 200°.

**Amidonaphthol** (2 : 8).



*Sulphonic acid* (2 : 8 : 6) (" G " or " γ-acid ").—Obtained by heating β-naphthylaminedisulphonic acid G (36 pts.) with caustic soda (30 pts.) and water (36 pts.) in an autoclave for 6 hours at 185° (Eng. Pats. 15176$^{89}$ and 16699$^{89}$). It forms colourless crystals, very sparingly soluble in water.

*Disulphonic acid* (2 : 8 : 3 : 6) (" 2R-acid ").—Obtained from β-naphthylaminetrisulphonic acid (2 : 3 : 6 : 8) by soda fusion (Ger. Pat. 53023). The acid is easily soluble in water.

*Phenylamidonaphtholsulphonic acid* (2 : 8 : 6) (" Phenyl-γ-acid ").—Obtained by heating dioxynaphthalenesulphonic acid (2 : 8 : 6) with aniline and aniline hydrochloride (Levinstein, Eng. Pat. 20548$^{95}$). Voluminous white needles. Sparingly soluble in cold water.

## HALOGEN COMPOUNDS

### Chlorobenzene

$C_6H_5Cl$

*Preparation.*—By passing chlorine (1 mol.) through benzene containing molybdenum chloride. The product is fractionated (Aronheim, *Ber.* **8**, 1400).

*Properties.*—Colourless liquid. B.p. 129°; sp. gr. 1·105. On nitration it gives a mixture of *o*- and *p*-chloronitrobenzene.

### Benzyl Chloride

$C_6H_5 \cdot CH_2Cl$ *i.e.*

*Preparation.*—By leading chlorine on to the surface of boiling toluene until it has increased in weight by 38%. The product is washed with water and separated by fractional distillation from unaltered toluene and from benzylidene dichloride and benzotrichloride, which are formed simultaneously.

*Properties.*—Colourless liquid. B.p. 179°; sp. gr. at 14° = 1·11. Insoluble in water. Pungent smell.

*Valuation.*—The commercial product is far from pure: it contains toluene, benzylidene chloride, benzotrichloride, and sometimes chlorotoluenes. It usually boils between 175° and 182°. The amount of benzotrichloride may be estimated by observing the amount of green colouring-matter produced on heating with dimethylaniline and zinc chloride. The quantity of chlorine present as *exo*-chloro substitution products is estimated by boiling a weighed sample with alcoholic silver nitrate and weighing the silver chloride produced; chlorine present in the nucleus is not eliminated by this treatment (Schulze, *Ber.* **17**, 1675).

### Benzylidene Dichloride (*Benzal Chloride*) and Benzotrichloride

$C_6H_5 \cdot CHCl_2$ and $C_6H_5 \cdot CCl_3$

*Preparation.*—Are formed together by the further chlorination of boiling toluene. They are usually not separated, but are employed at once for the preparation of benzaldehyde and benzoic acid by heating the mixture with milk of lime.

*Properties.*—Colourless oily liquids. Benzylidene dichloride has the sp. gr. at 15° = 1·25, and boils at 206°. Benzotrichloride has the sp. gr. at 14° = 1·38, and boils at 214°. On saponification benzylidene dichloride gives **benzaldehyde**, benzotrichloride gives **benzoic acid**.

### *o*-Chlorobenzyl Chloride

$C_6H_4Cl \cdot CH_2Cl[1:2]$

*Preparation.*—Formed as a by-product in the preparation of *o*-nitrobenzyl chloride by chlorination of *o*-nitrotoluene at 120° to 140° (see below). It is separated by fractional distillation in vacuo, or if required for conversion into the aldehyde the whole product is saponified by heating in alcoholic solution with sodium acetate and carbonate and the more volatile *o*-chlorobenzyl alcohol separated from *o*-nitrobenzyl alcohol by distillation with steam (Eng. Pat. $11260^{98}$).

***o*-Chlorobenzyl alcohol** obtained as above forms long white needles of m.p. 72°.

### *o*-Nitrobenzyl Chloride

$C_6H_4(NO_2) \cdot CH_2Cl[1:2]$

Prepared by chlorinating *o*-nitrotoluene, heated to 120° to 140°, with a stream of chlorine until about one-half of the theoretical quantity of chlorine has been absorbed. It can be separated from the unaltered nitrotoluene and from by-products of the reaction, by fractional distillation in vacuo. If required for preparing the aldehyde, its isolation is unnecessary, as it can be either converted into ***o*-nitrobenzyl alcohol** by treating the whole with sodium acetate and carbonate (Eng. Pats. $11259^{98}$; $11260^{98}$), or into ***o*-nitrobenzylaniline** or ***o*-nitrobenzylanilinesulphonic acid** by treatment with aniline or sodium sulphanilate (Eng. Pats. $15890^{97}$; $30118^{97}$; $1103^{98}$).

### *p*-Nitrobenzyl Chloride

$C_6H_4(NO_2) \cdot CH_2Cl[1:4]$

*Preparation.*—By passing chlorine into *p*-nitrotoluene heated to 185° to 190° (Wachendorff, *Ann.* **185**, 271); or by dropping benzyl chloride into fuming nitric acid cooled to −15° (Strakosch, *Ber.* **6**, 1056).

*Properties.*—Plates or needles. M.p. 71°.

## ALDEHYDES, KETONES, AND QUINONES

### Benzaldehyde (*Bitter-almond Oil*)

$C_6H_5\cdot CHO$ *i.e.*

*Preparation.*—(1) By heating the mixture of benzylidene dichloride and benzotrichloride, obtained by chlorinating toluene, with the calculated quantity of milk of lime under a pressure of 4 to 5 atmospheres. The benzaldehyde is distilled off with steam, whilst calcium benzoate, which is formed simultaneously, remains behind. (2) By heating the mixture of benzyl chloride (2 mols.) and benzylidene dichloride (1 mol.), obtained by chlorinating toluene until the sp. gr. of the liquid is 1·175, with finely powdered manganese dioxide (2 mols.) suspended in water (Schmidt, Ger. Pat. $20909^{82}$). (3) By oxidation of toluene in sulphuric acid solution by means of manganese dioxide (Eng. Pat. $22121^{97}$).

*Properties.*—Colourless liquid smelling of bitter almonds. B.p. 180°; sp. gr. $\frac{15}{4} = 1\cdot0504$. Slightly soluble in water, miscible with alcohol.

*Valuation.*—The commercial product, which is tolerably pure, should distil to the extent of 90% between 177° and 181°, and should have the correct specific gravity. It should dissolve almost completely in 10 times its volume of warm aqueous sodium bisulphite of sp. gr. 1·11; on extracting this solution with a little ether and evaporating off the ether, there should be no pungent smelling residue left (benzyl chloride, etc.). The presence of chlorine is detected by fusion with a scrap of metallic sodium and precipitation with silver nitrate. When it has been kept for some time it contains benzoic acid, which crystallises out. Adulteration with nitrobenzene is detected by the production of a green colour on heating with strong aqueous potash, and by the presence of nitrogen (formation of cyanide on ignition with sodium).

### Benzaldehyde-*o*-sulphonic acid

$C_6H_4(SO_3H)\cdot CHO[1:2]$

Prepared by heating *o*-chlorobenzaldehyde with a strong solution of sodium sulphite at 190° to 200° under pressure (Geigy, Ger. Pat. 88952). Also by oxidation of stilbenedisulphonic acid with potassium permanganate in the cold (Levinstein, Eng. Pat. $21968^{97}$). Syrupy. The sodium salt is easily soluble, the barium salt rather sparingly.

### *o*-Chlorobenzaldehyde

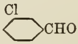
$C_6H_4Cl\cdot CHO[1:2]$

*Preparation.*—(1) By oxidation of *o*-chlorobenzyl alcohol (*q.v.*) with nitrosulphuric acid (Kalle, Eng. Pat. $11260^{98}$). (2) By chlorination of *o*-chlorotoluene (from diazotised *o*-toluidine and copper) (75 pts.) in presence of phosphorus pentachloride ($2\frac{1}{4}$ pts.) at a temperature of 150° to 180° until 40 pts. of chlorine are taken up. The crude *o*-chlorobenzylidene chloride thus obtained is converted into aldehyde by agitation with cold 100% sulphuric acid (420 pts.) until dissolved and the solution poured into water (Erdmann, *Ann.* **272**, 151).

*Properties.*—Colourless fluid. B.p. 214°; m.p. 3°; sp. gr. at 8° = 1·29.

### *m*-Chlorobenzaldehyde

$C_6H_4Cl\cdot CHO[1:3]$ *i.e.*



*Preparation.*—By chlorination of benzaldehyde in presence of zinc chloride (Müller, Ger. Pat. $33064^{88}$); or better from *m*-amidobenzaldehyde by diazotisation and treatment with cuprous chloride (Meister, Lucius, and Brüning).

*Properties.*—Oil. B.p. 210° to 213°; sp. gr. 1·246.

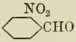
## Dichlorobenzaldehyde

$C_6H_3Cl_2 \cdot CHO[6:3:1]$

Obtained as chief product in the chlorination of benzaldehyde in presence of iodine or antimony (Gnehm, Am. Pat. 315932; *Ber.* **29**, 875).

## *o*-Nitrobenzaldehyde

$C_6H_4(NO_2)CHO[1:2]$ *i.e.*

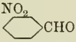


*Preparation.*—(1) By oxidation of *o*-nitrobenzyl alcohol (*q.v.*) with nitrosulphuric acid (Kalle, Eng. Pats. $11259^{98}$ and $11260^{98}$). (2) By oxidation of *o*-nitrobenzylaniline or its sulphonic acid to the corresponding *o*-nitrobenzylidene derivative and hydrolysis of the latter with acid (Meister, Lucius, and Brüning, Eng. Pats. $15890^{97}$ and $30118^{97}$). (3) By oxidation of *o*-nitrotoluene with oxide of manganese (Monnet, Eng. Pat. $613460^{98}$; Badische, Eng. Pat. $21947^{99}$).

*Properties.*—Long yellow needles. M.p. 46°. Gives indigo on treatment with acetone and aqueous soda.

## *m*-Nitrobenzaldehyde

$C_6H_4(NO_2)CHO[1:3]$ *i.e.*

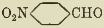


*Preparation.*—By slowly adding benzaldehyde (10 pts.) to potassium nitrate (11 pts.) dissolved in conc. sulphuric acid, keeping the temperature below 10° (Friedländer and Henriques, *Ber.* **14**, 2802; Ehrlich, *Ber.* **15**, 2010). The yield is 100 to 105%.

*Properties.*—Yellow needles. M.p. 58°.

## *p*-Nitrobenzaldehyde

$C_6H_4(NO_2)CHO[1:4]$ *i.e.*



*Preparation.*—By boiling *p*-nitrobenzyl chloride (1 pt.) with a solution of lead nitrate (5 pts.) in water (10 pts.) for 24 hours, or for 12 hours with a saturated solution of cupric nitrate. The yield is nearly theoretical (Faust, *Mon. Scien.* **1885**, 1262).

*Properties.*—Long thin prisms. M.p. 106°. Tolerably soluble in hot water, slightly in cold.

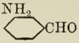
## *p*-Nitrobenzaldehyde-*o*-sulphonic acid

$C_6H_3(NO_2)(SO_3H) \cdot CHC[4:2:1]$

*Preparation.*—By oxidation of the sodium dinitrostilbenedisulphonate (200 pts.) in cold dilute aqueous solution with potassium permanganate (87½ pts.) (Levinstein, Eng. Pat. $19904^{97}$; Green and Wahl, *Ber.* **30**, 3101; Eng. Pat. $21825^{97}$).

*Properties.*—Small colourless crystals. Very soluble in water. It gives a yellow anilide and an orange-red hydrazone.

### *m*-**Amidobenzaldehyde**

$C_6H_4(NH_2)CHO[1:3]$ *i.e.* 

*Preparation.*—By reduction of the sodium bisulphite compound of *m*-nitrobenzaldehyde with ferrous hydrate (Meister, Lucius, and Brüning, Eng. Pat. $11049^{91}$; Ger. Pat. $62950^{91}$).

*Properties.*—The free base cannot be isolated, as when liberated from its salts it at once passes over into its anhydride $C_7H_5N$, a crystalline body of high melting-point and sparing solubility.

### *p*-**Amidobenzaldehyde**

$C_6H_4(NH_2)CHO[1:4]$ *i.e.* 

*Preparation.*—By boiling *p*-nitrotoluene (20 pts.) dissolved in alcohol (60 pts.) with a solution of sulphur (12 pts.) and caustic soda (20 pts.) in water (160 pts.) (Geigy and Co., Ger. Pat. $86874^{95}$).

*Properties.*—Flat plates. M.p. 71°. Soluble in water. Readily polymerises to a yellow insoluble product.

### *p*-**Dimethylamidobenzaldehyde**

$C_6H_4\{N(CH_3)_2\}CHO[1:4]$ *i.e.* 

*Preparation.*—(1) A mixture of dimethylaniline (12 pts.), anhydrous chloral (14 pts.), and phenol (9 pts.) is allowed to stand at the ordinary temperature for several days. The phenol is then removed by shaking with dilute caustic soda, and the crystalline residue is dissolved in boiling water and hydrochloric acid. On cooling, the sparingly soluble hydrochloride of the base $C_6H_4\{N(CH_3)_2\}\cdot CH(OH)\cdot CCl_3$ crystallises out, which is converted into *p*-dimethylamidobenzaldehyde and chloroform by heating with the theoretical quantity of alcoholic caustic soda (Bössneck, *Ber.* **18**, 1516; **19**, 365; Zierold, Ger. Pat. $61551^{90}$). (2) By hydrolysis of the benzylidene compound $(CH_3)_2N\cdot C_6H_4\cdot CH:N\cdot C_6H_4(SO_3H)$ obtained by the condensation of dimethylaniline, phenylhydroxylaminesulphonic acid (formed by reduction of *m*-nitrobenzenesulphonic acid) and formaldehyde (Geigy and Co., Eng. Pat. $17135^{98}$).

*Properties.*—Colourless plates. M.p. 73°. Soluble in hot water.

*Sulphonic acid* $C_6H_3\{N(CH_3)_2\}(SO_3H)\cdot CHO[4:2:1]$ is obtained from the *o*-chloro derivative by heating with sodium sulphite under pressure at 200° (Ger. Pat. $107918^{98}$).

### *p*-**Diethylamidobenzaldehyde**

$C_6H_4\{N(C_2H_5)_2\}CHO[1:4]$

Obtained from diethylaniline in the same way as the preceding. It forms colourless needles of m.p. 41°, soluble in water.

### *o*- and *p*-**Oxybenzaldehyde**

$C_6H_4(OH)CHO[1:2]$ & $[1:4]$

*Preparation.*—These two isomers are obtained together by boiling phenol (1 pt.), aqueous caustic soda of 20% NaOH (15 pts.), and chloroform (2 pts.). The acidified product is distilled with steam, when *o*-oxybenzaldehyde together with unaltered phenol and chloroform distil over and are separated by sodium bisulphite, whilst *p*-oxybenzaldehyde remains behind and crystallises from the residue on cooling (Tiemann and Reimer, *Ber.* **9**, 824; **10**, 63, 213).

*Properties.*—The *o*-compound is a pleasant-smelling liquid of b.p. 196° and sp. gr. at 14° = 1·173. The *p*-compound forms colourless needles of m.p. 116°. They are both soluble in hot water, and combine with alkaline bisulphites.

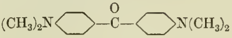
### *m*-Oxybenzaldehyde

$C_6H_4(OH)CHO[1:3]$

*Preparation.*—From *m*-amidobenzaldehyde by heating its diazo compound with water (Tiemann, *Ber.* **15**, 2045).

*Properties.*—Colourless needles. M.p. 104°; b.p. 240°. Soluble in hot water.

### *pp*-Tetramethyldiamidobenzophenone

$[4:1](CH_3)_2N \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot N(CH_3)_2[1:4]$ *i.e.* 

*Preparation.*—Carbonyl chloride is passed into dimethylaniline at the ordinary temperature until the latter has increased in weight by 40%. The product, which chiefly consists of dimethylamidobenzoyl chloride and dimethylaniline, is then heated for several hours at 100° to complete the reaction (Michler, *Ber.* **9**, 715, 1900).

*Properties.*—Colourless plates. M.p. 174° corr. Easily soluble in alcohol, insoluble in water.

*Chloride* $\{(CH_3)_2N \cdot C_6H_4\}_2CCl_2$.—Obtained by the action of phosphorus chlorides or oxychloride upon the ketone.

### *pp*-Tetraethyldiamidobenzophenone

$[4:1](C_2H_5)_2N \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot N(C_2H_5)_2[1:4]$

Obtained from diethylaniline and carbonyl chloride in the same way as the preceding. Small yellowish plates. M.p. 96°.

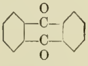
### *pp*-Tetramethyldiamidothiobenzophenone

$[4:1](CH_3)_2N \cdot C_6H_4 \cdot CS \cdot C_6H_4 \cdot N(CH_3)_2[1:4]$

*Preparation.*—By slowly adding thiocarbonyl chloride (10 pts.) diluted with carbon disulphide (30 pts.) to dimethylaniline (50 pts.), keeping the temperature at 0° to 10° by external cooling. After agitating for 10 or 12 hours, the mixture is made alkaline, the carbon disulphide and excess of dimethylaniline is distilled off with steam, and the thioketone remains behind (Kern, Eng. Pat. $12022^{86}$; Baither, *Ber.* **20**, 1732, 3290).

*Properties.*—Ruby-red plates with steel-blue reflex. M.p. 202°. On heating with dilute hydrochloric acid it is decomposed into tetramethyldiamidobenzophenone and hydric sulphide.

### Anthraquinone

$[2:1]C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4[1:2]$ *i.e.* 

*Preparation.*—By oxidation of anthracene with chromic acid, the operation being performed in the following manner:—Finely powdered commercial anthracene, containing 60 to 80% pure anthracene, is stirred up with a boiling solution of sodium or potassium bichromate (1 mol. of bichromate to every mol. of true anthracene present). A dilute solution of sulphuric acid (containing 4 mols. of sulphuric acid to every mol. of bichromate used) is then very slowly run in, the operation occupying 9 or 10 hours; the mixture is finally boiled for some time to complete the oxidation, and the crude anthraquinone is filtered off, dried, and ground. The product, which also contains the phenanthrene, carbazole, acridine, etc., present in the crude anthracene, is purified by heating it with 2 or 3 times its weight of conc. sulphuric acid at 110° for some time, and then pouring into water. By this treatment the impurities are converted into soluble compounds (sulphonic acids, etc.), which remain in solution whilst the anthraquinone is unattacked and precipitates as a nearly white crystalline powder. After washing with soda it is filtered off and dried. It contains 90 to 95% of pure anthraquinone, and is employed at once for the preparation of alizarin. By sublimation it can be obtained quite pure (Kopp, *Mon. Scien.* [3] **8**, 1159; Graebe and Liebermann, *Mon. Scien.* [3] **9**, 421).

*Properties.*—Sublimes in yellow needles. M.p. 277°. Very slightly soluble in alcohol and ether, more readily in benzene. Very stable. By treatment with fuming sulphuric acid it is first converted into a **monosulphonic acid** $C_{14}H_7O_2(SO_3H)$, and then into a mixture of two **disulphonic acids** $C_{14}H_6O_2(SO_3H)_2$. By fusion with caustic soda, the monosulphonic acid yields alizarin, the disulphonic acids give isopurpurin and flavopurpurin respectively

### Dinitroanthraquinones

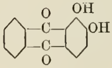
$C_{14}H_6O_2(NO_2)_2[1:5]$ & $[1:8]$

*Preparation.*—A mixture containing these two isomers, of which the first is of chief importance, is obtained by nitration of anthraquinone. For instance, dry sodium nitrate (10 pts.) is stirred into a solution of anthraquinone (10 pts.) in sulphuric acid (200 pts.), and the mixture kept at 60° to 80° for 12 hours. The product, of which the 1 : 5-isomer forms the chief part, is usually employed without separation. By repeatedly extracting the mixture with alcohol or acetone the 1 : 5-isomer is left as an insoluble powder (Römer, *Ber.* **16**, 366; Badische Anil. und Soda Fabrik, Eng. Pats. $19588^{91}$; $19589^{91}$; $974^{94}$).

*Properties.* — The 1 : 5-dinitroanthraquinone forms yellow needles or thick crystals (from nitrobenzene). M.p. much above 300°. Sublimable in needles. Very sparingly soluble in most solvents. Is employed for the preparation of the anthracene blues.

### 1 : 2-Dioxyanthraquinone (*Alizarine*)

$C_{14}H_6O_2(OH)_2[1:2]$ *i.e.*

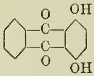


*Preparation.*—Anthraquinonemonosulphonate of soda (90 pts.) is heated at 160° with caustic soda (180 pts.) and sodium chlorate (16 pts.) dissolved in water (540 pts.). After 24 hours the vessel is closed and the heating continued under about 4 atmospheres pressure for a further 40 hours. The melt is then dissolved in water and precipitated boiling with acid.

*Properties.*—Yellow powder which sublimes at 160° to fine red needles. M.p. 290°. Insoluble in cold water. Its alkaline solution is violet. In addition to its employment in dyeing and printing it forms the raw product for the preparation of other anthracene colouring matters.

### 1 : 4-**Dioxyanthraquinone** (*Quinizarine*)

$C_{14}H_6O_2(OH)_2[1:4]$ *i.e.*

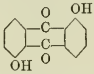


*Preparation.*—(1) By heating phthalic anhydride with hydroquinone in presence of sulphuric acid (*Ber.* **6**, 508). (2) By heating anthraquinone (1 pt.) and boric acid (1 pt.) with conc. sulphuric acid (20 pts.) at 260° to 280° for a short time (Eng. Pat. 973^94). (3) By heating a mixture of anthraquinone (10 pts.), conc. sulphuric acid (200 pts.), boric acid (10 pts.), and sodium nitrite (14 pts.) at 220° to 230° for 3 or 4 hours (Eng. Pat. 975^94).

*Properties.*—Red plates or needles. Sublimes in needles. M.p. 195°. Dissolves with a blue colour in alkalies.

### 1 : 5-**Dioxyanthraquinone** (*Anthrarufine*)

$C_{10}H_6O_2(OH)_2[1:5]$ *i.e.*

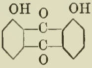


*Preparation.*—Together with a small quantity of chrysazine by heating a mixture of anthraquinone (5 pts.), dry boric acid (2 pts.), and sulphuric anhydride of 80% $SO_3$ (100 pts.) for 36 hours at 100° in a closed digestor (Ger. Pat. 101220^97).

*Properties.*—Yellow tables. M.p. 280°. Nearly insoluble in water. Its solution in caustic alkalies is yellow.

### 1 : 8-**Dioxyanthraquinone** (*Chrysazine*)

$C_{10}H_6O_2(OH)_2[1:8]$ *i.e.*

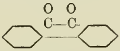


*Preparation.*—From (1 : 8)-dinitroanthraquinone by heating with methyl alcohol and caustic soda, and saponification of the ether obtained (Ger. Pat. 77818); or by reduction and subsequent diazotisation in strong sulphuric acid solution (Ger. Pat. 97688).

*Properties.*—Reddish brown needles. M.p. 191°. Its solution in austic alkalies is yellowish red.

### **Phenanthraquinone**

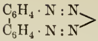
$C_{10}H_8O_2$ *i.e.*



*Preparation.*—By oxidation of phenanthrene (10 pts.) with sodium bichromate (120 pts.), water (300 pts.), and conc. sulphuric acid (180 pts.). The product is diluted with water and the phenanthraquinone filtered off and purified by solution in sodium bisulphite and reprecipitation (*cf.* Erdmann).

*Properties.*—Glistening yellowish plates or needles. M.p. 200°. Distils above 300°.

## DIAZO AND AZO COMPOUNDS

By the action of nitrous acid upon the salts of aromatic primary amines and diamines diazo compounds are produced; thus aniline hydrochloride gives **diazobenzene chloride** $C_6H_5 \cdot N:N \cdot Cl$, sulphanilic acid gives **diazobenzene sulphonic acid** $C_6H_4{<}\genfrac{}{}{0pt}{}{N:N}{SO_3}{>}$, benzidine sulphate gives **tetrazodiphenyl sulphate**  $\left.\begin{array}{l}C_6H_4 \cdot N:N \\ | \\ C_6H_4 \cdot N:N\end{array}\right> SO_4$, etc. These reactions take place with extreme readiness, it being only necessary to dissolve or suspend the amine salt or amidosulphonic or carboxylic acid in water, generally cooled with ice, and add the theoretical quantity of sodium nitrite and hydrochloric acid. The diazo compounds are mostly very unstable bodies, and when dry are explosive. For the preparation of the azo colours they are usually not isolated, but are at once combined with phenols or amines or their sulphonic or carboxylic acids, in alkaline or slightly acid aqueous solution. Thus diazobenzene chloride combines with *m*-phenylene diamine to form **diamidoazobenzene** ("Chrysoidine") $C_6H_5 \cdot N:N \cdot C_6H_3(NH_2)_2$; diazobenzene sulphonic acid combines with $\beta$-naphthol to form **$\beta$-naphtholazobenzenesulphonic acid** ("Orange II.") $C_6H_4(SO_3H) \cdot N:N \cdot C_{10}H_6 \cdot OH$.

These bodies are simple **monoazo compounds**; in certain cases, however, when the requisite positions are open, more especially with the dioxy-, diamido-, and amidoxy compounds, two diazo residues, similar or dissimilar, can be introduced into the same phenol or amine, producing a **disazo compound**; thus 2 mols. of diazobenzene chloride will combine with 1 mol. of $\alpha$-naphthol or with 1 mol. of *m*-phenylene diamine to form $C_6H_5 \cdot N:N \cdot C_{10}H_5(OH) \cdot N:N \cdot C_6H_5$ or $C_6H_5 \cdot N:N \cdot C_6H_2(NH_2)_2 \cdot N:N \cdot C_6H_5$. A second and more important class of disazo colouring matters is obtained by the action of nitrous acid upon certain amidoazo compounds (formed by combining diazo compounds with amines) and combining the diazoazo compound thus produced with another amine or phenol. Thus **amidoazonaphthalenedisulphonic acid** $C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot NH_2$, obtained by combining $\alpha$-diazonaphthalenedisulphonic acid with $\alpha$-naphthylamine, gives on treatment with nitrous acid the **diazoazonaphthalenedisulphonic acid** $C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot N:N \cdot OH$, which combines with $\beta$-naphthol disulphonic acid to form "Naphthol black" $C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot N:N \cdot C_{10}H_4(OH)(SO_3H)_2$. The amidoazo compounds employed for the preparation of these disazo colours are themselves colouring matters, but, with the exception of amidoazobenzene sulphonic acid, are not used for dyeing. They are usually not isolated, but are converted directly into the disazo compounds in the solution in which they are formed, by further disazotisation and combination. A third class of disazo compounds is obtained by treating a diamido compound with 2 mols. of nitrous acid and combining the tetrazo compound obtained with 2 mols. of a second component (phenol or amine) or with 1 mol. of each of two components.

By a further extension of the above methods compounds are obtainable containing three, four, or even more double-nitrogen groups in the molecule, and known as **trisazo compounds, tetrakisazo compounds,** etc. With the increase in the number of azo groups the shade of the colouring matter tends towards dark blue or black.

In certain cases the production of the azo colouring matter is effected upon the fibre, either by passing the fabric which has been padded with alkaline $\beta$-naphthol through a solution of the diazo compound (*e.g.* diazotised paranitraniline, $\alpha$-naphthylamine, dianisidine, etc.), or by diazotisation and combination of a previously fixed amido compound such as Primuline or Diaminogen ("*Ingrain colours*"). For the former process certain ready-prepared diazo compounds are brought upon the market under the name of "Azophor Red," "Nitrazol," etc.

Azo compounds derived from paradiamines (*i.e.* benzidine, *p*-phenylene diamine, etc.) and from dehydrothiotoluidine and its homologues possess the property of dyeing vegetable fibres without a mordant ("*Substantive cotton colours*").

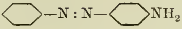
Azo compounds containing hydroxyl or carboxyl groups in certain positions enabling them to form lakes with metallic oxides are used for dyeing fast colours on wool ("*Chrome colours*").

Unsulphonated azo compounds derived from amidoammonium bases, safranines, or amidobenzylamines have strongly basic properties which render them suitable for dyeing tannin mordanted cotton or mixed fabrics of cotton and wool ("*Janus or Basic azo colours*").

The following are some of the more important of the amidoazo compounds employed as intermediate products:—

## *p*-Amidoazobenzene

$C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH_2[1:4]$ *i.e.*



*Preparation.*—By slowly running a solution of sodium nitrite (7 pts.) in water (10 pts.) into a mixture of aniline hydrochloride (26 pts.) dissolved in aniline (50 pts.), agitating and keeping the temperature between 30° and 40°. After the mixture has been kept at 40° for two hours, and has stood for a day at the ordinary temperature, the product is mixed with a slight excess of hydrochloric acid beyond that required to combine with the aniline, and is diluted with water (250 pts.). The amidoazobenzene hydrochloride which separates as a steel-blue crystalline precipitate is filtered off, washed, and dried. The excess of aniline employed is recovered from the filtrate by making alkaline and distilling with steam (Städel and Bauer, *Ber.* **19**, 1954).

*Properties.*—Orange needles or prisms. M.p. 127°; b.p. above 360°. Nearly insoluble in water, soluble in alcohol. Weak base, its salts, which are sparingly soluble, being decomposed on washing with water.

*Monosulphonic acid* $C_6H_4(SO_3H) \cdot N:N \cdot C_6H_4(NH_2)$.—Obtained by sulphonating amidoazobenzene with fuming sulphuric acid at a low temperature, until the product is soluble in alkalies. Small yellowish white needles, very sparingly soluble in water.

*Disulphonic acid* $C_6H_4(SO_3H) \cdot N:N \cdot C_6H_3(NH_2)(SO_3H)$.—Obtained by sulphonating amidoazobenzene with fuming sulphuric acid until the product is easily soluble in water. Steel-blue needles. A mixture of the sodium salts of this and the preceding acid is employed for dyeing under the name of "Acid yellow."

## Amidoazotoluene

$[2:1]C_6H_4(CH_3) \cdot N:N \cdot C_6H_3(CH_3)NH_2[1:3:4]$

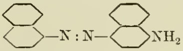
*Preparation.*—By slowly adding a saturated solution of sodium nitrite (1 mol.) to a mixture of *o*-toluidine (4 mols.) and conc. hydrochloric acid (2 mols.), keeping the temperature at 30° to 40°.

*Properties.*—Yellow plates or tables. M.p. 100°. Easily soluble in alcohol, nearly insoluble in water.

*Sulphonic acid.*—Obtained by treating amidoazotoluene with fuming sulphuric acid.

## *a*-Amidoazonaphthalene

$C_{10}H_7 \cdot N:N \cdot C_{10}H_6 \cdot NH_2[1:4]$ *i.e.*



*Preparation.*—By mixing equal mols. of *a*-diazonaphthalene chloride $C_{10}H_7 \cdot N_2 \cdot Cl$ (from *a*-naphthylamine hydrochloride and nitrous acid) and *a*-naphthylamine hydrochloride in cold aqueous solution, then slowly adding sodium carbonate till alkaline. The precipitate is filtered off and crystallised from xylene (Perkin and Church, *Ann.* **129**, 108; Friedländer, *Ber.* **22**, 590).

*Properties.*—Brownish red needles. M.p. 183° corr.

*Disulphonic acids* $C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot NH_2$. Obtained by combining the diazo compounds of the *a*-naphthylaminedisulphonic acids with *a*-naphthylamine hydrochloride (Cassella and Co., Eng. Pats. $9214^{85}$ and $14442^{88}$).

### Salicylic acid-azo-$\alpha$-naphthylamine

$[4:3:1]C_6H_3(OH)(CO_2H) \cdot N:N \cdot C_{10}H_6 \cdot NH_2[1:4]$

*Preparation.*—By combining the diazo compound of amidosalicylic acid with $\alpha$-naphthylamine (Bayer and Co., Ger. Pat. $51504^{89}$; Am. Pat. 438438).

*Properties.*—Small steel-blue needles. Dissolves in alkalies with a yellowish red colour.

## COMPOUNDS OF THE FATTY SERIES

### Carbonyl Chloride (*Phosgene Gas*)

$COCl_2$ *i.e.* $O=C=Cl_2$

*Preparation.*—By leading a mixture of equal volumes of carbonic oxide and chlorine over a condensing surface such as platinised asbestos, animal charcoal, etc. (Paternò, *Jahresber.* **1878**, 229).

*Properties.*—Pungent-smelling liquid, gaseous at ordinary temperatures. B.p. 8° corr.; sp. gr. at 0° = 1·392. Very soluble in benzene. Very slowly decomposed by cold water, quickly by hot into carbonic acid and hydrochloric acid.

### Thiocarbonyl Chloride (*Thiophosgene*)

$CSCl_2$ *i.e.* $S=C=Cl_2$

*Preparation.*—Chlorine is passed into cold carbon disulphide containing a trace of iodine until the liquid has increased in weight by 230% (*i.e.* 5 Cl to $CS_2$). The product $CCl_3 \cdot SCl$ is purified by distillation with steam and fractionation, and is converted into thiocarbonyl chloride by reduction with iron and acetic acid (Klasson, *Ber.* **20**, 2377; Kern and Sandoz, Ger. Pat. $5430^{87}$).

*Properties.*—Reddish liquid of irritant odour. B.p. 74°. On keeping, it is slowly converted into colourless crystals of the polymeric compound, which melt at 113°.

### Methyl Alcohol (*Wood Spirit*)

$CH_3 \cdot OH$

*Preparation.*—From the aqueous portion of the distillate obtained in the destructive distillation of wood, by treatment with lime and rectification.

*Properties.*—Colourless alcoholic liquid. B.p. 66°; sp. gr. at 15° = ·799. Miscible with water.

*Valuation.*—The purity of methyl alcohol, for use in the preparation of dimethylaniline, is of great consequence, especially in regard to freedom from acetone. 95% of it should distil within one degree, and its specific gravity should be correct. It should remain colourless when mixed with strong caustic soda, and only give a light yellow colour with twice its volume of conc. sulphuric acid. It should not at once decolorise $\frac{1}{5}$ of its volume of a 0·1% solution of potassium permanganate. It should not contain more that $\frac{1}{10}$ to $\frac{1}{4}$% of acetone, as determined by the following method:—1 to 2 c.c. of the methyl alcohol are put into a stoppered flask, and mixed with 20 to 30 c.c. of normal caustic potash solution (free from nitrite). 20 to 30 c.c. of $\frac{1}{5}$ normal iodine solution are then dropped in, and after shaking for $\frac{1}{2}$ minute the clear solution is acidified with a quantity of dilute hydrochloric acid of sp. gr. 1·025 equal in volume to the caustic potash solution employed. A measured excess of $\frac{1}{10}$ normal sodium thiosulphate is then added, and the latter is titrated back with $\frac{1}{5}$ normal iodine solution and starch. From the amount of iodine solution used up the percentage of acetone is calculated, since 1 mol. of acetone requires 6 atoms of iodine to convert into iodoform, *i.e.* 1 c.c. of $\frac{N}{5}$ iodine solution is equivalent to $\frac{\cdot 058}{6}$ grms. of acetone (Messinger, *Ber.* **21,** 3366).

## Methyl Chloride

$CH_3Cl$

*Preparation.*—Trimethylamine, obtained from the residues of beetroot molasses by distillation with lime, is heated with hydrochloric acid under pressure (Vincent, *Ding. pol. J.* **230,** 270; **234,** 294; *Jahresber.* **1878,** 1135).

*Properties.*—Colourless gas of pleasant ethereal smell. Under a pressure of 4 to 5 atmospheres it is liquid at ordinary temperatures. B.p. − 21°. Very soluble in alcohol, only slightly in water.

## Dimethyl Sulphate

$(CH_3)_2SO_4$

*Preparation.*—Fuming sulphuric acid of 25% $SO_3$ (4 pts.) is added to methyl alcohol (1 pt.) cooled to 30° to 40°. The mixture is then distilled in vacuo when dimethylsulphate passes over. Yield 130% of the alcohol (Berlin Aniline Co., Ger. Pat. $113239^{99}$).

*Properties.*—Colourless liquid. B.p. 188°; sp. gr. 1·324 at 22°. Very irritant and poisonous. Valuable methylating agent for amines and phenols.

## Formaldehyde (*Oxymethylene*)

$H_2C:O$

*Preparation.*—By leading a mixture of methyl alcohol vapour and air in theoretical proportions over heated copper gauze contained in a copper tube (Loew, *Journ. f. pr. Chem.* **33,** 321; Trillat, Ger. Pat. $55176^{89}$).

*Properties.*—Pungent-smelling gas. B.p − 21°. Very soluble in water, in which solvent it is usually collected. On keeping the solution it is slowly polymerised to trioxymethylene $C_3H_6O_3$, a crystalline solid of m.p. 152°.

*Valuation.*—The strength of aqueous solutions of formaldehyde can be determined by adding normal ammonia in excess and titrating with sulphuric acid; the quantity of ammonia employed in forming hexamethylenetetramine $(CH_2)_6N_4$ gives the percentage of formaldehyde present (Legler, *Ber.* **16,** 1333). The commercial solution usually contains 40%.

## Formic Acid

$H\cdot CO_2H$

*Preparation.*—Produced technically by passing carbonic oxide gas (CO) under 6 to 7 atmospheres pressure over powdered caustic soda at 150° to 170°, the sodium formiate produced being afterwards decomposed by a mineral acid (Goldschmidt, Ger. Pat. 86419).

*Properties.*—Pungent-smelling liquid. The anhydrous acid has the following physical constants:—M.p. 8°; B.p. 101°; sp. gr. 1·2256 at 15°.

## Dimethylamine

$(CH_3)_2NH$

*Preparation.*—By boiling nitrosodimethylaniline hydrochloride (165 pts.) with a solution of caustic soda (200 pts.) in water (8000 pts.). The dimethylamine which is evolved is collected in water or dilute hydrochloric acid.

*Properties.*—Pungent ammoniacal gas. B.p. 8°. Very soluble in water.

## Ethyl Bromide

$C_2H_5Cl$

*Preparation.*—Conc. sulphuric acid (2 pts.) is mixed with 96% alcohol (1 pt.), and after standing for some time is diluted with water ($\frac{1}{2}$ pt.). Potassium bromide (1 pt.) is then added, and the mixture is slowly heated, finally to 130°. The ethyl bromide, which distils over, is washed with water, and is freed from 7 or 8% of ether, which it contains, by shaking with conc. sulphuric acid in which only the ether dissolves (*Ding. pol. J.* **229**, 284).

*Properties.*—Colourless ethereal liquid. B.p. 38°; sp. gr. at 15° = 1·476.

## Acetic Acid (*Glacial acetic acid*)

$CH_3 \cdot CO_2H$

*Preparation.*—By distillation of crude calcium acetate ("pyrolignite of lime," obtained by neutralisation of wood vinegar with lime) with hydrochloric or sulphuric acid, and fractional distillation of the product (*cf.* Klar, *J. Soc. Chem. Ind.* **1897**, 667 and 722).

*Properties.*—Liquid or crystalline solid. B.p. 118°; m.p. 17°; sp. gr. 1·05 at 20°.

*Valuation.*—It should not contain more than 1 to $1\frac{1}{2}$% of water, *i.e.* its m.p. should not be lower than 14°. On evaporation it should leave no appreciable residue. It should give no precipitate with silver nitrate or barium chloride. 5 g. diluted with 15 c.c. of water should not decolorise more than 3 c.c. of $\frac{N}{100}$ permanganate by 15 minutes' standing.

## Chloroacetic Acid

$CH_2Cl \cdot CO_2H$

*Preparation.*—By passing chlorine (1 mol.) into boiling glacial acetic acid containing some iodine, sulphur, or phosphorus (cf. *Ber.* **22**, 762; **25**, 334).

*Properties.*—Needles. B.p. 186°; m.p. 63°; sp. gr. 1·395 at 73°.

## Acetoacetic Ether

$CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5$ and $CH_3 \cdot C(OH) : CH \cdot CO_2C_2H_5$

*Preparation.*—By the action of dry sodium ethylate upon dry acetic ether.

*Properties.*—Liquid. B.p. 181°; sp. gr. 1·025.

## Oxalacetic Ether

$CO_2(C_2H_5) \cdot CO \cdot CH_2 \cdot CO_2(C_2H_5)$

*Preparation.*—Dry acetic ether (110 pts. by vol.) is slowly added to a mixture of oxalic ether (135 pts. by vol.) and ether (800 pts. by vol.) containing sodium wire (23 pts.). After some hours the product has solidified to a mass of sodium oxalacetic ether which is pressed and decomposed with acid. The yield is 70 to 80% of the theoretical (Erdmann).

*Properties.*—Colourless liquid. B.p. 132° in a vacuum of 24 mm. Insoluble in water. Its sodium compound forms fine felted needles soluble in water. Its copper compound forms brilliant green glistening needles of m.p. 162°.

## Succinic Acid

$CO_2H \cdot CH_2 \cdot CH_2 \cdot CO_2H$

*Preparation.*—By the dry distillation of amber at 280°; or by the fermentation of a solution of ammonium tartrate at 25° to 30° (König, *Ber.* **15**, 172).

*Properties.*—Colourless monoclinic prisms. M.p. 180°; b.p. 235°. At its boiling-point it is converted into the anhydride $C_2H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$. It is tolerably soluble in water (6 pts. in 100 pts. at 15°).

## Dioxytartaric Acid

$CO_2H \cdot C(OH)_2 \cdot C(OH)_2 \cdot CO_2H$ or $CO_2H \cdot CO \cdot CO \cdot CO_2H$

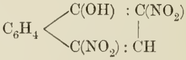
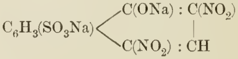
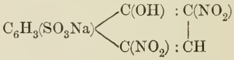
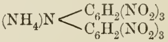
*Preparation.*—By the spontaneous decomposition of the nitrate of tartaric acid ("nitrotartaric acid") in aqueous solution. Tartaric acid (1 pt.) is gently warmed with fuming nitric acid (2 pts.) till dissolved, mixed with an equal volume of conc. sulphuric acid and allowed to stand overnight. The crystalline magma is then stirred into ice and water, and the solution left to stand for 3 or 4 days, after which it is neutralised with sodium carbonate, and the nearly insoluble sodium dioxytartrate which separates out is filtered off, washed, and dried. The yield is good.

*Properties.*—The acid is very unstable. The sodium salt is a colourless crystalline powder ($+ 2H_2O$), which decomposes on heating into tartronic acid and carbonic acid. By reaction with phenylhydrazine-*p*-sulphonic acid it yields "Tartrazine."

## SECTION II

# COLOURING MATTERS

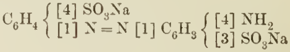
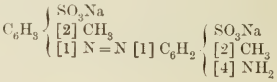
## I. NITRO

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 1 | **Picric Acid.**<br>**Carbazotic Acid.** | Symmetrical trinitrophenol. | $C_3H_3N_3O_7$ | $C_6H_2\left\{\begin{array}{l}[1]\ OH\\ [2]\ NO_2\\ [4]\ NO_2\\ [6]\ NO_2\end{array}\right.$ |
| 2 | **Victoria Yellow.**<br>**English Yellow.**<br>**Victoria Orange.**<br>**Saffron Substitute.**<br>**Aniline Orange.** | Mixture of the potassium (or ammonium) salts of dinitro-*o*-cresol and dinitro-*p*-cresol. | $C_7H_5N_2O_5K$ | $C_6H_2\left\{\begin{array}{l}[1]\ OK\\ [2]\ CH_3\\ (NO_2)_2\end{array}\right.$ and $C_6H_2\left\{\begin{array}{l}[1]\ OK\\ [4]\ CH_3\\ (NO_2)_2\end{array}\right.$ |
| 3 | **Martius Yellow.**<br>**Naphthol Yellow.**<br>**Primrose.**<br>**Jaune d'or.**<br>**Manchester Yellow.** | Ammonium, sodium, or calcium salt of dinitro-α-naphthol. | *Ammonium salt :*<br>$C_{10}H_9N_3O_5$<br>*Sodium salt :*<br>$C_{10}H_5N_2O_5Na + H_2O$<br>*Calcium salt :*<br>$C_{20}H_{10}N_4O_{10}Ca$ | *Free acid :*  $C_6H_4\left<\begin{array}{l}C(OH)\ :C(NO_2)\\ \qquad\qquad\ \ \vert\\ C(NO_2):CH\end{array}\right.$ |
| 4 | **Naphthol Yellow S.**<br>[*B.*]<br>**Naphthol Yellow.**<br>**Acid Yellow S.**<br>**Citronine A.** [*L.*] | Sodium (or potassium) salt of dinitro-α-naphthol-β-monosulphonic acid. | $C_{10}H_4N_2O_8SNa_2$ |  $C_6H_3(SO_3Na)\left<\begin{array}{l}C(ONa):C(NO_2)\\ \qquad\qquad\quad\ \ \vert\\ C(NO_2)\ :CH\end{array}\right.$<br>$[ONa : NO_2 : NO_2 : SO_3Na = 1 : 2 : 4 : 7]$ |
| 5 | **Brilliant Yellow.**<br>[*Sch.*]<br>**Naphthol Yellow RS.** [*By.*] | Sodium salt of dinitro-α-naphthol-α-monosulphonic acid. | $C_{10}H_5N_2O_8SNa$ |  $C_6H_3(SO_3Na)\left<\begin{array}{l}C(OH)\ :C(NO_2)\\ \qquad\qquad\ \ \vert\\ C(NO_2):CH\end{array}\right.$<br>$[OH : NO_2 : NO_2 : SO_3Na = 1 : 2 : 4 : 8]$ |
| 6 | **Aurantia.**<br>**Imperial Yellow.** | Ammonium salt of hexanitrodiphenylamine. | $C_{12}H_8N_8O_{12}$ |  $(NH_4)N\left<\begin{array}{l}C_6H_2(NO_2)_3\\ C_6H_2(NO_2)_3\end{array}\right.$ |

## COLOURING MATTERS.

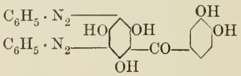
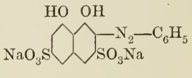
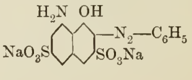
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of nitric acid upon phenol or upon phenolsulphonic acids. | 1771.<br>1842.<br>1869. | Woulfe.<br>(from indigo.)<br>Laurent.<br>(from phenol.)<br>Ann. (1843) **43**, 208.<br>R. Schmitt and L. Glutz.<br>(from phenolsulphonic acids.)<br>Ber. **2**, 52. | **Appearance of dyestuff**: light yellow crystals.—**In water**: sparingly soluble in the cold, more easily on boiling. Soluble in alcohol, benzene, etc. Melts at 122°·5. Tastes bitter.—**On boiling with potassium cyanide**: brown solution.—**Dyes**: wool and silk greenish yellow from an acid bath. |
| Action of nitric acid upon a mixture of the sulphonic acids of *o*- and *p*-cresol, or upon diazotoluene. | 1869. | Mittentzwey.<br>Wagner's Jahresber. **15**, 593; Ber. (1869) **2**, 206, 581; (1873) **6**, 974; (1874) **7**, 176; (1875) **8**, 685; (1881) **14**, 567, 898, 986; (1882) **15**, 1858; (1884) **17**, 370, 608; (1885) **18**, 252. | **Appearance of dyestuff**: reddish yellow powder.—**In water**: soluble with orange yellow colour.—**On addition of hydrochloric acid to aqueous solution**: white precipitate of dinitrocresol.—**On addition of caustic soda to aqueous solution**: no change of colour.—**On heating the powder**: the potassium salt deflagrates, the ammonium salt burns quietly.—**In conc. sulphuric acid**: light yellow solution.—**Dyes**: wool and silk orange. Used for colouring liqueurs, butter, etc. |
| Action of nitric acid upon α-naphthylamine, α-diazonaphthalene, α-naphthol, or (usual method) upon the (1 . 2 : 4) disulphonic acid of α-naphthol. | 1864. | Martius.<br>Zeits. f. Chem. (1868) **4**, 80.<br>Dale, Caro, and Martius.<br>Eng. Pat. $2785^{64}$.<br>Ballo.<br>Ber. (1870) **3**, 288.<br>Darmstädter and Wichelhaus.<br>Ber. **2**, 113; Ann. **152**, 299.<br>F. Bender.<br>Ber. **22**, 996 (note). | **Appearance of dyestuff**: Ammonium and sodium salts, small glistening orange yellow plates, calcium salt yellowish red crystals.—**In water**: soluble with a yellow colour; the ammonium salt is also soluble in alcohol.—**Addition of hydrochloric acid to the aqueous solution**: precipitates dinitronaphthol of m.p. 138°.—**On heating**: the sodium salt deflagrates, the ammonium salt burns quietly.—**Dyes**: wool golden yellow from an acid bath. |
| (*a*) Action of nitric acid upon α-naphthol-trisulphonic acid (1 : 2 : 4 : 7).<br>(*b*) Action of nitric acid upon α-naphthol-disulphonic acid (1 : 2 : 7) or upon the nitroso compound of the latter (usual method). | 1879. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $5305^{79}$.<br>Am. Pat. $225108^{80}$.<br>Ger. Pat. $10785^{79}$.<br>Fr. Pat. $134632^{80}$.<br>Leonhardt & Co.<br>Eng. Pat. $11318^{87}$.<br>Lauterbach.<br>Ber. **14**, 2028.<br>C. Graebe.<br>Ber. **18**, 1126. | **Appearance of dyestuff**: orange yellow powder.—**In water**: easily soluble.—**Addition of hydrochloric acid to the aqueous solution**: yellow without forming a precipitate.—**Caustic potash added to the aqueous solution**: flocculent yellow precipitate.—**On heating the powder**: burns with deflagration.—**Dyes**: wool and silk yellow from an acid bath. |
| Action of nitric acid upon α-naphthol-disulphonic acid Sch. or its nitroso derivative. | 1884. | Mensching.<br>The Schöllkopf Aniline & Chemical Co.<br>Eng. Pat. $15775^{85}$.<br>Am. Pat. 333036.<br>Ger. Pat. $40571^{85}$. | **Appearance of dyestuff**: golden yellow powder.—**On heating**: does not deflagrate, but swells up.—**In water**: soluble with a brownish yellow colour.—**On addition of hydrochloric acid to aqueous solution**: clear yellow solution.—**On addition of caustic soda to aqueous solution**: orange yellow precipitate, dissolves on warming.—**In conc. sulphuric acid**: pale yellow solution.—**Dyes**: wool and silk yellow from an acid bath. |
| Action of nitric acid upon diphenylamine. | 1873. | Kopp. Gnehm.<br>Ber. **7**, 1399; **9**, 1245. | **Appearance of dyestuff**: reddish brown crystals.—**On heating**: burns with deflagration.—**In water**: soluble with orange yellow colour.—**On addition of acids to aqueous solution**: precipitates bright yellow hexanitrodiphenylamine of m.p. 238°.—**Dyes**: wool and silk orange from an acid bath. |

## II. MONO-AZO

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 7 | **Aniline Yellow.**<br>**Spirit Yellow.**<br>**Jaune d'aniline.**<br>(As a dyestuff no longer in commerce.) | Hydrochloride of amidoazobenzene. | $C_{12}H_{12}N_3Cl$ | $C_6H_5-N=N-C_6H_4-NH_2HCl$ [1 : 4] |
| 8 | **Acid Yellow.** [*A.*]<br>**Fast Yellow G.** [*K.*]<br>**Acid Yellow G.**<br>**Fast Yellow.** [*B.*] [*By.*]<br>**Fast Yellow Extra.** [*By.*]<br>**Jaune acide.**<br>**New Yellow L.** [*K.*] | Mixture of sodium amidoazobenzene-disulphonate with some sodium amidoazobenzene-monosulphonate. | $C_{12}H_9N_3S_2O_6Na_2$ |  $C_6H_4\left\{\begin{array}{l}{[4]}\ SO_3Na\\ {[1]}\ N=N\ {[1]}\ C_6H_3\left\{\begin{array}{l}{[4]}\ NH_2\\ {[3]}\ SO_3Na\end{array}\right.\end{array}\right.$ |
| 9 | **Fast Yellow R.** [*K.*]<br>**Fast Yellow.** [*B.*]<br>**Yellow W.** [*By.*] | Sodium salt of amidoazotoluene-disulphonic acid. | $C_{14}H_{13}N_3S_2O_6Na_2$ |  $C_6H_3\left\{\begin{array}{l}SO_3Na\\ {[2]}\ CH_3\\ {[1]}\ N=N\ {[1]}\ C_6H_2\left\{\begin{array}{l}SO_3Na\\ {[2]}\ CH_3\\ {[4]}\ NH_2\end{array}\right.\end{array}\right.$ |
| 10 | **Sudan G.**<br>[*A.*] [*F.*] [*Ib.*] [*W.*]<br>**Carminaph J.** [*D. H.*]<br>**Cerasine Orange G.** [*C.*] | Dioxyazobenzene or Benzeneazoresorcinol. | $C_{12}H_{10}N_2O_2$ | $C_6H_5-N=N-C_6H_3(OH)_2$ [1 : 2 : 4] & [1 : 2 : 6] |
| 11 | **Sudan I.**<br>[*A.*] [*F.*] [*Ib.*] [*W.*]<br>**Carminaph.** [*D. H.*] | Benzene-azo-$\beta$-naphthol. | $C_{16}H_{12}N_2O$ | $C_6H_5-N=N-C_{10}H_6\cdot OH\ [\beta]$ |
| 12 | **Cochineal Scarlet G.** [*Sch.*] | Sodium salt of benzene-azo-$\alpha$-naphthol-monosulphonic acid. | $C_{16}H_{11}N_2O_4SNa$ | $C_6H_5-N=N-C_{10}H_5(OH)(SO_3Na)$ [2 : 1 : 5] |
| 13 | **Ponceau 4 GB.** [*A.*]<br>**Croceïne Orange.** [*By.*] [*K.*]<br>**Brilliant Orange.** [*M.*]<br>**Orange GRX.** [*B.*] | Sodium salt of benzene-azo-$\beta$-naphthol-$\beta$-sulphonic acid. | $C_{16}H_{11}N_2O_4SNa$ | $C_6H_5-N=N-C_{10}H_5(OH)(SO_3Na)$ [1 : 2 : 6] |

## COLOURING MATTERS.

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Warming diazobenzeneanilide (diazoamidobenzene) dissolved in aniline, with aniline hydrochloride. | | 1861.<br>1862. | Mène.<br>Jahresber. 1861, 496;<br>Jour. f. Pr. Chem. **82**, 462.<br>P. Griess.<br>Ann. (1862) **121**, 262 (note).<br>Simpson, Maule, & Nicholson (oxalate).<br>*Zeits. f. Chem.* (1866) **2**, 132.<br>Dale and Caro.<br>Eng. Pat. $3307^{63}$.<br>Kekulé.<br>Chemie der Benzolderivate, p. 204.<br>Martius and Griess.<br>Berl. Acad. Ber. 1865, 633. | **Appearance of dyestuff**: steel blue crystals.—**In water**: soluble sparingly with a yellow colour; on boiling it is partially decomposed with precipitation of the yellow base of m.p. 127°.—**In conc. sulphuric acid**: brown solution; red on dilution with water.—**Employment**: for preparation of acid yellow and indulines. |
| Action of fuming sulphuric acid upon amidoazobenzene hydrochloride. | | 1878. | Grässler.<br>Eng. Pat. $43^{79}$.<br>Am. Pat. 253598.<br>Ger. Pats. $4186^{79}$ & $7094^{79}$.<br>Chem. Ind. (1879) **2**, 48 and 346.<br>Griess.<br>Ber. **15**, 2185.<br>Eger.<br>Ber. **22**, 847. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: orange.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: brownish yellow solution, becoming orange yellow on dilution with water.—**Dyes**: wool and silk yellow from an acid bath. |
| Action of fuming sulphuric acid upon amidoazotoluene hydrochloride. | | 1878. | Grässler.<br>Eng. Pat. $43^{79}$.<br>Am. Pat. 253598.<br>Ger. Pat. $4186^{78}$.<br>Griess.<br>Ber. (1882) **15**, 2187. | **Appearance of dyestuff**: brownish yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid to aqueous solution**: magenta red.—**On addition of caustic soda to aqueous solution**: no change.—**In conc. sulphuric acid**: yellowish brown solution, becoming magenta red on dilution.—**Dyes**: wool reddish yellow from an acid bath. |
| Aniline. | Resorcinol. | 1875. | Baeyer and Jaeger.<br>Ber. **8**, 151.<br>Will & Pukall.<br>Ber. **20**, 1122. | **Appearance of dyestuff**: brown powder.—**In hot water**: partially soluble with a yellow colour.—**On addition of hydrochloric acid to the aqueous solution**: light brown precipitate.—**On addition of caustic soda**: brown solution.—**In conc. sulphuric acid**: brownish yellow solution; on dilution, light brown precipitate.—**In alcohol**: soluble with a yellow colour.—**Employment**: for colouring oils, varnishes, etc. |
| Aniline. | β-Naphthol. | 1883. | C. Liebermann.<br>Ber. (1883) **16**, 2860. | **Appearance of dyestuff**: brick red powder.—**In water**: insoluble.—**In conc. sulphuric acid**: magenta red solution; orange yellow precipitate on dilution with water.—**In alcohol**: soluble with an orange yellow colour.—**Employment**: for colouring oils, varnishes, etc. |
| Aniline. | α-Naphthol-monosulphonic acid L. (1:5.) | 1883. | Gaess.<br>Mon. Scien. 1884, 335.<br>Gattermann & Schulze.<br>Ber. **30**, 51.<br>Am. Pat. 333041. | **Appearance of dyestuff**: brick red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: thick precipitate.—**On addition of caustic soda to the aqueous solution**: orange yellow colour.—**In conc. sulphuric acid**: cherry red solution; brownish red precipitate on dilution with water.—**Dyes**: wool brick red from an acid bath. |
| Aniline. | β-Naphthol-monosulphonic acid S. | 1878. | P. Griess.<br>Ber. (1878) **11**, 2197. | **Appearance of dyestuff**: bright red powder.—**In water**: very soluble, with an orange yellow colour.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution**: brownish yellow solution.—**In conc. sulphuric acid**: orange yellow solution, giving a yellowish brown precipitate on dilution with water.—**Dyes**: wool orange yellow from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 14 | **Orange G.**<br>[*A.*] [*M.*] [*B.*]<br>**Orange GG.** [*C.*] | Sodium salt of benzene-azo-β-naphthol-disulphonic acid G. | $C_{16}H_{10}N_2S_2O_7Na_2$ | $C_6H_5-N=N-[1]\ C_{10}H_4\left\{\begin{array}{l}[2]\ OH\\ [6]\ SO_3Na\\ [8]\ SO_3Na\end{array}\right.$ |
| 15 | **Ponceau 2 G.**<br>[*A.*] [*B.*] [*M.*] [*C.*]<br>**Orange R.** [*H.*] | Sodium salt of benzene-azo-β-naphthol-disulphonic acid R. | $C_{16}H_{10}N_2O_7S_2Na_2$ | $C_6H_5-N=N-[1]\ C_{10}H_4\left\{\begin{array}{l}[2]\ OH\\ [3]\ SO_3Na\\ [6]\ SO_3Na\end{array}\right.$ |
| 16 | **Butter Yellow.**<br>**Oil Yellow.** [*W.*] | Dimethylamidoazobenzene or benzeneazodimethylaniline. | $C_{14}H_{15}N_3$ | $C_6H_5-N=N-[1]C_6H_4\ [4]N(CH_3)_2$ |
| 17 | **Chrysoïdine Y.**<br>[*H.*] [*W.*] [*Lev.*]<br>**Chrysoïdine Crystals.*** | Hydrochloride of diamidoazobenzene.<br>Hydrochloride of benzene-azo-*m*-phenylenediamine. | $C_{12}H_{13}N_4Cl$ | $C_6H_5-N=N-C_6H_3(NH_2)_2HCl\ [1:2:4]$ |
| 18 | **Chrysoïdine R.**<br>[*H.*] [*W.*] [*Lev.*]<br>[*G.*] [*I.*]<br>**Cerotine Orange C extra.** [*C.J.*]<br>**Gold Orange for Cotton.**<br>[*T.M.*] [*D.H.*] | Hydrochloride of benzene-azo-*m*-tolylene diamine. | $C_{13}H_{15}N_4Cl$ | $C_6H_5-N=N-C_6H_2(CH_3)(NH_2)_2HCl[1:5:2:4]$ |
| 19 | **Wool Yellow.**<br>[*B.*]<br>**Patent Fustin.**<br>[*Wood & Bedford.*] | Mixture of benzene-azo-morin and benzene-azo-maclurin, chiefly the latter. | | *Benzene-azo-maclurin :*<br> |
| 20 | **Chromotrope 2 R.**<br>[*M.*]<br>**Biebrich Acid Red 4 B.** [*K.*] | Sodium salt of benzene-azo-(1 : 8)-dioxynaphthalene-(3 : 6)-disulphonic acid. | $C_{16}H_{10}N_2S_2O_8Na_2$ |  |
| 21 | **Fast Acid Fuchsine B.** [*By.*] | Sodium salt of benzene-azo-(1 : 8)-amido-naphthol-(3 : 6)-disulphonic acid. | $C_{16}H_{11}N_3S_2O_7Na_2$ |  |

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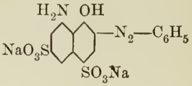
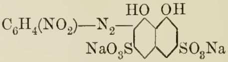
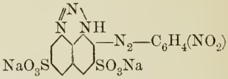
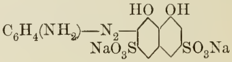
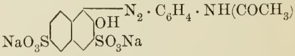
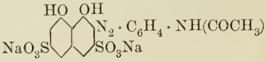
* Chrysoïdine Crystals also contain the

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| **Aniline.** | *β*-Naphthol-disulphonic acid G. | 1878. | Baum.<br>Meister, Lucius, and Brüning.<br>Eng. Pat. 1715$^{78}$.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff:** yellowish red powder.—**In water:** orange yellow solution.—**On addition of hydrochloric acid to aqueous solution:** no change.—**On addition of caustic soda to aqueous solution:** yellowish red.—**In conc. sulphuric acid:** orange yellow solution, not altered on dilution with water.—**Dyes:** wool orange yellow from an acid bath. |
| **Aniline.** | *β*-Naphthol-disulphonic acid R. | 1878. | Baum.<br>Meister, Lucius, and Brüning.<br>Eng. Pat. 1715$^{78}$.<br>Am. Pat. 251162.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff:** bright red powder.—**In water:** orange solution.—**On addition of hydrochloric acid to the aqueous solution:** hardly changed.—**On addition of caustic soda to the aqueous solution:** somewhat yellower.—**In. conc. sulphuric acid:** cherry red solution; on dilution with water, orange.—**Dyes:** wool a reddish orange from an acid bath. |
| **Aniline.** | Dimethyl-aniline. | 1875.<br>1876. | O. N. Witt.<br>P. Griess.<br>Ber. (1877) 10, 528. | **Appearance of dyestuff:** yellow plates of m.p. 115°.—**In water:** insoluble.—**In aqueous hydrochloric acid:** red solution, from which caustic soda throws down an orange yellow precipitate of the base.—**In conc. sulphuric acid:** yellow solution, becoming red on dilution with water.—**In oils:** soluble.—**Employment:** for colouring butter, oils, etc. |
| **Aniline.** | *m*-Phenylene diamine. | 1875.<br>1876. | H. Caro.<br>O. N. Witt.<br>A. W. Hofmann.<br>Ber. 10, 213.<br>O. N. Witt.<br>Ber. 10, 350, 654.<br>P. Griess.<br>Ber. 10, 388. | **Appearance of dyestuff:** large shining black crystals or reddish brown powder.—**In water:** orange brown solution.—**On addition of hydrochloric acid to the aqueous solution:** orange brown precipitate.—**On addition of caustic soda to the aqueous solution:** reddish brown precipitate.—**In conc. sulphuric acid:** brownish yellow solution, becoming cherry red on dilution with water.—**Dyes:** wool, silk, and tannined cotton, orange. |
| **Aniline.** | *m*-Tolylene diamine. | | | **Appearance of dyestuff:** yellowish brown lumps.—**In water or alcohol:** soluble with a yellow colour.—**On addition of hydrochloric acid to the aqueous solution:** red.—**On addition of caustic soda to the aqueous solution:** yellow precipitate of the base [m.p. 165° to 166°].—**In conc. sulphuric acid:** greenish yellow solution, becoming on dilution bluish red and then yellowish red. |
| **Aniline.** | Fustic extract. | 1887. | Ch. S. Bedford.<br>Eng. Pat. 12667$^{87}$.<br>Am. Pat. 409384.<br>Ger. Pat. 47274$^{88}$.<br>J. Herzfeld.<br>Färberztg. 1, 104, 338. | **Appearance of dyestuff:** brownish yellow powder or brownish yellow paste.—**In water:** nearly insoluble.—**In alcohol and caustic soda:** yellowish brown solution.—**In conc. sulphuric acid:** yellowish brown solution.—**Dyes:** wool mordanted with chrome brownish yellow. |
| **Aniline.** | 1 : 8-Dioxy-naphthalene-3 : 6-sulphonic acid. | 1890. | Meister, Lucius, & Brüning.<br>Eng. Pat. 9258$^{90}$.<br>Ger. Pat. 69095$^{90}$.<br>Fr. Pat. 206439.<br>Compare Ber. 1893, ref. 659. | **Appearance of dyestuff:** brownish red powder.—**In water:** magenta red solution.—**Addition of caustic soda or hydrochloric acid:** no change.—**In conc. sulphuric acid:** ruby red solution, yellowish red on dilution.—**Dyes:** wool from an acid bath bluish red, becoming plum blue to violet black on chroming. Shades are very level and fast to light acids, sulphur, and rubbing, but not very fast to milling. |
| **Aniline.** | 1 : 8-Amido-naphthol-3 : 6-disulphonic acid ("H-acid.") | | | **Appearance of dyestuff:** brown powder.—**In water:** magenta red solution —**On addition of hydrochloric acid:** red solution or precipitate.—**On addition of caustic soda:** orange red solution. —**In conc. sulphuric acid:** magenta red solution; bright red on adding water. |

homologues from *o*- and *p*-toluidine

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 22 | **Tolane Red B & G.** [*K.*] | Sodium salt of benzene-azo-(1 : 8)-amidonaphthol-(4 : 6)-disulphonic acid. | $C_{16}H_{11}N_3S_2O_7Na_2$ |  |
| 23 | **Orange III. Orange No. 3.** [*P.*] | Sodium salt of *m*-nitrobenzene-azo-*β*-naphthol-disulphonic acid. | $C_{16}H_9N_3O_9S_2Na_2$ | $C_6H_4 \left\{ \begin{matrix} [3]\,NO_2 \\ [1]-N=N-[1]\,C_{10}H_4 \end{matrix} \right. \left\{ \begin{matrix} [2]\,OH \\ [3]\,SO_3Na \\ [6]\,SO_3Na \end{matrix} \right.$ |
| 24 | **Alizarine Yellow GG.** [*M.*] | *m*-Nitrobenzene-azo-salicylic acid. | $C_{13}H_9N_3O_5$ | $C_6H_4 \left\{ \begin{matrix} [3]\,NO_2 \\ [1]\,N=N\,[1]\,C_6H_3 \end{matrix} \right. \left\{ \begin{matrix} [4]\,OH \\ [3]\,CO_2H \end{matrix} \right.$ |
| 25 | **Prage Alizarine Yellow G.** [*Ki.*] | *m*-Nitrobenzene-azo-resorcylic acid. | $C_{18}H_9N_3O_6$ | $C_6H_4 \left\{ \begin{matrix} [3]\,NO_2 \\ [1]\,N=N-C_6H_2 \end{matrix} \right. \left\{ \begin{matrix} (OH)_2 \\ CO_2H \end{matrix} \right.$ |
| 26 | **Alizarine Yellow R.** [*M.*] [*C. R.*] [*By.*] **Terracotta R.** [*G.*] | *p*-Nitrobenzene-azo-salicylic acid. | $C_{13}H_9N_3O_5$ | $C_6H_4 \left\{ \begin{matrix} [4]\,NO_2 \\ [1]\,N=N\,[1]\,C_6H_3 \end{matrix} \right. \left\{ \begin{matrix} [4]\,OH \\ [3]\,CO_2H \end{matrix} \right.$ |
| 27 | **Prage Alizarine Yellow R.** [*Ki.*] | *p*-Nitrobenzene-azo-resorcylic acid. | $C_{13}H_9N_3O_6$ | $C_6H_4 \left\{ \begin{matrix} [4]\,NO_2 \\ [1]\,N=N-C_6H_2 \end{matrix} \right. \left\{ \begin{matrix} (OH)_2 \\ CO_2H \end{matrix} \right.$ |
| 28 | **Archil Substitute V.** [*P.*] [*C. R.*] [*H.*] | Sodium salt of *p*-nitrobenzene-azo-*α*-naphthylamine-*p*-sulphonic acid. | $C_{16}H_{11}N_4O_5SNa$ | $C_6H_4 \left\{ \begin{matrix} [4]\,NO_2 \\ [1]\,N=N\,[2]\,C_{10}H_5 \end{matrix} \right. \left\{ \begin{matrix} [1]\,NH_2 \\ [4]\,SO_3Na \end{matrix} \right.$ |
| 29 | **Archil Substitute 3 VN.** [*P.*] **Archil Substitute V.** [*A.*] | Sodium salt of *p*-nitrobenzene-azo-*α*-naphthylamine-sulphonic acid. | $C_{16}H_{11}N_4O_5SNa$ | $C_6H_4 \left\{ \begin{matrix} [4]\,NO_2 \\ [1]\,N=N-C_{10}H_5 \end{matrix} \right. \left\{ \begin{matrix} [1]\,NH_2 \\ [5]\,SO_3Na \end{matrix} \right.$ |
| 30 | **Apollo Red.** [*G.*] **Archil Substitute extra.** [*C.*] | Sodium salt of *p*-nitrobenzene-azo-*α*-naphthylamine-disulphonic acid. | $C_{16}H_{10}N_4O_8S_2Na_2$ | $C_6H_4 \left\{ \begin{matrix} [4]\,NO_2 \\ [1]\,N=N\,[2]\,C_{10}H_4 \end{matrix} \right. \left\{ \begin{matrix} [1]\,NH_2 \\ [4]\,SO_3Na \\ [6\text{ or }7]\,SO_3Na \end{matrix} \right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment, |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Aniline. | 1 : 8-Amidonaphthol-4 : 6-disulphonic acid ("K-acid.") | 1893. | ROSENBERG & KRECHE.<br>KALLE & Co.<br>Eng. Pat. $515^{94}$.<br>Am. Pat. 563383.<br>Ger. Pat. 99164. | **Appearance of dyestuff:** brown powder.—**In water:** magenta red solution.—**On addition of hydrochloric acid:** yellowish brown solution or precipitate.—**On addition of caustic soda:** orange red solution.—**In conc. sulphuric acid:** magenta red; yellowish brown on dilution.—**Dyes:** wool from an acid bath a brilliant red, tolerably fast to light and milling. |
| *m*-Nitraniline. | *β*-Naphthol-disulphonic acid R. | 1878. | Z. ROUSSIN &<br>A. J. POIRRIER.<br>Ger. Pat. $6715^{78}$.<br>Chem. Ind. (1879) **2**, 292.<br>H. STEBBINS.<br>Chem. News, **43**, 58.<br>Chem. Ind. (1881) **4**, 87. | **Appearance of dyestuff:** reddish brown powder.—**In water:** reddish yellow solution.—**On addition of hydrochloric acid to the aqueous solution:** orange yellow precipitate, soluble in much water.—**On addition of caustic soda:** yellowish brown solution. **In conc. sulphuric acid:** orange yellow solution; on dilution with water, first an orange yellow precipitate then a yellow solution.—**Dyes:** wool orange from an acid bath. |
| *m*-Nitraniline. | Salicylic acid. | 1885. | R. NIETZKI.<br>Eng. Pat. $17583^{87}$.<br>Am. Pat. 424019.<br>Ger. Pat. $44170^{87}$.<br>J. Soc. Chem. Ind. (1890) 53; (1892) 599.<br>J. Soc. Dyers and Colorists (1889), 106.<br>Bull. de Mulhouse (1892), 198. | **Appearance of dyestuff:** yellow paste (20 %).—**In water:** insoluble. **In alcohol:** yellow solution.—**On addition of caustic soda to the paste:** orange yellow solution.—**In conc. sulphuric acid:** orange solution; on dilution with water a bright yellow precipitate.—**Dyes:** yellow on chrome mordanted wool. |
| *m*-Nitraniline. | *β*-Resorcylic acid. | 1894. | KINZLBERGER.<br>Ger. Pat. 81501.<br>Cf. Ber. 1895, ref. 705. | **Appearance of dyestuff:** yellow powder.—**In water or alcohol:** yellow solution.—**On addition of hydrochloric acid:** yellow precipitate.—**On addition of caustic soda:** orange coloration.—**In conc. sulphuric acid:** yellow solution; yellow precipitate on dilution.—**Dyes:** chrome mordanted cotton pure yellow, chromed wool brownish yellow. |
| *p*-Nitraniline. | Salicylic acid. | 1885. | R. MELDOLA.<br>J. Chem. Soc. (1885) **47**, 666.<br>Jahresber. (1885) 1058.<br>J. Soc. Chem. Ind. (1890) 53; (1892) 599.<br>J. Soc. Dyers and Colorists (1889) 106.<br>Bull. de Mulhouse (1892) 198.<br>Eng. Pat. $13920^{88}$. | **Appearance of dyestuff:** light brown paste (20%).—**In alcohol:** reddish yellow solution.—**In water:** insoluble.—**On addition of caustic soda:** blood red solution. **In conc. sulphuric acid:** orange yellow solution; brownish yellow precipitate on dilution with water.—**Dyes:** chrome mordanted wool yellowish brown. |
| *p*-Nitraniline. | *β*-Resorcylic acid. | 1894. | KINZLBERGER.<br>Ger. Pat. 81501. | **Appearance of dyestuff:** orange yellow powder.—**In water or alcohol:** orange yellow solution.—**On addition of hydrochloric acid:** orange yellow precipitate.—**On addition of caustic soda:** bluish violet solution.—**In conc. sulphuric acid:** orange yellow.—**Dyes:** chromed wool and cotton orange yellow. |
| *p*-Nitraniline. | Naphthionic acid. | 1878. | Z. ROUSSIN and A. J. POIRRIER.<br>Eng. Pat. $4490^{78}$.<br>Ger. Pat. $6715^{78}$.<br>Chem. Ind. (1879) 2, 292. | **Appearance of dyestuff:** brown paste.—**In water:** reddish brown solution.—**On addition of hydrochloric acid to the aqueous solution:** brownish red precipitate.—**On addition of caustic soda to the aqueous solution:** brownish red precipitate, soluble in water.—**In conc. sulphuric acid:** magenta red solution; brownish red precipitate on dilution with water.—**Dyes:** wool archil red from an acid bath. |
| *p*-Nitraniline. | *a*-Naphthylamine-sulphonic acid L. | 1887. | SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES.<br>Eng. Pat. $12692^{87}$.<br>Ger. Pat. $45787^{87}$.<br>Fr. Pat. 185908. | **Appearance of dyestuff:** dark brown powder.—**In water:** red solution.—**In alcohol:** slightly soluble.—**On addition of hydrochloric acid to the aqueous solution:** bluish precipitate.—**On addition of caustic soda to the aqueous solution:** brownish coloration.—**In conc. sulphuric acid:** red solution.—**Dyes:** wool archil red from an acid bath. |
| *p*-Nitraniline. | *a*-Naphthylamine-disulphonic acid D. | 1887. | A. MYLIUS.<br>J. R. GEIGY & Co.<br>Eng. Pat. $9468^{87}$.<br>Am. Pat. $376392^{88}$.<br>Fr. Pat. $184638^{87}$. | **Appearance of dyestuff:** brown powder. **In water:** brownish red solution.—**On addition of hydrochloric acid to the aqueous solution:** magenta red coloration. **On addition of caustic soda to the aqueous solution:** brown precipitate, soluble in water.—**In conc. sulphuric acid:** magenta red solution; no change of colour on dilution.—**Dyes:** wool archil red from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 31 | **Paranitraniline Red.**<br>**Azophor Red.**<br>[*M.*]<br>**Discharge Lake**<br>[*M.*] | *p*-Nitrobenzene-azo-*β*-naphthol. | $C_{16}H_{11}N_3O_3$ | $C_6H_4\left\{\begin{array}{l}[4]\,NO_2\\ [1]\,N=N\,[1]\,C_{10}H_6\,[2]\,OH\end{array}\right.$ |
| 32 | **Chromotrope 2 B.**<br>[*M.*] | Sodium salt of *p*-nitrobenzene-azo-1 : 8-dioxynaphthalene-3 : 6-disulphonic acid. | $C_{16}H_9N_3O_{10}S_2Na_2$ |  |
| 33 | **Brilliant Archil C.**<br>[*C.*] | Sodium salt of the azimide of *p*-nitrobenzene-azo-(1 : 8)-naphthylene diamine disulphonic acid. | $C_{16}H_8N_6S_2O_8Na_2$ |  |
| 34 | **Wool Violet S.**<br>[*B.*] | Sodium salt of dinitrobenzene-azo-diethyl-metasulphanilic acid. | $C_{16}H_{16}N_5SO_7Na$ | $C_6H_3\left\{\begin{array}{l}(NO_2)_2\\ N=N\,[1]\,C_6H_3\left\{\begin{array}{l}[2]\,SO_3Na\\ [4]\,N(C_2H_5)_2\end{array}\right.\end{array}\right.$ |
| 35 | **Brown PM.**<br>[*Mo.*] | Hydrochloride of *p*-amidobenzene-azo-*m*-phenylene diamine. | $C_{12}H_{14}N_5Cl$ | $C_6H_4\left\{\begin{array}{l}[4]\,NH_2\\ [1]\,N=N\,[1]\,C_6H_3\left\{\begin{array}{l}[2]\,NH_2HCl\\ [4]\,NH_2\end{array}\right.\end{array}\right.$ |
| 36 | **Victoria Violet. 4 BS.*** [*M.*] | Sodium salt of *p*-amidobenzene-azo-1 : 8-dioxynaphthalene disulphonic acid. | $C_{16}H_{11}N_3S_2O_8Na_2$ |  |
| 37 | **Azocoralline.**<br>[*D.*] | Sodium salt of *p*-acetamidobenzene-azo-*β*-naphthol disulphonic acid. | $C_{18}H_{13}N_3S_2O_8Na_2$ |  |
| 38 | **Chromotrope 6 B.**<br>[*M.*] | Sodium salt of *p*-acetamidobenzene-azo-1:8-dioxynaphthalene disulphonic acid. | $C_{17}H_{13}N_3S_2O_9Na_2$ |  |
| 39 | **Azophosphine GO.**<br>[*M.*] | Chloride of *m*-trimethylamidobenzene-azo-resorcin. | $C_{14}H_{18}N_3O_2Cl$ | $C_6H_4\left\{\begin{array}{l}[3]\,N(CH_3)_3Cl\\ [1]\,N=N\,[1]\,C_6H_3\left\{\begin{array}{l}[2]\,OH\\ [4]\,OH\end{array}\right.\end{array}\right.$ |

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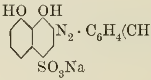
* To the same class belong **Victoria Violet 8 BS** [*M.*], which gives purer and bluer shades than the 4 BS and is

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Combination of diazo compound of *p*-nitraniline with β-naphthol either in substance or upon the fibre. | | 1880.<br>1889. | *Production on fibre:*<br>READ, HOLLIDAY & CO.<br>ULLRICH & v. GALLOIS.<br>Färberzeitung, **1**, 44; **2**, 298, 381; **5**, 121, 285, 333; **6**, 99, 295.<br>A. G. GREEN.<br>J. Soc. Dyers, 1897, 17; 1898, 95. | **Dyes:** when produced upon the cotton fibre a brilliant scarlet, very fast to washing, chlorine, and light. In order to produce the colour the cotton is first padded in an alkaline solution of β-naphthol, dried, and then immersed or printed with a solution of *p*-nitrodiazobenzene acetate. The latter is either produced by diazotisation of PARANITRANILINE [*M.*] [*C.*] [*Cl. Co.*] as required, or ready-prepared diazo compounds of the latter are employed, *e.g.* NITROSAMINE [*B.*], AZOPHOR RED [*M.*], NITRAZOL [*C.*].<br>**Employment in substance:** as a discharge colour for printing, and in the preparation of lakes for paper staining, etc. |
| *p*-Nitraniline. | 1 : 8-Dioxynaphthalene-3 : 6-disulphonic acid. | 1890. | KUZEL.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $9258^{90}$.<br>Ger. Pat. 69095.<br>Fr. Pat. 206439. | **Appearance of dyestuff:** reddish brown powder.—**In water:** yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution:** yellower.—**On addition of caustic soda:** bluish red solution.—**In conc. sulphuric acid:** dark violet solution; yellowish red on dilution.—**Dyes:** wool from an acid bath bluish red shades, becoming blue to black on chroming. Fast to acids, sulphur, and rubbing; not so fast to milling. |
| Action of nitrous acid upon the product from diazotised *p*-nitraniline and 1 : 8-naphthylene diamine-3 : 6-disulphonic acid. | | | Eng. Pat. $24714^{93}$.<br>Ger. Pat. 77425.<br>Fr. Pat. 234837. | **Appearance of dyestuff:** brownish red powder.—**In water:** magenta red solution.—**On addition of hydrochloric acid:** crimson red solution.—**On addition of caustic soda:** blue.—**In conc. sulphuric acid:** blue solution; violet red on dilution.—**Dyes:** wool in very level shades of moderate fastness to washing. |
| From diazotised dinitraniline and diethyl-*m*-sulphanilic acid. | | 1894. | JULIUS.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $6197^{94}$.<br>Am. Pat. 525656.<br>Ger. Pat. 86071.<br>Fr. Pat. 239096. | **Appearance of dyestuff:** black powder.—**In water or alcohol:** reddish violet solution.—**On addition of hydrochloric acid:** orange red solution.—**On addition of caustic soda:** bluish violet precipitate.—**In conc. sulphuric acid:** scarlet red solution; orange red on dilution.—**Dyes:** wool reddish violet from an acid bath. |
| From diazotised *p*-phenylene diamine and *m*-phenylene diamine. | | 1884. | GUILLIARD, MONNET, & CARTIER.<br>Ger. Pat. 32502.<br>Fr. Pat. 166371. | **Appearance of dyestuff:** brown powder.—**In water:** brown solution.—**On addition of hydrochloric acid or caustic soda:** yellowish brown precipitate.—**In conc. sulphuric acid:** reddish brown solution.—**Dyes:** tannined cotton a darker brown than Bismarck Brown. |
| Alkaline reduction of Chromotrope 2 B or splitting off the acetyl group from Chromotrope 6 B. | | 1891. | OTTO.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $8270^{92}$.<br>Ger. Pat. 70885.<br>Fr. Pat. 221363. | **Appearance of dyestuff:** grayish green powder.—**In water:** dark violet solution.—**On addition of hydrochloric acid:** yellowish red solution.—**On addition of caustic soda:** reddish yellow solution.—**In conc. sulphuric acid:** bluish red solution; yellowish red solution or precipitate on dilution.—**Dyes:** wool from an acid bath level shades of bluish violet, fast to washing and rubbing, moderately fast to light and milling. |
| Acetyl-*p*-phenylene diamine. | β-Naphthol-disulphonic acid R. | 1884. | NIETZKI.<br>Ber. 17, 344. | **Appearance of dyestuff:** cinnamon brown powder.—**In water:** orange red solution; **On addition of hydrochloric acid:** little change.—**On addition of caustic soda:** yellower.—**In conc. sulphuric acid:** yellowish red; orange red on dilution.—**Dyes:** wool fairly level shades from an acid bath. |
| Acetyl-*p*-phenylene diamine. | (1 : 8) Dioxynaphthalene-(3 : 6)-disulphonic acid. | 1890. | MEISTER, LUCIUS, & BRÜNING.<br>Ger. Pat. 75738.<br>Cf. Ber. 1894, ref. 907. | **Appearance of dyestuff:** grayish brown powder.—**In water:** violet red solution.—**On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** yellower.—**In conc. sulphuric acid:** ruby red solution; bluish red precipitate on dilution.—**Dyes:** wool from an acid bath level violet red shades, fast to light, acids, rubbing, and sulphur; not fast to milling. |
| *m*-Amidophenyl-trimethyl-ammonium-chloride. | Resorcin. | 1895. | KÖNIG.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $14494^{95}$.<br>Ger. Pat. 87257.<br>Fr. Pat. 249227. | **Appearance of dyestuff:** brown powder.—**In water:** easily soluble with yellowish red colour.—**On addition of hydrochloric acid:** orange red solution.—**On addition of caustic soda:** orange red solution.—**In conc. sulphuric acid:** brownish red solution; orange yellow on dilution.—**Dyes:** unmordanted cotton direct from an acid bath. Employed for dyeing union goods. |

employed in wool printing; and **Azo Acid Blue B** [*M.*], which dyes wool pure blue. Compare Ger. Pat. 70385.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 40 | **Azogalleine.** [*G.*] | *p*-Dimethylamido-benzene-azo-pyrogallol. | $C_{14}H_{15}N_3O_3$ | $C_6H_4\left\{\begin{matrix}[4]\,N(CH_3)_2\\ [1]\,N=N\,[1]\,C_6H_2(OH)_3\,[2:3:4]\end{matrix}\right.$ |
| 41 | **Chrysoïdine R.** [*D. H.*] | Hydrochloride of toluene-azo-*m*-tolylene diamine. | $C_{14}H_{17}N_4Cl$ | $C_6H_4\left\{\begin{matrix}[2]\,CH_3\\ [1]\,N=N\,[1]\,C_6H_2\left\{\begin{matrix}[2]\,NH_2HCl\\ [4]\,NH_2\\ [5]\,CH_3\end{matrix}\right.\end{matrix}\right.$ |
| 42 | **Cochineal Scarlet 2 R.** [*Sch.*] | Sodium salt of toluene-azo-α-naphthol-sulphonic acid. | $C_{17}H_{13}N_2O_4SNa$ | $C_6H_4(CH_3)-N=N-C_{10}H_5\left\{\begin{matrix}[1]\,OH\\ [5]\,SO_3Na\end{matrix}\right.$ |
| 43 | **Orange GT.** [*By.*]<br>**Orange RN.** [*C.*]<br>**Orange O.** [*M.*]<br>**Orange N.** [*K.*] | Sodium salt of toluene-azo-β-naphthol-sulphonic acid. | $C_{17}H_{13}N_2O_4SNa$ | $C_6H_4(CH_3)-N=N-[1]\,C_{10}H_5\left\{\begin{matrix}[2]\,OH\\ [6]\,SO_3Na\end{matrix}\right.$ |
| 44 | **Ponceau RT.** | Sodium salt of toluene-azo-β-naphthol-disulphonic acid. | $C_{17}H_{12}N_2O_7S_2Na_2$ | $C_6H_4(CH_3)-N=N-[1]\,C_{10}H_4\left\{\begin{matrix}[2]\,OH\\ [3]\,SO_3Na\\ [6]\,SO_3Na\end{matrix}\right.$ |
| 45 | **Azofuchsine B.** [*By.*] | Sodium salt of toluene-azo-1 : 8-dioxynaphthalene-sulphonic acid. | $C_{17}H_{13}N_2SO_5Na$ |  |
| 46 | **Persian Yellow.** [*G.*] | Nitrotoluene-azo-nitro-salicylic acid. | $C_{14}H_{10}N_4O_7$ | $C_6H_3\left\{\begin{matrix}[1]\,N=N\,[1]\,C_6H_2\left\{\begin{matrix}[3]\,CO_2H\\ [4]\,OH\\ [5]\,NO_2\end{matrix}\right.\\ [2]\,NO_2\\ [4]\,CH_3\end{matrix}\right.$ |
| 47 | **Tannin Orange R.** [*C.*] | *Exo*-dimethylamido-toluene-azo-β-naphthol. | $C_{19}H_{19}N_3O$ | $C_6H_4\left\{\begin{matrix}[4]\,CH_2\cdot N(CH_3)_2\\ [1]\,N=N\,[1]\,C_{10}H_6\,[2]\,OH\end{matrix}\right.$ |
| 48 | **New Phosphine G.** [*C.*] | *Exo*-dimethylamido-toluene-azo-resorcin. | $C_{15}H_{17}N_3O_2$ | $C_6H_4\left\{\begin{matrix}[3]\,CH_2\cdot N(CH_3)_2\\ [1]\,N=N\,[1]\,C_6H_3(OH)_2\,[2:4]\end{matrix}\right.$ |
| 49 | **Sudan II.** [*A.*]<br>**Red B.** [*B.*] [*Fi.*]<br>**Scarlet G.** [*C. J.*] | Xylene-azo-β-naphthol. | $C_{18}H_{16}N_2O$ | $C_6H_3(CH_3)_2-N=N-C_{10}H_6(OH)\,\beta$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Dimethyl-*p*-phenylene diamine. | Pyrogallol. | 1894. | C. Ris.<br>J. R. Geigy & Co.<br>Ger. Pat. 81376.<br>Fr. Pat. 230937. | **Appearance of dyestuff**: blackish brown powder.—**In water**: sparingly soluble with grayish yellow colour.—**In alcohol**: yellow solution.—**On addition of caustic soda**: reddish brown solution. —**In conc. sulphuric acid**: yellow solution.—**Dyes**: chromed wool blackish violet.—**In printing**: gives dark violet with a chrome mordant. |
| *o*-Toluidine. | *m*-Tolylene diamine. | 1876. | Witt. | **Appearance of dyestuff**: crystalline violet powder.—**In water and alcohol**: red solution.—**On addition of hydrochloric acid**: light brown precipitate.—**On addition of caustic soda**: yellow precipitate.—**In conc. sulphuric acid**: brown solution.—**Dyes**: tannin mordanted cotton brownish yellow. |
| Toluidine. | α-Naphthol-sulphonic acid L. | 1883. | Gaess.<br>Mon. Scien. (1884) 335. | **Appearance of dyestuff**: cinnabar red powder.—**In hot water**: soluble with yellowish red colour.—**On addition of hydrochloric acid to the aqueous solution**: red flocks.—**On addition of caustic soda to the aqueous solution**: orange coloration.—**In conc. sulphuric acid**: magenta red colour; red flocks on dilution. —**Dyes**: wool red from an acid bath. |
| Toluidine. | β-Naphthol-monosulphonic acid S. | 1879. | Levinstein.<br>Ber. (1880) 13, 586. | **Appearance of dyestuff**: scarlet powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brown oily drops.—**On addition of caustic soda to the aqueous solution**: dark brownish red solution.—**In conc. sulphuric acid**: magenta red solution; brown oily drops on dilution with water. **Dyes**: wool orange from an acid bath. |
| Toluidine. | β-Naphthol-disulphonic acid R. | 1878. | Baum.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $1715^{78}$.<br>Ger. Pat. $3229^{78}$. | **Appearance of dyestuff**: red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: yellowish brown coloration.—**In conc. sulphuric acid**: cherry red solution; yellowish red on dilution with water.—**Dyes**: wool reddish orange from an acid bath. |
| Toluidine. | Dioxynaphthalene sulphonic acid S. | 1889. | Ullrich & Duisberg.<br>Bayer & Co.<br>Eng. Pat. $18517^{89}$.<br>Ger. Pat. 54116.<br>Am. Pats. 466841 & 468142.<br>Fr. Pat. 203744. | **Appearance of dyestuff**: blackish brown powder.—**In water**: bluish red solution, bluer on addition of caustic soda.—**On addition of hydrochloric acid**: reddish brown solution or precipitate.—**In conc. sulphuric acid**: violet solution; bluish red on dilution.—**Dyes**: wool from an acid bath magenta red, becoming violet black on chroming, very fast to acids and light, moderately fast to alkalies and milling. Silk in a strongly acid bath is left undyed. |
| Nitration of the compound from diazotised toluidine and salicylic acid. | | 1888. | Walter.<br>J. R. Geigy & Co.<br>Eng. Pat. $13920^{88}$.<br>Am. Pat. 431297.<br>Fr. Pat. 193190. | **Appearance of dyestuff**: brownish yellow paste (20%).—**In boiling water or alcohol**: yellow solution.—**On addition of caustic soda**: orange brown solution.—**In conc. sulphuric acid**: orange yellow solution; brownish yellow precipitate on dilution.—**Dyes**: chromed wool yellow.—**In cotton printing**: yellow with chromium acetate. |
| Amidobenzyl-dimethylamine. | β-Naphthol. | 1892. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $22572^{93}$.<br>Am. Pat. 515100.<br>Ger. Pat. 70678.<br>Fr. Pat. 225968. | **Appearance of dyestuff**: brown powder or paste (50%).—**In water**: sparingly soluble with a brown colour.—**In alcohol**: easily soluble.—**On addition of hydrochloric acid**: orange brown precipitate.—**On addition of caustic soda**: yellowish brown precipitate.—**In conc. sulphuric acid**: cherry red solution; orange brown precipitate on dilution.—**Dyes**: leather and tannin mordanted cotton orange. |
| Amidobenzyl-dimethylamine. | Resorcin. | 1892. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $22572^{93}$.<br>Am. Pat. 515100.<br>Ger. Pat. 70678.<br>Fr. Pat. 225968. | **Appearance of dyestuff**: yellowish brown powder.—**In water**: yellowish brown solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: redder and deeper.—**In conc. sulphuric acid**: yellowish brown solution; no change on dilution.—**Dyes**: leather and tannined cotton yellow. |
| Xylidine. | β-Naphthol. | 1883. | Meister, Lucius, & Brüning.<br>Eng. Pat. $1715^{78}$.<br>Ger. Pat. $3229^{78}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: insoluble. —**In conc. sulphuric acid**: magenta red solution; pale yellow precipitate on dilution with water.—**In alcohol**: yellowish red solution.—**Employment**: for colouring oils, varnishes, etc. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 50 | **Azococcine 2 R.** [*A.*]<br>**Double Scarlet R.** [*Lev.*] | Sodium salt of xylene-azo-α-naphthol-*p*-sulphonic acid. | $C_{18}H_{15}N_2O_4SNa$ | $C_6H_3(CH_3)_2 - N = N - [2]\,C_{10}H_5 \left\{\begin{matrix}[1]\,OH\\ [4]\,SO_3Na\end{matrix}\right.$ |
| 51 | **Cochineal Scarlet 4 R.** [*Sch.*] | Sodium salt of xylene-azo-α-naphthol-sulphonic acid. | $C_{18}H_{15}N_2O_4SNa$ | $C_6H_3(CH_3)_2 - N = N - C_{10}H_5 \left\{\begin{matrix}[1]\,OH\\ [5]\,SO_3Na\end{matrix}\right.$ |
| 52 | **Wool Scarlet R.** [*Sch.*] | Sodium salt of xylene-azo-α-naphthol-disulphonic acid. | $C_{18}H_{14}N_2O_7S_2Na_2$ | $C_6H_3(CH_3)_2 - N = N - [2]\,C_{10}H_4 \left\{\begin{matrix}[1]\,OH\\ [4]\,SO_3Na\\ [8]\,SO_3Na\end{matrix}\right.$ |
| 53 | **Palatine Scarlet.*** [*B.*] | Sodium salt of *m*-xylene-azo-naphthol disulphonic acid. | $C_{18}H_{14}N_2S_2O_7Na_2$ | $C_6H_3(CH_3)_2 - N = N - [2]\,C_{10}H_4 \left\{\begin{matrix}OH\,[1]\\ (SO_3Na)_2\,[3:6]\end{matrix}\right.$ |
| 54 | **Scarlet GR.** [*A.*]<br>**Scarlet R.** [*By.*]<br>**Brilliant Orange R.** [*M.*]<br>**Orange L.** [*Lev.*] | Sodium salt of xylene-azo-β-naphthol-monosulphonic acid. | $C_{18}H_{15}N_2O_4SNa$ | $C_6H_3(CH_3)_2 - N = N - [1]\,C_{10}H_5 \left\{\begin{matrix}[2]\,OH\\ [6]\,SO_3Na\end{matrix}\right.$ |
| 55 | **Ponceau R,**† **2 R, G, & GR.** [*A.*] [*B.*] [*M.*] [*Lev.*] [*H.*] [*C.*]<br>**Xylidine Red.**<br>**Xylidine Scarlet.** | Sodium salt of xylene-azo-β-naphthol-disulphonic acid. | $C_{18}H_{14}N_2O_7S_2Na_2$ | $C_6H_3(CH_3)_2 - N = N - [1]\,C_{10}H_4 \left\{\begin{matrix}[2]\,OH\\ [3]\,SO_3Na\\ [6]\,SO_3Na\end{matrix}\right.$ |
| 56 | **Ponceau 3 R.** ‡ [*A.*] [*B.*] [*M.*]<br>**Ponceau 4 R.** [*A.*]<br>**Cumidine Red.**<br>**Cumidine Ponceau.** | Sodium salt of ψ-cumene-azo-β-naphthol-disulphonic acid. | $C_{19}H_{16}N_2O_7S_2Na_2$ | $C_6H_2 \left\{\begin{matrix}[5]\,CH_3\\ [4]\,CH_3\\ [2]\,CH_3\\ [1]\,N = N - C_{10}H_4 \left\{\begin{matrix}OH\\ (SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$ |
| 57 | **Ponceau 3 R.** [*M.*] | Sodium salt of ethyldimethylbenzene-azo-β-naphthol-disulphonic acid. | $C_{20}H_{18}N_2S_2O_7Na_2$ | $C_6H_2 \left\{\begin{matrix}C_2H_5\\ (CH_3)_2\\ N = N - C_{10}H_4 \left\{\begin{matrix}OH\beta\\ (SO_3Na)_2\end{matrix}\right.\end{matrix}\right.$ |
| 58 | **Benzoyl Pink.**<br>**Rose de Benzoyl.** [*P.*] | Sodium salt of benzoyl-amido-ditolyl-azo-α-naphtholsulphonic acid. | | $\begin{array}{l}C_6H_4(CH_3)\cdot NH\cdot CO\cdot C_6H_5\\ \vert\\ C_6H_4(CH_3)\cdot N_2\cdot C_{10}H_6(OH)(SO_3Na)\,[2:1:4]\end{array}$ |
| 59 | **Sudan Brown.** [*A.*]<br>**Pigment Brown.** [*B.*] | α-Naphthalene-azo-α-naphthol. | $C_{20}H_{14}N_2O$ | $C_{10}H_7\,[\alpha]\,N = N - C_{10}H_6(OH)\,[\alpha]$ |

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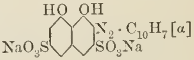
* To this group also belong the light- and sulphur-

† The marks G and GR are made from crude xylidine and crude β-naphthol-

‡ The mark 3 R is made from crude cumidine or amido-

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Xylidine. | α-Naphthol-monosulphonic acid NW. | 1882. | O. N. WITT.<br>VEREIN CHEM. FABRIKEN MANNHEIM.<br>Eng. Pat. 2237$^{83}$.<br>Ger. Pat. 26012$^{83}$. | **Appearance of dyestuff**: reddish brown powder.—**On addition of hydrochloric acid to the aqueous solution**: brownish red flocks.—**On addition of caustic soda**: solution becomes brownish yellow. **In conc. sulphuric acid**: magenta red solution; brownish red precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| Xylidine. | α-Naphthol-monosulphonic acid L. | 1883. | GAESS.<br>Mon. Scien. (1884) 335. | **Appearance of dyestuff**: fiery red powder.—**In water**: sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution**: reddish brown precipitate.—**On addition of caustic soda**: yellowish red solution.—**In conc. sulphuric acid**: magenta red solution; reddish precipitate on dilution.—**Dyes**: wool red from an acid bath. |
| Xylidine. | α-Naphthol-disulphonic acid Sch. | 1884. | MENSCHING.<br>THE SCHÖLLKOPF ANILINE & CHEMICAL CO.<br>Eng. Pats. 15775$^{85}$ and 15781$^{85}$.<br>Am. Pat. 333035.<br>Ger. Pat. 40571$^{85}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: becomes bluish red.—**On addition of caustic soda**: yellowish red solution.—**In conc. sulphuric acid**: cherry red; red on dilution with water.—**Dyes**: wool red from an acid bath. |
| *m*-Xylidine. | α-Naphthol-disulphonic acid (1 : 3 : 6). | 1886.<br>1889. | RUDOLPH & GÜRCKE.<br>Ger. Pat. app. G 3636.<br>BAD. ANIL. & SODA FABRIK. | **Appearance of dyestuff**: brownish red powder.—**In water and in alcohol**: soluble with a scarlet red colour. **On addition of hydrochloric acid**: gelatinous yellowish brown precipitate.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: bluish red solution; yellowish brown precipitate on dilution.—**Dyes**: wool scarlet from an acid bath. |
| Xylidine. | β-Naphthol-monosulphonic acid S. | 1879. | LEVINSTEIN.<br>Ber. (1880) 13, 586. | **Appearance of dyestuff**: cinnabar red powder.—**In water**: orange solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate.—**On addition of caustic soda**: unchanged.—**In conc. sulphuric acid**: cherry red solution; brownish red precipitate on dilution with water.—**Dyes**: wool yellowish red from an acid bath. |
| Xylidine. (Chiefly meta.) | β-Naphthol-disulphonic acid R. | 1878. | BAUM.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. 1715$^{78}$.<br>Am. Pat. 210233.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: easily soluble.—**On addition of hydrochloric acid or of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: cherry red solution; reddish yellow on dilution with water.—**Dyes**: wool scarlet from an acid bath. |
| ψ-Cumidine. | β-Naphthol-disulphonic acid R. | 1878. | BAUM.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. 1715$^{78}$.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff**: dark red powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: yellow precipitate.—**In conc. sulphuric acid**: cherry red solution; no change on dilution with water.—**Dyes**: wool bluish scarlet from an acid bath. |
| Amido-ethyl-dimethyl-benzene. | β-Naphthol-disulphonic acid. | 1878. | MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. 1715$^{78}$.<br>Am. Pat. 251163.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff**: dark red powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: yellow precipitate.—**In conc. sulphuric acid**: cherry red solution; not altered on dilution with water.—**Dyes**: wool bluish scarlet from an acid bath. |
| Benzoyl-*o*-tolidine. | α-Naphthol-sulphonic acid (1 : 4). | 1891. | CHAPUIS.<br>SOC. ANON. DES MAT. COL. DE ST. DENIS.<br>Ger. Pat. 60332. | **Appearance of dyestuff**: brick red paste.—**On addition of hydrochloric acid**: violet precipitate.—**On addition of caustic soda**: brick red solution.—**In conc. sulphuric acid**: bluish red solution.—**Dyes**: unmordanted cotton pink. |
| α-Naphthylamine. | α-Naphthol. | 1878. | BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 786$^{78}$.<br>Ger. Pat. 5411$^{78}$. | **Appearance of dyestuff**: brown powder.—**In water**: insoluble; dissolves sparingly with a wine red colour on adding caustic soda.—**In conc. sulphuric acid**: blue solution; brown precipitate on dilution.—**In alcohol**: soluble.—**Employment**: for colouring oils, soap, etc. |

fast scarlets: **Brilliant Cochineal 2 R and 4 R** [*C.*].
disulphonic acid; **R** from crude xylidine, and **2 R** from *m*-xylidine and **R**-salt.
ethyldimethylbenzene, **4 R** from pure ψ-cumidine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 60 | **Carminaph Garnet.** [*D. H.*]<br>**Scarlet 2 R.** [*C. J.*]<br>**Naphthylamine Bordeaux** (on fibre). | α-Naphthalene-azo-β-naphthol. | $C_{20}H_{14}N_2O$ | $C_{10}H_7[\alpha]N=N-C_{10}H_6(OH)[\beta]$ |
| 61 | **Buffalo Rubine.** [*Sch.*]<br>**Azo Bordeaux.** [*By.*] | Sodium salt of α-naphthalene-azo-α-naphthol disulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_7[\alpha]N=N-C_{10}H_4\left\{\begin{matrix}[\alpha]OH\\(SO_3Na)_2\end{matrix}\right.$<br>$[N_2:OH:SO_3H:SO_3H=2:1:4:8]$ |
| 62 | **Palatine Red.*** [*B.*]<br>**Naphthorubine.** [*By.*] | Sodium salt of α-naphthalene-azo-α-naphthol-disulphonic acid. | $C_{20}H_{12}N_2S_2O_7Na_2$ | $C_{10}H_7[\alpha]N=N-C_{10}H_4\left\{\begin{matrix}OH[1]\\(SO_3Na)_2[3:6]\end{matrix}\right.$ |
| 63 | **Fast Red B T.** [*By.*] [*Lev.*] [*D. H.*] | Sodium salt of α-naphthalene-azo-β-naphthol-monosulphonic acid. | $C_{20}H_{13}N_2O_4SNa$ | $C_{10}H_7[\alpha]N=N[1]C_{10}H_5\left\{\begin{matrix}[2]OH\\[6]SO_3Na\end{matrix}\right.$ |
| 64 | **Crystal Scarlet 6 R.** [*C.*] [*M.*]<br>**Crystal Ponceau.** [*A.*] [*B.*] | Sodium salt of α-naphthalene-azo-β-naphthol disulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_7[\alpha]N=N-[1]C_{10}H_4\left\{\begin{matrix}[2]OH\\[6]SO_3Na\\[8]SO_3Na\end{matrix}\right.$ |
| 65 | **Fast Red B.** [*B.*]<br>**Bordeaux B.** [*A.*] [*M.*] [*Lev.*] [*H.*]<br>**Bordeaux BL.** [*C.*]<br>**Bordeaux R extra.** [*M.*] | Sodium salt of α-naphthalene-azo-β-naphthol disulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_7[\alpha]N=N-[1]C_{10}H_4\left\{\begin{matrix}[2]OH\\[3]SO_3Na\\[6]SO_3Na\end{matrix}\right.$ |
| 66 | **Sulphamine Brown A.** [*D.*]<br>**Naphthine Brown α.** [*P.*] | | | |
| 67 | **Chromotrope 10 B.** [*M.*] | Sodium salt of α-naphthalene-azo-1:8-dioxy-naphthalene-disulphonic acid. | $C_{20}H_{12}N_2S_2O_8Na_2$ |  |
| 68 | **Sulphamine Brown B.** [*D.*]<br>**Naphthine Brown β.** [*P.*] | | | |

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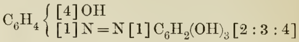
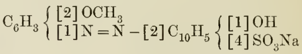
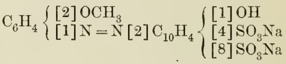
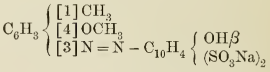
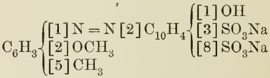
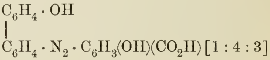
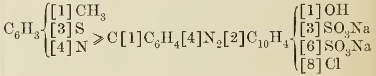
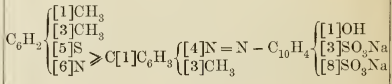
* Allied to Palatine Red

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| α-Naphthylamine. | β-Naphthol. | | | **Appearance of dyestuff**: reddish brown paste.—**In water**: insoluble.—**In alcohol**: red solution.—**In conc. sulphuric acid**: blue solution; reddish brown precipitate on dilution.—**Employment in dyeing and printing**: as a pigment colour when printed with albumen; and produced upon the fibre by padding with β-naphthol and application of diazotised α-naphthylamine ("Naphthylamine Bordeaux"). |
| α-Naphthylamine. | α-Naphthol-disulphonic acid Sch. | 1884. | Mensching.<br>Schöllkopf Anil. & Chem. Co.<br>Eng. Pats. 15775$^{85}$ and 15781$^{85}$.<br>Ger. Pat. 40571$^{85}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid or of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution; magenta red on dilution with water.—**Dyes**: wool red from an acid bath. |
| α-Naphthylamine. | Naphthol-disulphonic acid of Gürcke & Rudolf. | 1886.<br>1888. | O. Gürcke & C. Rudolf.<br>Eng. Pat. 15716$^{86}$.<br>Ger. Pat. 38281$^{85}$.<br>Bad. Anil. & Soda Fabrik. | **Appearance of dyestuff**: brown powder.—**In water and alcohol**: bluish red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: blue solution; on dilution with water, brown precipitate.—**Dyes**: wool bluish red. |
| α-Naphthylamine. | β-Naphthol-monosulphonic acid S. | 1878. | Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 786$^{78}$ (expired).<br>Am. Pat. 204799.<br>Ger. Pat. 5411$^{78}$. | **Appearance of dyestuff**: red powder.—**In water**: red solution.—**In alcohol**: slightly soluble.—**On the addition of hydrochloric acid to the aqueous solution**: dark reddish brown precipitate.—**On the addition of caustic soda**: brown coloration.—**In conc. sulphuric acid**: dark violet solution; dark brownish violet precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| α-Naphthylamine. | β-Naphthol-disulphonic acid G. | 1883. | Meinhard Hoffmann.<br>Meister, Lucius, & Brüning.<br>Ger. Pat. 36491$^{84}$, add. to Ger. Pat. 3229.<br>L. Cassella & Co.<br>Eng. Pat. 816$^{84}$.<br>Am. Pat. 332528$^{85}$. | **Appearance of dyestuff**: beautiful brownish red crystals with golden reflex.—**In water**: scarlet red solution.—**Addition of hydrochloric acid to the aqueous solution**: colour rather darker; an excess precipitates brown crystalline flakes.—**On addition of caustic soda**: the solution becomes brown.—**In conc. sulphuric acid**: violet solution, becoming scarlet on dilution with water.—**Dyes**: wool scarlet from an acid bath. |
| α-Naphthylamine. | β-Naphthol-disulphonic acid R. | 1878. | Baum.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 1715$^{78}$.<br>Am. Pat. 251164.<br>Ger. Pat. 3229$^{78}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: solution becomes yellowish brown.—**In conc. sulphuric acid**: blue solution; on dilution with water, magenta red.—**Dyes**: wool red from an acid bath. |
| Action of diazotised α-naphthylamine upon the sodium bisulphite compound of nitroso-β-naphthol. | | 1894. | Bürger & Ashworth.<br>Dahl & Co.<br>Ger. Pat. 79583.<br>Fr. Pat. 239100. | **Appearance of dyestuff**: brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: reddish brown precipitate.—**In conc. sulphuric acid**: green solution.—**Dyes**: chromed wool dark brown of good fastness. The fastness to light and milling is increased by coppering. |
| α-Naphthylamine. | 1:8-Dioxynaphthalene-3:6-disulphonic acid. | 1890. | Meister, Lucius, & Brüning.<br>Eng. Pat. 9258$^{90}$.<br>Ger. Pat. 69095.<br>Fr. Pat. 206439. | **Appearance of dyestuff**: violet brown powder.—**In water or alcohol**: violet solution.—**On addition of hydrochloric acid**: solution becomes bluer.—**On addition of caustic soda**: yellowish red solution.—**In conc. sulphuric acid**: greenish blue solution; reddish violet on addition of water.—**Dyes**: wool from an acid bath reddish violet shades fast to light, acids, sulphur, and rubbing, but not fast to milling. |
| Action of diazotised β-naphthylamine upon the sodium bisulphite compound of nitroso-β-naphthol. | | 1894. | Bürger & Ashworth.<br>Ger. Pat. 79583.<br>Fr. Pat. 239100. | **Appearance of dyestuff**: brown powder.—**In water**: yellowish brown solution.—**On addition of hydrochloric acid or caustic soda**: yellowish brown precipitates.—**In conc. sulphuric acid**: violet solution; yellowish brown on dilution.—**Dyes**: chromed wool chocolate brown. |

is **Azo Red A** [*C.*].

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 69 | **Azochromine.**<br>[*G.*] | Tetraoxyazobenzene. | $C_{12}H_{10}O_4N_2$ |  $C_6H_4\left\{\begin{array}{l}[4]\,OH\\ [1]\,N=N\,[1]\,C_6H_2(OH)_3\,[2:3:4]\end{array}\right.$ |
| 70 | **Azarine S.**<br>[*M.*] | Ammonium bisulphite compound of dichloro-phenolazo-$\beta$-naphthol. | $C_{16}H_{15}Cl_2N_3SO_5$ | $C_6H_2Cl_2(OH)\cdot NH\cdot N(SO_3NH_4)\cdot C_{10}H_6\cdot OH\beta$ |
| 71 | **Azoeosine.**<br>[*By.*] | Sodium salt of anisol-azo-$\alpha$-naphthol-$p$-sulphonic acid. | $C_{17}H_{13}N_2O_5SNa$ |  $C_6H_3\left\{\begin{array}{l}[2]\,OCH_3\\ [1]\,N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,OH\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 72 | **Azocochineal.**<br>[*By.*] | Sodium salt of anisol-azo-$\alpha$-naphthol-disulphonic acid. | $C_{17}H_{12}N_2S_2O_8$ |  $C_6H_4\left\{\begin{array}{l}[2]\,OCH_3\\ [1]\,N=N\,[2]\,C_{10}H_4\left\{\begin{array}{l}[1]\,OH\\ [4]\,SO_3Na\\ [8]\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 73 | **Coccinine B.**<br>[*M.*] | Sodium salt of $p$-methoxy-toluene-azo-$\beta$-naphthol-disulphonic acid. | $C_{18}H_{14}N_2O_8S_2Na_2$ |  $C_6H_3\left\{\begin{array}{l}[1]\,CH_3\\ [4]\,OCH_3\\ [3]\,N=N-C_{10}H_4\left\{\begin{array}{l}OH\beta\\ (SO_3Na)_2\end{array}\right.\end{array}\right.$ |
| 74 | **Eosamine B.**<br>[*A.*] | Sodium salt of $p$-cresol-methyl-ether-azo-$\alpha$-naphthol-disulphonic acid. | $C_{18}H_{14}N_2S_2O_8Na_2$ |  $C_6H_3\left\{\begin{array}{l}[1]\,N=N\,[2]\,C_{10}H_4\left\{\begin{array}{l}[1]\,OH\\ [3]\,SO_3Na\\ [8]\,SO_3Na\end{array}\right.\\ [2]\,OCH_3\\ [5]\,CH_3\end{array}\right.$ |
| 75 | **Diamond Flavine G.** [*By.*] | $p$-Oxydiphenylazo-salicylic acid. | $C_{19}H_{14}N_2O_4$ |  $\begin{array}{l}C_6H_4\cdot OH\\ \vert\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)(CO_2H)\,[1:4:3]\end{array}$ |
| 76 | **Dutch Yellow.**<br>[*Pick, Lange, & Co.*] | | | |
| 77 | **Diamine Rose.**<br>[*C.*]<br>**Diamine Pink.**<br>[*C.*] | Sodium salt of benzenyl-amido-thio-phenol-azo-chloro-naphthol disulphonic acid. | $C_{24}H_{15}N_3ClS_3O_7Na_2$ |  $C_6H_3\left\{\begin{array}{l}[1]\,CH_3\\ [3]\,S\\ [4]\,N\end{array}\right.\geqslant C\,[1]\,C_6H_4[4]N_2[2]C_{10}H_4\left\{\begin{array}{l}[1]\,OH\\ [3]\,SO_3Na\\ [6]\,SO_3Na\\ [8]\,Cl\end{array}\right.$ |
| 78 | **Erika B.**<br>[*A.*] | Sodium salt of methyl-benzenyl-amido-thio-xylenol-azo-$\alpha$-naphthol-disulphonic acid. | $C_{26}H_{19}N_3O_7S_3Na_2$ |  $C_6H_2\left\{\begin{array}{l}[1]CH_3\\ [3]CH_3\\ [5]S\\ [6]N\end{array}\right.\geqslant C[1]C_6H_3\left\{\begin{array}{l}[4]N=N-C_{10}H_4\left\{\begin{array}{l}[1]OH\\ [3]SO_3Na\\ [8]SO_3Na\end{array}\right.\\ [3]CH_3\end{array}\right.$ |

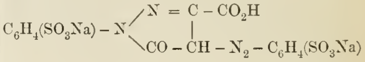
| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Diazo compound of *p*-amidophenol combined with pyrogallol. | | 1893. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $11902^{93}$.<br>Am. Pat. 548460.<br>Fr. Pat. 230937.<br>Ger. Pat. 81109. | **Appearance of dyestuff**: dark brown paste (30%).—**In water**: insoluble cold, dark yellow solution on boiling.—**In alcohol**: dull yellow solution.—**In conc. hydrochloric acid**: red solution.—**In caustic soda**: brown solution.—**In conc. sulphuric acid**: brown solution; brown precipitate on dilution.—**Dyes**: chromed wool dark brown.—**In cotton printing**: dark brown with a chrome mordant. |
| Action of ammonium bisulphite upon the combination product from diazodichlorophenol and *β*-naphthol. | | 1883. | A. Spiegel.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $5767^{83}$.<br>Am. Pats. 302790 & 306546.<br>Ger. Pat. 29067.<br>Ber. **18**, 1479. | **Appearance of dyestuff**: yellow paste.—**In water**: sparingly soluble with a yellow colour.—**In alcohol**: easily soluble.—**On addition of hydrochloric acid**: orange yellow precipitate.—**On addition of caustic soda**: violet precipitate; on boiling, red solution.—**In conc. sulphuric acid**: magenta red solution; reddish brown precipitate on dilution.—**Employment**: for fast reds and pinks in calico-printing, and for dyeing silk. |
| *o*-Anisidine. | *α*-Naphthol-monosulphonic acid NW. | 1885. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $2237^{83}$. | **Appearance of dyestuff**: red powder.—**In water**: red solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: the solution becomes yellowish brown.—**In conc. sulphuric acid**: carmine red solution; brownish red precipitate on dilution with water —**Dyes**: wool eosine red from an acid bath. |
| *o*-Anisidine. | *α*-Naphthol-disulphonic acid S. | 1892. | C. Duisberg.<br>Fr. Bayer & Co.<br>Ger. Pat. 40571. | **Appearance of dyestuff**: red powder.—**In water**: red solution.—**On addition of hydrochloric acid or caustic soda**: no change.—**In conc. sulphuric acid**: dark red solution; yellowish red on addition of water.—**Dyes**: wool from an acid bath red, very fast to alkalies, acids, and sulphur, moderately fast to light. |
| Amido-*p*-cresol-methyl ether. | *β*-Naphthol-disulphonic acid R. | 1878. | Baum.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $4914^{78}$.<br>Am. Pat. 250038.<br>Ger. Pat. $7217^{78}$. | **Appearance of dyestuff**: dark red powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid**: the solution becomes somewhat darker.—**On addition of caustic soda**: brown precipitate: soluble with a reddish brown colour.—**In conc. sulphuric acid**: cherry red solution; not altered on dilution with water.—**Dyes**: wool red from an acid bath. |
| *m*-Amido-*p*-cresol-methyl ether. | *α*-Naphthol-*ε*-disulphonic acid. | 1894. | G. Schultz. | **Appearance of dyestuff**: reddish brown powder.—**In water**: bluish red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: yellower.—**In conc. sulphuric acid**: violet blue solution; bluish red on dilution.—**Dyes**: wool and silk a very level bluish red of good fastness to light. |
| Boiling the intermediate product from tetrazotised benzidine and 1 mol. of salicylic acid. | | 1891. | Kahn.<br>Fr. Bayer & Co.<br>Ger. Pat. 60373. | **Appearance of dyestuff**: pale yellowish brown paste.—**In water**: insoluble; dissolves on adding sodium acetate.—**In boiling alcohol**: yellowish brown solution.—**In caustic soda**: dark reddish orange solution.—**In conc. sulphuric acid**: blood red solution; brown precipitate on dilution.—**Dyes**: chromed wool a full yellow, fast to milling. |
| Action of sodium bisulphite upon the intermediate product from tetrazotised benzidine and 1 mol. of salicylic acid. | | 1891. | M. Lange.<br>Ger. Pat. 68953. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: light brown precipitate —**On addition of caustic soda**: yellowish red solution.—**In conc. sulphuric acid**: bordeaux red solution; yellow precipitate on dilution.—**Dyes**: chromed wool brownish yellow. |
| Dehydro-thio-*p*-toluidine. | 1 : 8-Chloro-*α*-naphthol-3 : 6-disulphonic acid. | 1893. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $1920^{94}$.<br>Am. Pat. 535037.<br>Fr. Pat. 235271.<br>Ger. Pats. 79055 & 96768. | **Appearance of dyestuff**: dull red powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid**: red solution or precipitate.—**On addition of caustic soda**: bluer and darker.—**In conc. sulphuric acid**: reddish violet solution; red on dilution **Dyes**: unmordanted cotton, half-wool, and half-silk, fairly fast pink shades. |
| Dehydro-thio-*m*-xylidine. | *α*-Naphthol-*ε*-disulphonic acid. | 1889. | G. Schultz.<br>Ber. (1889) **22**, 583.<br>Actienges. f. Anilinfabrikn.<br>Eng. Pat. $17333^{88}$.<br>Am. Pat. 418657.<br>Fr. Pat. 194406.<br>Soc. Dyers aud Cols., 1889, 106. | **Appearance of dyestuff**: reddish brown powder.—**In water**: red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: red precipitate.—**On the addition of caustic soda to the aqueous solution**: bluish red precipitate.—**In conc. sulphuric acid**: red solution; on dilution with water, red precipitate.—**Dyes**: unmordanted cotton rose pink. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 79 | **Salmon Red.**<br>[*A.*] | Sodium salt of methyl-benzenyl-amido-thioxylenol-azo-β-naphthylamine disulphonic acid. | $C_{26}H_{20}N_4O_6S_3Na_2$ | $\mathrm{C_6H_2}\left\{\begin{matrix}\mathrm{[1]CH_3} \\ \mathrm{{[3]}CH_3} \\ \mathrm{{[5]}S} \\ \mathrm{{[6]}N}\end{matrix}\right. \geqslant \mathrm{C[1]C_6H_3}\left\{\begin{matrix}\mathrm{[4]N=N[1]C_{10}H_4}\left\{\begin{matrix}\mathrm{[2]NH_2} \\ \mathrm{{[3]}SO_3Na} \\ \mathrm{{[6]}SO_3Na}\end{matrix}\right. \\ \mathrm{{[3]}CH_3}\end{matrix}\right.$ |
| 80 | **Emin Red.**<br>[*A.*] | Sodium salt of methyl-benzenyl-amido-thioxylenol-azo-β-naphthol-sulphonic acid. | $C_{26}H_{20}N_3O_4S_2Na$ | $\mathrm{C_6H_2}\left\{\begin{matrix}\mathrm{[1]CH_3} \\ \mathrm{{[3]}CH_3} \\ \mathrm{{[5]}S} \\ \mathrm{{[6]}N}\end{matrix}\right. \geqslant \mathrm{C[1]C_6H_3}\left\{\begin{matrix}\mathrm{[2]N=N[1]C_{10}H_5}\left\{\begin{matrix}\mathrm{[2]OH} \\ \mathrm{{[7]}SO_3Na}\end{matrix}\right. \\ \mathrm{{[5]}CH_3}\end{matrix}\right.$ |
| 81 | **Diazine Green.**<br>[*K.*]<br>**Janus Green B & G.**<br>[*M.*] | Chloride of safranine-azo-dimethylaniline. | | $\mathsf{S}-N=N-C_6H_4\cdot N(CH_3)_2$<br>($\mathsf{S}$ = residue of safranine.) |
| 82 | **Diazine Black.**<br>[*K.*] | Safranine-azo-phenol. | | $\mathsf{S}-N=N-C_6H_4-OH$ |
| 83 | **Indoine Blue R.**<br>[*B.*] [*G.*]<br>**Janus Blue.** [*M.*]<br>**Naphthindone.** [*C.*]<br>**Bengaline.** [*K.*]<br>**Vac Blue.** [*H.*]<br>**Fast Cotton Blue R.** [*O.*]<br>**Indole Blue R.** [*A.*]<br>**Diazine Blue.** [*K.*] | Safranine-azo-β-naphthol. | | $\mathsf{S}-N=N-C_{10}H_6\cdot OH\beta$ |
| 84 | **Resorcin Yellow.**<br>[*A.*]<br>**Tropæoline O.** [*C.*]<br>**Tropæoline R.**<br>**Chrysoine.** [*B.*]<br>**Chryseoline.**<br>**Yellow T.** [*I.*]<br>**Gold Yellow.** [*By.*]<br>**Acme Yellow.** [*L.*] | Sodium salt of *p*-sulphobenzene-azo-resorcinol. | $C_{12}H_9N_2O_5SNa$ | $\mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{[4]\,SO_3Na} \\ \mathrm{{[1]}\,N=N-[4]\,C_6H_3}\left\{\begin{matrix}\mathrm{[1]\,OH} \\ \mathrm{{[3]}\,OH}\end{matrix}\right.\end{matrix}\right.$ |
| 85 | **Orange I.**<br>**Alphanaphthol Orange.**<br>**Naphthol Orange.**<br>[*A.*]<br>**Tropæoline 000 No. 1.**<br>**Orange B.** [*L.*] | Sodium salt of *p*-sulphobenzene-azo-α-naphthol. | $C_{16}H_{11}N_2O_4SNa$ | $\mathrm{C_6H_4}\left\{\begin{matrix}\mathrm{[4]\,SO_3Na} \\ \mathrm{{[1]}\,N=N-[4]\,C_{10}H_6\,[1]\,OH}\end{matrix}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Dehydro-thio-*m*-xylidine. | β-Naphthylamine-disulphonic acid R. | | G. Schultz.<br>Paul.<br>Zeit. f. angew. Chem. 1896, 680.<br>J. Soc. Chem. Ind. 1897, 730. | **Appearance of dyestuff**: red powder.—**In water**: orange red solution.—**On addition of hydrochloric acid**: garnet red precipitate.—**In conc. sulphuric acid**: violet solution; garnet red precipitate on dilution.—**Dyes**: cotton direct salmon red. |
| Isodehydrothio-*m*-xylidine. | β-Naphthol-sulphonic acid S. | 1891. | G. Schultz & A. Sansone.<br>Paul.<br>Zeit. f. angew. Chem. 1896, 680.<br>J. Soc. Chem. Ind. 1897, 730. | **Appearance of dyestuff**: red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: red precipitate.—**On addition of caustic soda**: yellower.—**In conc. sulphuric acid**: carmine red solution; red precipitate on dilution.—**Dyes**: wool from an acid bath red. |
| Safranine. | Dimethylaniline. | 1897. | L. Cassella & Co.<br>Ger. Pat. $95668^{97}$.<br>Compare Monit. Scien. 1896, 984. | **Appearance of dyestuff**: brown or dark green powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: soluble blue precipitate.—**On addition of caustic soda**: black precipitate.—**In conc. sulphuric acid**: olive green solution; on dilution becoming greenish blue and then pure blue.—**Dyes**: cotton a fairly fast dull bluish green. |
| Safranine. | Phenol. | | Monit. Scien. 1896, 984. | **Appearance of dyestuff**: blackish brown powder.—**In water**: blackish green blue solution.—**In alcohol**: reddish blue solution.—**On addition of hydrochloric acid**: soluble blackish green precipitate.—**On addition of caustic soda**: red precipitate.—**In conc. sulphuric acid**: green solution; on dilution, violet and then blackish green.—**Dyes**: tannined cotton black of good fastness to light and soap. |
| Safranine. | β-Naphthol. | 1891. | Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $4543^{91}$ & $18769^{93}$.<br>Am. Pats. 524251 & 524254.<br>Ger. Pats. 61692 & 85690.<br>Fr. Pat. 212276.<br>*Patents by other Firms:*<br>Eng. Pats. $3488^{95}$; $23985^{98}$.<br>Ger. Pats. $85932^{95}$; $91721^{95}$; $92015^{95}$; $105433^{98}$; $108497^{98}$.<br>Fr. Pats. 245239; 250239; 283013; 285360. | **Appearance of dyestuff**: dark coloured paste or bronzy powder.—**In water**: violet solution.—**In alcohol**: bluish violet solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: blackish violet precipitate.—**In conc. sulphuric acid**: greenish brown solution, becoming green, and then giving a violet precipitate when diluted.—**Dyes**: unmordanted or tannined cotton very fast indigo-blue shades. Discharged by stannous salts it gives a red pattern on a blue ground. |
| *p*-Sulphanilic acid. | Resorcinol. | 1875.<br>1876. | P. Griess.<br>Ber. (1878) **11**, 2195.<br>O. N. Witt. | **Appearance of dyestuff**: brown powder.—**In water**: orange solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: solution becomes reddish brown.—**In conc. sulphuric acid**: yellow solution, becoming reddish yellow on solution.—**Dyes**: wool reddish yellow from an acid bath. |
| *p*-Sulphanilic acid. | α-Naphthol. | 1876.<br>1877. | P. Griess. Z. Roussin.<br>O. N. Witt.<br>Liebermann.<br>Ann. (1882) **211**, 61.<br>Ber. (1881) **14**, 1796.<br>O. Mühlhäuser.<br>Ding. Pol. J. **264**, 181, 238.<br>J. Soc. Chem. Ind. 1887, 591. | **Appearance of dyestuff**: reddish brown powder.—**In water**: orange red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: the solution becomes cherry red.—**In conc. sulphuric acid**: magenta red solution, becoming reddish brown on dilution.—**Dyes**: wool orange from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 86 | **Orange II.** [*P.*]<br>**Betanaphthol Orange.**<br>**Tropæoline OOO No. 2.**<br>**Mandarin G extra.** [*A.*]<br>**Chrysaureïne.**<br>**Gold Orange.** [*By.*]<br>**Orange extra.** [*C.*]<br>**Atlas Orange.** [*B.S.S.*]<br>**Orange A.** [*L.*] | Sodium salt of *p*-sulphobenzene-azo-$\beta$-naphthol. | $C_{16}H_{11}N_2O_4SNa$ | $C_6H_4\left\{\begin{array}{l}[4]\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_6\,[2]\,OH\end{array}\right.$ |
| 87 | **Orange III.** [*P.*]<br>**Methyl Orange.**<br>**Dimethylaniline Orange.**<br>**Helianthine.** [*B.*]<br>**Tropæoline D.** | Sodium salt of *p*-sulphobenzene-azo-dimethylaniline. | $C_{14}H_{14}N_3SO_3Na$ | $C_6H_4\left\{\begin{array}{l}[4]\,SO_3Na\\ {[1]}\,N=N-[1]\,C_6H_4\,[4]\,N(CH_3)_2\end{array}\right.$ |
| 88 | **Diphenylamine Orange.**<br>**Orange IV.** [*P.*]<br>**Tropæoline OO.** [*C.*]<br>**Orange M.** [*I.*]<br>**Fast Yellow.** [*B.S.S.*]<br>**Orange G S.**<br>**New Yellow.** [*By.*]<br>**Orange N.** [*B.*]<br>**Acid Yellow D.** [*A.*] | Sodium salt of *p*-sulphobenzene-azo-diphenylamine. | $C_{18}H_{14}N_3O_3SNa$ | $C_6H_4\left\{\begin{array}{l}[4]\,SO_3Na\\ {[1]}\,N=N-[1]\,C_6H_4\,[4]\,NH\cdot C_6H_5\end{array}\right.$ |
| 89 | **Brilliant Yellow S.** [*B.*] [*T. M.*]<br>**Yellow WR.** [*I.*]<br>**Curcumine.** [*G.*] | Sodium salt of *p*-sulphobenzene-azo-diphenylamine-sulphonic acid. | $C_{18}H_{13}N_3O_6S_2Na_2$ | |
| 90 | **Narceïne.** [*D. H.*] | Sodium bisulphite compound of *p*-sulphobenzene-azo-$\beta$-naphthol. | $C_{16}H_{12}N_2O_7S_2Na_2$ | $C_6H_4\left\{\begin{array}{l}[4]\,SO_3Na\\ {[1]}\,NH-N(SO_3Na)-[1]\,C_{10}H_6\,[2]\,OH\end{array}\right.$ |
| 91 | **Curcumeïne.** [*A.*]<br>**New Yellow.** [*T. M.*]<br>**Citronine.** | Mixture of nitrated diphenylamine yellow with nitro-diphenylamine. | | |
| 92 | **Azo Acid Yellow.** [*A.*]<br>**Azo Yellow.** [*M.*]<br>**Azoflavine.** [*B.*]<br>**Indian Yellow.** [*By.*] | Mixture of nitrated diphenylamine yellow with nitro-diphenylamine. | | |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| *p*-Sulphanilic acid. | *β*-Naphthol. | 1876. | Z. Roussin.<br>P. Griess.<br>Ber. (1878) **11**, 2198.<br>A. W. Hofmann.<br>Ber. (1877) **10**, 1378.<br>W. V. Miller.<br>Ber. (1880) **13**, 268.<br>Chem. Ind. (1880), **3**, 147.<br>O. Mühlhäuser.<br>Ding. Pol. J. **264**, 181, 238.<br>J. Soc. Chem. Ind. (1887) 591. | **Appearance of dyestuff:** bright orange powder.—**In water:** orange solution.—**On addition of hydrochloric acid to the aqueous solution:** brownish yellow precipitate.—**On addition of caustic soda:** solution becomes dark brown.—**In conc. sulphuric acid:** magenta red solution; brownish yellow precipitate on dilution with water.—**Dyes:** wool orange from an acid bath. |
| *p*-Sulphanilic acid. | Dimethyl-aniline. | 1875.<br>1876. | P. Griess.<br>Ber. (1877) **10**, 528.<br>O. N. Witt. Z. Roussin. | **Appearance of dyestuff:** ochre yellow powder.—**In water:** orange yellow solution.—**On addition of hydrochloric acid:** solution becomes magenta red.—**On addition of caustic soda to the aqueous solution:** orange yellow precipitate, soluble in much water.—**In conc. sulphuric acid:** brown solution; magenta red on dilution with water.—**Dyes:** wool orange from an acid bath. It is employed as an indicator in alkalimetry, as it is not reddened by carbonic acid. |
| *p*-Sulphanilic acid. | Diphenylamine. | 1876.<br>1877. | P. Griess. O. N. Witt.<br>Ber. (1879) **12**, 262.<br>Z. Roussin. | **Appearance of dyestuff:** orange yellow plates or yellow powder.—**In water:** orange yellow solution; the colour crystallises out from the hot aqueous solution on cooling in orange spangles.—**On addition of hydrochloric acid to aqueous solution:** violet precipitate.—**On addition of caustic soda to the aqueous solution:** yellow precipitate.—**In conc. sulphuric acid:** violet solution; violet precipitate on dilution with water.—**Dyes:** wool orange yellow from an acid bath. |
| Sulphonation of Orange IV. | | | Dall & Co.<br>Ger. Pat. 21093. | **Appearance of dyestuff:** orange yellow powder.—**In water:** yellow solution.—**On addition of hydrochloric acid:** solution becomes violet red.—**Caustic soda:** small quantity, no change; excess, violet red colour.—**In conc. sulphuric acid:** bluish red solution; magenta red on dilution.—**Dyes:** wool and silk yellow. |
| Sulphanilic acid.<br>And treatment with sodium bisulphite. | *β*-Naphthol. | 1879. | Prud'homme.<br>E. Nölting.<br>Mon. Scien. (1886) 319. | **Appearance of dyestuff:** orange yellow powder.—**In water:** yellow solution.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda:** solution becomes brownish red.—**In conc. sulphuric acid:** yellowish brown solution; evolves sulphurous acid on dilution and warming.—**Employment:** for calico printing. |
| Action of nitric acid upon diphenylamine yellow. | | 1880. | E. Knecht. | **Appearance of dyestuff:** ochre yellow powder.—**In water:** sparingly soluble in cold, more readily in hot.—**On addition of hydrochloric acid to the aqueous solution:** magenta red colour.—**On addition of caustic soda:** yellowish brown colour.—**In conc. sulphuric acid:** reddish violet solution; olive brown on dilution.—**Dyes:** wool yellow from an acid bath. |
| Action of nitric acid upon diphenylamine yellow. | | 1880. | E. Knecht. | **Appearance of dyestuff:** ochre yellow powder.—**In hot water:** lemon yellow solution.—**On addition of hydrochloric acid:** the colour of the solution becomes browner and deeper.—**On addition of caustic soda:** solution becomes yellowish brown.—**In conc. sulphuric acid:** magenta red solution; on dilution with water, yellowish brown precipitate.—**Dyes:** wool yellow from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 93 | **Azo-fuchsine G.**<br>[*By.*] | Sodium salt of *p*-sulpho-benzene-azo-dioxy-naphthalene-sulphonic acid. | $C_{16}H_{10}N_2S_2O_8Na_2$ | $C_6H_4\begin{cases}[4]\,SO_3Na\\ [1]-N=N[2]C_{10}H_4\begin{cases}[1]\,OH\\ [8]\,OH\\ [4]\,SO_3Na\end{cases}\end{cases}$ |
| 94 | **Tartrazine.**<br>[*B.*] [*I.*] [*H.*]<br>**Hydrazine Yellow.**<br>[*O.*] | Sodium salt of benzene-azo-pyrazalone-carboxy-disulphonic acid. | $C_{16}H_{10}N_4S_2O_9Na_2$ |  |
| 95 | **Metanil Yellow.*** <br>[*O.*] [*B.*] [*A.*]<br>**Orange M N.**<br>[*I.*]<br>**Tropæoline G.**<br>[*C.*] | Sodium salt of *m*-sulphobenzene-azo-diphenylamine. | $C_{18}H_{14}N_3O_3SNa$ | $C_6H_4\begin{cases}[3]\,SO_3Na\\ [1]\,N=N-[1]\,C_6H_4\,[4]\,NH\cdot C_6H_5\end{cases}$ |
| 96 | **Phenoflavine.**<br>[*O.*] | Sodium salt of *m*-sulphobenzene-azo-amidophenol sulphonic acid. | $C_{12}H_9N_3S_2O_7Na_2$ | $C_6H_4\begin{cases}[3]\,SO_3Na\\ [1]\,N=N\,[1]\,C_6H_2\begin{cases}[2]\,NH_2\\ [4]\,OH\\ [6]\,SO_3Na\end{cases}\end{cases}$ |
| 97 | **Orange T.** [*K.*]<br>**Mandarin G. R.** [*A.*]<br>**Orange R.** [*I.*]<br>**Kermesin Orange.**<br>[*L.*] | Sodium salt of sulpho-*o*-toluene-azo-*β*-naphthol. | $C_{17}H_{13}N_2O_4SNa$ | $C_6H_3(SO_3Na)\begin{cases}[2]\,CH_3\\ [1]\,N=N-[1]\,C_{10}H_6\,[2]\,OH\end{cases}$ |
| 98 | **Fast Yellow N.**<br>[*P.*]<br>**Jaune solide N.**<br>**Curcumeïn.** | Sodium salt of sulpho-*p*-toluene-azo-diphenylamine. | $C_{19}H_{16}N_3O_3SNa$ | $C_6H_3\begin{cases}[4]\,CH_3\\ [3]\,SO_3Na\\ [1]\,N=N-[1]\,C_6H_4\,[4]\,NH\cdot C_6H_5\end{cases}$ |
| 99 | **Orange R R.** [*I.*]<br>**Orange R.** [*B.*] | Sodium salt of sulphoxylene-azo-*β*-naphthol. | $C_{18}H_{15}N_2O_4SNa$ | $C_6H_2(CH_3)_2(SO_3Na)-N=N-C_{10}H_6\cdot OH\beta$ |
| 100 | **Cuba Orange.**<br>[*Pick, Lange.*] | | | $\begin{matrix}N\cdot C_{10}H_6\cdot SO_3Na\\ \|\\ N\cdot C_{10}H_6\cdot SO_3Na\end{matrix}$ (?) |
| 101 | **Fast Brown N.** [*B.*]<br>**Naphthylamine Brown.**<br>**Azo Brown O.**<br>[*M.*] | Sodium salt of *p*-sulphonaphthalene-azo-*α*-naphthol. | $C_{20}H_{13}N_2O_4SNa$ | $C_{10}H_6\begin{cases}[4]\,SO_3Na\\ [1]\,N=N-[4]\,C_{10}H_6\,[1]\,OH\end{cases}$ |

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* **Acid Yellow 2 G** is the sulphonic acid of

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Sulphanilic acid. | (1 : 8)-dioxy-naphthalene-monosulphonic acid Sch. | 1889. | M. Ulrich & C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $18517^{89}$.<br>Ger. Pat. $54116^{89}$.<br>Am. Pats. 466841 & 468142. | **Appearance of dyestuff :** reddish brown powder.—**In water :** bluish red solution.—**On addition of hydrochloric acid to the aqueous solution :** colour becomes yellower.—**On addition of caustic soda :** colour becomes bluer.—**In conc. sulphuric acid :** violet solution ; bluish red on dilution.—**Dyes :** wool magenta red from an acid bath, very fast to light and acids, moderately fast to milling. |
| 1. Action of phenylhydrazine sulphonic acid (2 mols.) upon dioxytartaric acid (1 mol.).<br>2. Action of phenylhydrazine sulphonic acid (1 mol.) upon oxalacetic ether (1 mol.), coupling the product with diazotised sulphanilic acid and saponifying. | | 1884. | A. Ziegler.<br>Ber. **20**, 834.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $9858^{85}$, $5693^{93}$.<br>Am. Pat. $324630^{85}$.<br>Ger. Pat. $34294^{85}$.<br>Fr. Pat. $169964^{85}$.<br>R. Anschütz.<br>Ann. **294**, 232 ; **306**, 1.<br>Bernthsen.<br>Chem. Ztg. 1898, 456. | **Appearance of dyestuff :** bright orange yellow powder.—**In water :** easily soluble with golden yellow colour.—**On addition of hydrochloric acid :** no alteration.—**On addition of caustic soda :** colour becomes redder.—**In conc. sulphuric acid :** yellow.—**Dyes :** wool and silk yellow from an acid bath, very fast to light acids and alkalies, moderately fast to milling. |
| *m*-Sulphanilic acid. | Diphenyl-amine. | 1879.<br>1882. | Fr. Bayer & Co.<br>Eng. Pat. $1226^{79}$.<br>Ed. Hepp. K. Oehler.<br>Eng. Pat. $4966^{80}$ | **Appearance of dyestuff :** brownish yellow powder.—**In water :** orange yellow solution.—**On addition of hydrochloric acid to the aqueous solution :** magenta red colour, with separation of a precipitate.—**On addition of caustic soda to the aqueous solution :** no change.—**In conc. sulphuric acid :** violet solution ; magenta red on dilution.—**Dyes :** wool orange yellow from an acid bath. |
| *m*-Sulphanilic acid. | Amidophenol-sulphonic acid III. | 1892. | Rudolph. K. Oehler.<br>Ger. Pat. 71229. | **Appearance of dyestuff :** brownish yellow powder.—**In water :** yellow solution.—**On addition of hydrochloric acid or caustic soda :** orange solution.—**In conc. sulphuric acid :** yellow solution.—**Dyes :** wool yellow from an acid bath. |
| *o*-Toluidine-monosulphonic acid. | β-Naphthol. | | R. Nietzki.<br>Organ. Farbstoffe (1886), 49.<br>O. Mühlhäuser.<br>Ding. Pol. J. **264**, 181, 238.<br>J. Soc. Chem. Ind. (1887) 591. | **Appearance of dyestuff :** brick red powder.—**In water :** orange solution.—**On addition of hydrochloric acid to aqueous solution :** yellowish brown flocks.—**On addition of caustic soda :** solution becomes reddish brown.—**In conc. sulphuric acid :** magenta red solution ; yellowish brown flocks on dilution with water. **Dyes :** wool orange from an acid bath. |
| *p*-Toluidine-*o*-sulphonic acid. | Diphenylamine. | 1878. | Z. Roussin.<br>Eng. Pat. $4491^{78}$. | **Appearance of dyestuff :** orange powder.—**In water :** yellow solution.—**On addition of hydrochloric acid to the aqueous solution :** steel blue precipitate.—**In conc. sulphuric acid :** bluish green solution ; steel blue precipitate on dilution with water.—**Dyes :** wool orange from an acid bath. |
| Xylidine-sulphonic acid. | β-Naphthol. | 1877. | Bad. Anil. & Soda Fabrik.<br>O. Mühlhäuser.<br>Ding. Pol. J. **264**, 181, 238.<br>J. Soc. Chem. Ind. (1887) 591. | **Appearance of dyestuff :** bright red powder.—**In water :** orange solution.—**On addition of hydrochloric acid to the aqueous solution :** brownish red precipitate.—**On addition of caustic soda :** solution becomes brownish yellow.—**In conc. sulphuric acid :** cherry red solution ; brown precipitate on dilution with water.—**Dyes :** wool orange from an acid bath. |
| Action of sodium sulphite (1 mol.) upon diazonaphthalene-sulphonic acid (2 mols.). | | 1894. | M. Lange.<br>Ger. Pat. 78225 | **Appearance of dyestuff :** reddish yellow powder.—**In water :** orange solution.—**With caustic soda :** yellow crystalline precipitate.—**In conc. sulphuric acid :** blue solution.—**Dyes :** wool orange. |
| Naphthionic acid. | α-Naphthol. | 1878. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $786^{78}$ (expired).<br>Am. Pat. 204799 (expired).<br>Ger. Pat. $5411^{78}$. | **Appearance of dyestuff :** brown powder.—**In water :** yellowish brown solution.—**On addition of hydrochloric acid :** the aqueous solution becomes magenta red.—**On addition of caustic soda :** the solution becomes reddish brown.—**In conc. sulphuric acid :** violet solution ; magenta red on dilution with water.—**Dyes :** wool brown from an acid bath. |

etanil Yellow, and has a greener shade.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 102 | **Fast Red.**<br>**Fast Red A.** [*B.*]<br>**Roccelline.** [*D.H.*]<br>**Rauracienne.**<br>**Ceracine.**<br>**Orcelline No. 4.**<br>**Rubidine.** | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol. | $C_{20}H_{13}N_2O_4SNa$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_6\,[2]\,OH\end{array}\right.$ |
| 103 | **Azorubine S.** [*A.*]<br>**Fast Red C.** [*B.*]<br>**Carmoisine.** [*By.*]<br>**Azorubine A.** [*C.*]<br>**Azo Acid Rubine.** [*D.*] | Sodium salt of *p*-sulphonaphthalene-azo-α-naphthol-*p*-sulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 104 | **Croceïne 3 BX.** [*By.*] [*K.*]<br>**Coccine 2 B.** [*A.*]<br>**Scarlet 000.** [*H.*] | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol-mono-sulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[8]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 105 | **Fast Red E.** [*B.*] [*By.*]<br>**Fast Red.** [*A.*] | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol-mono-sulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 106 | **New Coccine.** [*A.*]<br>**Brilliant Scarlet.** [*C.*] [*Lev.*]<br>**Cochineal Red A.** [*B.*]<br>**Croceïne Scarlet 4 BX.** [*K.*] | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol-disulphonic acid. | $C_{20}H_{11}N_2O_{10}S_3Na_3$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[6]}\,SO_3Na\\ {[8]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 107 | **Fast Red D.** [*B.*]<br>**Bordeaux S.** [*A.*]<br>**Amaranth** [*M.*] [*C.*]<br>**Azo Acid Rubine 2 B.** [*D.*]<br>**Fast Red E B.** [*B.*] | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol-disulphonic acid. | $C_{20}H_{11}N_2O_{10}S_3Na_3$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 108 | **Scarlet 6 R.**<br>**Ponceau 6 R.** [*M.*] [*B.*] | Sodium salt of *p*-sulphonaphthalene-azo-*β*-naphthol-trisulphonic acid. | $C_{20}H_{10}N_2O_{13}S_4Na_4$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-C_{10}H_3\left\{\begin{array}{l}OH\beta\\ (SO_3Na)_3\end{array}\right.\end{array}\right.$ |
| 109 | **Roxamine.** [*D.H.*] | Sodium salt of dioxy-azo-naphthalene sulphonic acid. | $C_{20}H_{13}N_2O_5SNa$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[7]}\,OH\end{array}\right.\end{array}\right.$ |
| 110 | **Chromotrope 8 B.** [*M.*] | Sodium salt of *p*-Sulphonaphthalene-azo-dioxy-naphthalene disulphonic acid. | $C_{20}H_{11}N_2S_3O_{11}Na_3$ | $C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N\,[2]\,C_{10}H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Naphthionic acid. | β-Naphthol. | 1877. | H. Caro. Z. Roussin.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $786^{78}$ (expired).<br>Am. Pat. 204799 (expired).<br>Ger. Pat. $5411^{78}$.<br>Fr. Pat. $123148^{78}$.<br>P. Griess.<br>Ber. 11, 2199; 12, 1364.<br>E. Roussel.<br>Monit. de la teinture (1883), 271. | **Appearance of dyestuff**: brownish red powder.—**In water**: sparingly soluble cold, more easily hot, with a red colour.—**On addition of hydrochloric acid to the aqueous solution**: yellowish brown precipitate.—**On addition of caustic soda to the aqueous solution**: the colour becomes rather duller and darker. **In conc. sulphuric acid**: violet solution; yellowish brown precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | α-Naphthol-monosulphonic acid NW. | 1883. | O. N. Witt.<br>Verein. Chem. Fabriken Mannheim.<br>Eng. Pats. $2237^{83}$ and $4237^{83}$.<br>Ger. Pat. $26012^{83}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown gelatinous precipitate.—**On addition of caustic soda**: the solution becomes rather yellower.—**In conc. sulphuric acid**: violet solution; magenta red on dilution with water.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | β-Naphthol-sulphonic acid α or B. | 1882. | Eugen Frank.<br>Fr. Bayer & Co.<br>Eng. Pat. $2030^{81}$.<br>Am. Pat. 256376.<br>Ger. Pat. $20402^{82}$. | **Appearance of dyestuff**: scarlet red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: the aqueous solution becomes yellowish brown.—**In conc. sulphuric acid**: reddish violet solution; yellowish red on dilution with water.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | β-Naphthol-monosulphonic acid S. | 1878. | Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $786^{78}$ (expired).<br>Ger. Pat. $5411^{78}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: bordeaux red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: solution becomes brown.—**In conc. sulphuric acid**: violet solution; red on dilution.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | β-Naphthol-disulphonic acid G. | 1878. | Actienges. f. Anilinfabrikn.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $816^{84}$.<br>Am. Pat. 314938.<br>Ger. Pat. $36491^{84}$. | **Appearance of dyestuff**: scarlet red powder.—**In water**: easily soluble.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: solution becomes brown.—**In conc. sulphuric acid**: magenta red solution; yellowish red on dilution.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | β-Naphthol-disulphonic acid R. | 1878. | Meister, Lucius, & Brüning.<br>Ger. Pat. $3229^{78}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: colour becomes darker.—**In conc. sulphuric acid**: violet; magenta red on dilution with water.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | β-Naphthol-trisulphonic acid. | 1881. | L. Limpach.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $2544^{82}$ (lapsed).<br>Am. Pat. 268506.<br>Ger. Pat. $22038^{82}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: solution becomes reddish brown.—**In conc. sulphuric acid**: violet solution; magenta red on dilution.—**Dyes**: wool red from an acid bath. |
| Naphthionic acid. | (2 : 7)-Dioxy-naphthalene. | 1889. | Durand & Huguenin. | **Appearance of dyestuff**: brick red powder.—**In water**: scarlet solution.—**Addition of hydrochloric acid**; no change.—**Addition of caustic soda**: solution becomes darker.—**In conc. sulphuric acid**: intense violet solution.—**Dyes**: wool red from an acid bath; used as an orchil substitute. |
| Naphthionic acid. | 1 : 8-Dioxy-naphthalene-3 : 6-disulphonic acid. | 1890. | Kuzel.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $9258^{90}$.<br>Ger. Pat. 69095.<br>Fr. Pat. 206439. | **Appearance of dyestuff**: greyish violet powder.—**In water**: violet red solution.—**On addition of hydrochloric acid**: bluer.—**On addition of caustic soda**: darker.—**In conc. sulphuric acid**: indigo blue solution, on dilution becoming violet.—**Dyes**: wool from acid bath reddish violet, fast to light, rubbing, acids, and sulphur, not so fast to milling. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 111 | **Fast Brown 3 B.** [*A.*] | Sodium salt of sulphonaphthalene-azo-α-naphthol. | $C_{20}H_{13}N_2O_4SNa$ | $C_6H_4 \left\{ \begin{array}{l} [6]\,SO_3Na \\ [2]\,N=N-[4]\,C_{10}H_6\,[1]\,OH \end{array} \right.$ |
| 112 | **Double Brilliant Scarlet G.** [*A.*] [*Lev.*]<br>**Scarlet for silk.** [*M.*] | Sodium salt of sulphonaphthalene-azo-β-naphthol. | $C_{20}H_{13}N_2O_4SNa$ | $C_{10}H_6 \left\{ \begin{array}{l} [6]\,SO_3Na \\ [2]\,N=N-[1]\,C_{10}H_6\,[2]\,OH \end{array} \right.$ |
| 113 | **Double Scarlet Extra S.** [*A.*]<br>**Double Brilliant Scarlet 3 R.** [*By.*]<br>**Brilliant Ponceau 4 R.** [*By.*] | Sodium salt of sulphonaphthalene-azo-α-naphthol-monosulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_6 \left\{ \begin{array}{l} [6]\,SO_3Na \\ [2]\,N=N-[2]\,C_{10}H_5 \left\{ \begin{array}{l} [1]\,OH \\ [4]\,SO_3Na \end{array} \right. \end{array} \right.$ |
| 114 | **Fast Acid Scarlet.**<br>**Acid Ponceau.** [*D. H.*]<br>**Ponceau S for silk.** [*I.*] | Sodium salt of sulphonaphthalene-azo-β-naphthol. | $C_{20}H_{13}N_2O_4SNa$ | $C_{10}H_6 \left\{ \begin{array}{l} SO_3Na \\ N=N-[1]\,C_{10}H_6\,[2]\,OH \end{array} \right.$ |
| 115 | **Pyrotine RRO.** [*D.*] | Sodium salt of sulphonaphthalene-azo-α-naphthol-monosulphonic acid. | $C_{20}H_{12}N_2O_7S_2Na_2$ | $C_{10}H_6 \left\{ \begin{array}{l} [5]\,SO_3Na \\ [2]\,N=N-[2]\,C_{10}H_5 \left\{ \begin{array}{l} [1]\,OH \\ [4]\,SO_3Na \end{array} \right. \end{array} \right.$ |
| 116 | **Milling Yellow.** [*D.*] [*Lev.*]<br>**Chrome Yellow D.** [*By.*]<br>**Anthracene Yellow B N.** [*C.*]<br>**Mordant Yellow O.** [*B.*] [*M.*]<br>**Chrome Fast Yellow.** [*A.*] | Sodium salt of sulphonaphthalene-azo-salicylic acid. | $C_{17}H_{10}N_2O_5SNa_2$ | $C_{10}H_6 \left\{ \begin{array}{l} SO_3Na \\ N=N\,[4]\,C_6H_3 \left\{ \begin{array}{l} [1]\,OH \\ [2]\,CO_2Na \end{array} \right. \end{array} \right.$ |
| 117 | **Crumpsall Yellow.** [*Lev.*] | Sodium salt of di-sulphonaphthalene-azo-salicylic acid. | $C_{17}H_{10}N_2S_2O_9Na_2$ | $C_{10}H_5 \left\{ \begin{array}{l} [8]\,SO_3Na \\ [6]\,SO_3Na \\ [2]\,N=N\,[1]\,C_6H_3 \left\{ \begin{array}{l} [3]\,CO_2H \\ [4]\,OH \end{array} \right. \end{array} \right.$ |
| 118 | **Lanacyl Violet B.** [*C.*] | Sodium salt of di-sulpho-oxy-naphthalene-azo-ethyl-alpha-naphthylamine. | $C_{22}H_{17}N_3S_2O_7Na_2$ | $C_{10}H_4 \left\{ \begin{array}{l} [8]\,OH \\ [6]\,SO_3Na \\ [3]\,SO_3Na \\ [1]\,N=N\,[1]\,C_{10}H_6\,[4]\,NH \cdot C_2H_5 \end{array} \right.$ |
| 119 | **Lanacyl Blue BB.*** [*C.*] | Sodium salt of di-sulpho-oxy-naphthalene-azo-amido-naphthol. | $C_{20}H_{13}N_3S_2O_8Na_2$ | $C_{10}H_4 \left\{ \begin{array}{l} [8]\,OH \\ [6]\,SO_3Na \\ [3]\,SO_3Na \\ [1]\,N=N\,[2]\,C_{10}H_5 \left\{ \begin{array}{l} [1]\,OH \\ [5]\,NH_2 \end{array} \right. \end{array} \right.$ |

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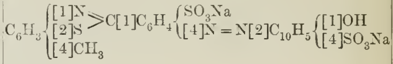
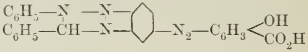
* To this group also belongs **Lanacyl**

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| β-Naphthylamine monosulphonic acid Br. | α-Naphthol. | 1882. | H. Prinz.<br>Farbfabrik vorm. Brönner.<br>Eng. Pat. 3724$^{82}$.<br>Ger. Pat. 22547$^{82}$.<br>Am. Pat. 332829. | **Appearance of dyestuff**: brown.—**In water**: brownish red solution. **On addition of hydrochloric acid to the aqueous solution**: reddish violet.—**On addition of caustic soda to the aqueous solution**: magenta red.—**In conc. sulphuric acid**: blue; reddish violet precipitate on dilution.—**Dyes**: wool brown from an acid bath. |
| β-Naphthylamine monosulphonic acid Br. | β-Naphthol. | 1882. | H. Prinz.<br>Farbfabrik vorm. Brönner.<br>Eng. Pat. 3724$^{82}$.<br>Ger. Pat. 22547$^{8}$ .<br>Am. Pat. 332829, | **Appearance of dyestuff**: reddish brown powder.—**In water**: scarlet solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: reddish brown precipitate, soluble in much water.—**In conc. sulphuric acid**: magenta red solution; brownish red precipitate on dilution with water.—**Dyes**: wool a yellow scarlet from an acid bath, silk fast to washing. |
| β-Naphthylamine monosulphonic acid Br. | α-Naphthol-monosulphonic acid NW. | 1882. | H. Prinz.<br>Farbfabrik vorm. Brönner.<br>Eng. Pat. 3724$^{82}$.<br>Ger. Pat. 22547$^{82}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: yellowish brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: magenta red solution; scarlet on dilution.—**Dyes**: wool scarlet from an acid bath. |
| β-Naphthylamine sulphonic acid (chiefly α and γ). | β-Naphthol. | | L. Durand, Huguenin & Co. | **Appearance of dyestuff**: scarlet red powder.—**In water**: soluble in hot water, sparingly in cold.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: the solution becomes browner.—**In conc. sulphuric acid**: magenta red solution; brown precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| β-Naphthylamine monosulphonic acid D (chiefly γ). | α-Naphthol-monosulphonic acid NW. | 1884. | Dahl & Co.<br>Eng. Pats. 7712$^{84}$, 7713$^{84}$, 11002$^{84}$.<br>Ger. Pats. 29084$^{84}$, 32271$^{84}$, 32276$^{84}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: solution becomes bluer.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: magenta red solution; on dilution with water, red.—**Dyes**: wool red from an acid bath. |
| β-Naphthylamine monosulphonic acid. | Salicylic acid. | 1890. | Nietzki. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: solution brown, depositing after some time a brown precipitate.—**On addition of caustic soda**: the solution becomes deep orange red.—**In conc. sulphuric acid**: yellowish red solution.—**Dyes**: wool yellow from an acid bath; chromed wool yellow, fast to milling and light. |
| β-Naphthylamine-γ-disulphonic acid. | Salicylic acid. | 1894. | Hirschberger.<br>Levinstein & Co.<br>Eng. Pat. 12145$^{94}$.<br>Ger. Pat. 87483. | **Appearance of dyestuff**: yellow powder.—**In water**: easily soluble with yellow colour.—**On addition of hydrochloric acid**: orange red coloration.—**On addition of caustic soda**: greenish yellow coloration.—**In conc. sulphuric acid**: orange red solution.—**Dyes**: wool, chromed or unchromed, yellow. |
| 1 : 8-Amidonaphthol-3 : 6-disulphonic acid ("*H-acid*"). | Ethyl-α-naphthylamine. | 1896. | L. Cassella & Co.<br>Eng. Pat. 12556$^{95}$.<br>Ger. Pat. 94288$^{96}$.<br>Fr. Pat. 257136. | **Appearance of dyestuff**: dark brown powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: solution becomes orange red.—**In conc. sulphuric acid**: greenish blue solution; on dilution blue and then violet.—**Dyes**: wool from an acid bath shades of good fastness to light, milling, acids, and alkalies. |
| 1 : 8-Amidonaphthol-3 : 6-disulphonic acid ("*H-acid*"). | 1 : 5-Amidonaphthol. | 1896. | L. Cassella & Co.<br>Eng. Pat. 29134$^{96}$.<br>Ger. Pat. 95190$^{96}$.<br>Fr. Pat. 260848. | **Appearance of dyestuff**: black powder.—**In water**: reddish or bluish violet solution.—**On addition of hydrochloric acid**: little change.—**On addition of caustic soda**: solution becomes orange red.—**In conc. sulphuric acid**: blue solution; on dilution first blue and then violet.—**Dyes**: wool from an acid bath, blue of good fastness to light and acids. |

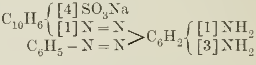
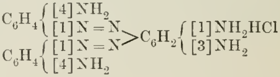
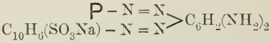
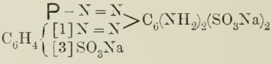
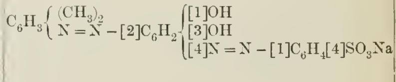
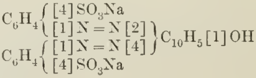
**Blue R and Lanacyl Navy Blue B [*C.*].**

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 120 | **Yellow fast-to-soap.**<br>**Jaune resistant-au-savon.** [*P.*] | Sodium salt of *m*-carboxybenzene-azo-diphenylamine. | $C_{19}H_{14}N_3O_2Na$ | $C_6H_4\left\{\begin{array}{l}[3]\,CO_2Na\\ [1]-N=N-[1]\,C_6H_4\,[4]\,NH\cdot C_6H_5\end{array}\right.$ |
| 121 | **Diamond Yellow G.** [*By.*] | Sodium salt of *m*-carboxy-benzene-azo-salicylic acid. | $C_{14}H_{10}N_2O_5$ | $C_6H_4\left\{\begin{array}{l}[3]\,CO_2Na\\ [1]-N=N-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,OH\\ [2]\,CO_2Na\end{array}\right.\end{array}\right.$ |
| 122 | **Diamond Yellow R.** [*By.*] | Sodium salt of *o*-carboxy-benzene-azo-salicylic acid. | $C_{14}H_{10}N_2O_5$ | $C_6H_4\left\{\begin{array}{l}[2]\,CO_2Na\\ [1]-N=N-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,OH\\ [2]\,CO_2Na\end{array}\right.\end{array}\right.$ |
| 123 | **Chrome Brown RR.** [*G.*] | Sodium salt of disulpho-oxybenzene-azo-pyrogallol. | $C_{12}H_8N_2S_2O_{10}Na_2$ | $C_6H_2\left\{\begin{array}{l}[4]\,OH\\ [3]\,SO_3Na\\ [5]\,SO_3Na\\ [1]\,N=N\,[1]\,C_6H_2\left\{\begin{array}{l}[4]\,OH\\ [3]\,OH\\ [2]\,OH\end{array}\right.\end{array}\right.$ |
| 124 | **Dianil Yellow.** [*M.*] | | | $P-N=N-CH{<}\begin{array}{l}CO\cdot CH_3\\ CO_2C_2H_5\end{array}$<br>[P = radicle of primuline or of dehydrothiotoluidine sulphonic acid.] |
| 125 | **Oriol Yellow.** [*G.*]<br>**Cotton Yellow R.** [*B.*]<br>**Alkali Yellow.** [*D.*] | Sodium salt of primuline-azo-salicylic acid. | | $P-N=N-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,OH\\ [2]\,CO_2Na\end{array}\right.$ |
| 126 | **Alkali Brown.** [*D.*]<br>**Benzo Brown 5 R.** [*By.*] | Sodium salt of primuline-azo-phenylene diamine. | | $P-N=N-C_6H_3(NH_2)_2\,[1:2:4]$ |
| 127 | **Atlas Red.** [*B.S.S.*] | Sodium salt of primuline-azo-tolylene diamine. | | $P-N=N-C_6H_2(CH_3)(NH_2)_2\,[1:3:4:6]$ |
| 128 | **Cotton Yellow G.** [*B.*] | Sodium salt of primuline-azo-*m*-phenylene-diamine-disulphonic acid. | | $P-N=N-[2]\,C_6H\left\{\begin{array}{l}[1]\,NH_2\\ [3]\,NH_2\\ [4]\,SO_3Na\\ [6]\,SO_3Na\end{array}\right.$ |
| 129 | **Clayton Cloth Red.** [*Cl. Co.*]<br>**Stanley Red.** [*Cl. Co.*] | Ammonium or sodium salt of sulphobenzenyl-amido-thiocresol-azo-β-naphthol. | $C_{24}H_{21}N_4O_4S_2$ | $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}[1]N\\ [2]S\end{array}\right>C[1]C_6H_4\left\{\begin{array}{l}SO_3NH_4\\ [4]N=N-[1]C_{10}H_6[2]OH\end{array}\right.\\ [4]CH_3\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| *m*-Amido-benzoic acid. | Diphenyl-amine. | 1884. | Rosenstiehl.<br>Soc. Anon. des Mat. Color. et des Produits Chim. de St. Denis.<br>Eng. Pat. $4621^{83}$.<br>Am. Pat. 157755.<br>Ger. Pat. $29991^{84}$. | **Appearance of dyestuff**: brown paste.—**In water**: slightly soluble. **On addition of hydrochloric acid to the aqueous solution**: reddish violet colour.—**On addition of caustic soda to the aqueous solution**: scarcely any change.—**In conc. sulphuric acid**: violet solution; magenta red on dilution.—**Employment in cotton printing**: orange with a chrome mordant. |
| *m*-Amido-benzoic acid. | Salicylic acid. | 1889. | R. Lauch & C. Krekeler.<br>Fr. Bayer & Co.<br>Eng. Pat. $8299^{89}$.<br>Ger. Pat. appl. F. 4438. | **Appearance of dyestuff**: grayish yellow paste.—**In water**: sparingly soluble with yellow colour, easily in presence of sodium carbonate or acetate.—**In conc. sulphuric acid**: reddish yellow solution, yellow gelatinous precipitate on dilution with water.—**Dyes**: chrome mordanted wool greenish yellow. |
| o-Amido-benzoic acid. | Salicylic acid. | 1889. | R. Lauch & C. Krekeler.<br>Fr. Bayer & Co.<br>Eng. Pat. $8299^{89}$.<br>Ger. Pat. appl. F. 4438. | **Appearance of dyestuff**: brown paste.—**In water**: sparingly soluble with yellow colour, easily in presence of sodium carbonate or acetate.—**In conc. sulphuric acid**: reddish yellow solution; brownish yellow precipitate on dilution with water.—**Dyes**: chrome mordanted wool reddish yellow. |
| *p*-Amido-phenol-*α*-di-sulphonic acid. | Pyrogallol. | 1893. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $11902^{93}$.<br>Am. Pat. 548460.<br>Ger. Pat. 81109.<br>Fr. Pat. 230937. | **Appearance of dyestuff**: dark brown powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: solution becomes reddish brown.—**In conc. sulphuric acid**: brown solution; brownish yellow on dilution.—**Dyes**: chromed wool brown.—**In cotton printing**: reddish brown with a chrome mordant. |
| Primuline or dehydrothio-*p*-toluidine-sulphonic acid. | Acetacetic ether. | 1898. | Scholl.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $17328^{97}$.<br>Am. Pat. 662056.<br>Ger. Pat. $98761^{97}$.<br>Fr. Pat. 256647 & 269001. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**In alcohol**: sparingly soluble.—**On addition of hydrochloric acid**: yellow precipitate.—**On addition of caustic soda**: brown precipitate.—**In conc. sulphuric acid**: brown solution; yellow precipitate on dilution.—**Dyes**: cotton moderately fast to light, washing, and acids. |
| Primuline or dehydrothio-*p*-toluidine-sulphonic acid. | Salicylic acid. | 1888. | J. R. Geigy & Co.<br>Am. Pat. $398990^{88}$.<br>Dahl & Co.<br>Ger. Pat. $48465^{88}$.<br>Fr. Pat. 192628. | **Appearance of dyestuff**: red powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: yellow precipitate.—**On addition of caustic soda**: the solution becomes rather redder.—**In conc. sulphuric acid**: scarlet red solution; on dilution brownish yellow precipitate.—**Dyes**: unmordanted cotton yellow from a boiling alkaline bath. |
| Primuline or dehydrothio-*p*-toluidine-sulphonic acid. | *m*-Phenylene diamine. | 1887. | A. G. Green.<br>Dahl & Co. | **Appearance of dyestuff**: dark brown powder.—**In water**: brownish red solution.—**In alcohol**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: dark brown precipitate.—**On addition of caustic soda to the aqueous solution**: red precipitate.—**In conc. sulphuric acid**: bluish violet solution; dark brown precipitate on dilution—**Dyes**: unmordanted cotton a reddish brown from an alkaline bath. |
| Primuline or dehydrothio-*p*-toluidine-sulphonic acid. | *m*-Tolylene diamine. | 1889. | A. G. Green.<br>Brooke, Simpson, & Spiller.<br>Eng. Pat. $10448^{90}$. | **Appearance of dyestuff**: dark red powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid**: dark precipitate.—**Dyes**: unmordanted cotton terra-cotta red from an alkaline bath. Gives deep ingrain brown shades by diazotisation and development on the fibre. |
| Primuline. | *m*-Phenylene-diamine-di-sulphonic acid. | 1893. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $14678^{93}$<br>Am. Pat. 524262.<br>Ger. Pat. $73369^{93}$.<br>Fr. Pat. $231694^{93}$. | **Appearance of dyestuff**: brown powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid**: reddish precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: brownish orange solution; reddish precipitate on dilution. **Dyes**: unmordanted cotton from a boiling bath orange yellow. |
| Dehydrothio-*p*-toluidine-sulphonic acid. | *β*-Naphthol. | 1887.<br>1889. | A. G. Green.<br>Ch. Dreyfus.<br>The Clayton Aniline Co.<br>Eng. Pat. $18901^{89}$.<br>J. Soc. Dyers and Colorists (1890), 32. | **Appearance of dyestuff**: dark red powder.—**In water**: reddish brown solution.—**On addition of hydrochloric acid to aqueous solution**: red precipitate.—**Dyes**: wool and silk red from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 130 | **Rosophenine 10 B.**<br>[*Cl. Co.*]<br>**Rosophenine Pink.**<br>[*Cl. Co.*] | Sodium salt of sulphobenzenyl-amido-thiocresol-azo-α-naphthol-sulphonic acid. | $C_{24}H_{16}N_3S_3O_7Na$ |  $C_6H_3\left\{\begin{matrix}\left.\begin{matrix}{[1]}N\\ {[2]}S\end{matrix}\right>C[1]C_6H_4\left\{\begin{matrix}SO_3Na\\ {[4]}N=N[2]C_{10}H_5\left\{\begin{matrix}{[1]}OH\\ {[4]}SO_3Na\end{matrix}\right.\end{matrix}\right.\\ {[4]}CH_3\end{matrix}\right.$ |
| 131 | **Chrome Fast Yellow G.**<br>[*A.*] | Sodium salt of diphenyl-phenotriazine-azo-salicylic-di-(and tri-) sulphonic acid. | | *Di- and tri-sulphonic acid of:*<br> |
| 132 | **Fast Sulphone Violet 5 BS.***<br>[*K. S.*] | | | A mono-azo compound, composition unknown. |

## III. DISAZO

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 133 | **Acid Brown R.**<br>[*A.*] | Sodium salt of *p*-sulphonaphthalene-azo-phenylene-diamine-azo-benzene. | $C_{22}H_{17}N_6O_3SNa$ |  $\left.\begin{matrix}C_{10}H_6\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N\end{matrix}\right.\\ C_6H_5-N=N\end{matrix}\right>C_6H_2\left\{\begin{matrix}{[1]}NH_2\\ {[3]}NH_2\end{matrix}\right.$ |
| 134 | **Leather Brown.**<br>[*O.*] | Hydrochloride of bi-*p*-amidobenzene-disazo-*m*-phenylene-diamine. | $C_{18}H_{19}N_8Cl$ |  $\left.\begin{matrix}C_6H_4\left\{\begin{matrix}{[4]}NH_2\\ {[1]}N=N\end{matrix}\right.\\ C_6H_4\left\{\begin{matrix}{[1]}N=N\\ {[4]}NH_2\end{matrix}\right.\end{matrix}\right>C_6H_2\left\{\begin{matrix}{[1]}NH_2HCl\\ {[3]}NH_2\end{matrix}\right.$ |
| 135 | **Terra Cotta F.**<br>[*G.*] | Sodium salt of primuline-azo-phenylene-diamine-azo-naphthalene-sulphonic acid. | |  $\left.\begin{matrix}P-N=N\\ C_{10}H_6(SO_3Na)-N=N\end{matrix}\right>C_6H_2(NH_2)_2$<br>[P = residue of primuline or dehydrothiotoluidine sulphonic acid.] |
| 136 | **Cotton Orange R.**<br>[*B.*] | Sodium salt of primuline-azo-disulpho-*m*-phenyl-ene-diamine-azo-benzene-*m*-sulphonic acid. | |  $\left.\begin{matrix}P-N=N\\ C_6H_4\left\{\begin{matrix}{[1]}N=N\\ {[3]}SO_3Na\end{matrix}\right.\end{matrix}\right>C_6(NH_2)_2(SO_3Na)_2$ |
| 137 | **Resorcin Brown.**<br>[*A.*] | Sodium salt of xylene-azo-resorcin-azo-benzene-*p*-sulphonic acid. | $C_{20}H_{17}N_4O_5SNa$ |  $C_6H_3\left\{\begin{matrix}(CH_3)_2\\ N=N-[2]C_6H_2\left\{\begin{matrix}{[1]}OH\\ {[3]}OH\\ {[4]}N=N-[1]C_6H_4[4]SO_3Na\end{matrix}\right.\end{matrix}\right.$ |
| 138 | **Fast Brown G.**<br>[*T. M.*]<br>**Acid Brown.**<br>[*D.*] | Sodium salt of bi-sulphobenzene-disazo-α-naphthol. | $C_{22}H_{14}N_4O_7S_2Na_2$ |  $\left.\begin{matrix}C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N[2]\end{matrix}\right.\\ C_6H_4\left\{\begin{matrix}{[1]}N=N[4]\\ {[4]}SO_3Na\end{matrix}\right.\end{matrix}\right\}C_{10}H_5[1]OH$ |

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* To the same class belong **Brilliant Sulphone Red B** [*K. S.*]

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Dehydrothio-*p*-toluidine-sulphonic acid. | *a*-Naphthol-sulphonic acid (1 : 4). | 1893. | A. G. Green.<br>The Clayton Aniline Co. | **Appearance of dyestuff**: dark red powder.—**In water**: crimson red colour.—**On addition of hydrochloric acid**: violet red precipitate.—**In conc. sulphuric acid**: violet red solution; violet red precipitate on dilution.—**Dyes**: unmordanted cotton direct, in pink to red shades, fast to acids. |
| Sulphonic acid (di- and tri-) of the triazine from chrysoïdine and benzaldehyde. | Salicylic acid. | 1895. | Nölting & Herzberg.<br>Compare Ber. **30**, 2598. | **Appearance of dyestuff**: orange yellow powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid**: yellow flocculent precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: orange yellow solution; lighter on dilution.—**Dyes**: chromed wool yellow. |
| | | 1899. | Böniger. | **In water**: very soluble to a violet solution.—**In alcohol**: easily soluble with a violet blue colour.—**On addition of hydrochloric acid**: brick red precipitate.—**On addition of caustic soda**: brownish red solution.—**In conc. sulphuric acid**: red solution; brick red precipitate on dilution.—**Dyes**: wool and silk from an acid bath, very level bright bluish violet shades, very fast to light, sulphur, and washing. |

## COLOURING MATTERS.

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Componnd from | Combined with | | | |
| Naphthionic acid. | Chrysoïdine. | 1882. | W. Wolff.<br>Actienges. f. Anilin-fabrikn.<br>Ger. Pat. 22714. | **Appearance of dyestuff**: brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: dull olive green solution; brown precipitate on dilution.—**Dyes**: wool brown from an acid bath. |
| Combination of 2 mols. of *p*-diazo-acetanilide with 1 mol. of *m*-phenylene-diamine and heating the product with conc. hydrochloric acid. | | 1890. | Chr. Rudolph & G. Palm.<br>K. Oehler.<br>Ger. Pat. $57429^{90}$. | **Appearance of dyestuff**: blackish powder.—**In water**: brown solution.—**On addition of hydrochloric acid**: the solution becomes yellower.—**On addition of caustic soda**: brown precipitate.—**In conc. sulphuric acid**: brown solution; yellowish brown on dilution.—**Dyes**: leather and jute brown. |
| Primuline and naphthionic acid. | *m*-Phenylene diamine. | 1890. | Joh. Walter.<br>J. R. Geigy & Co.<br>Eng. Pat. $1688^{90}$.<br>Am. Pat. $440288^{90}$.<br>Fr. Pat. $203439^{90}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: reddish violet solution; brown precipitate on dilution with water.—**Dyes**: unmordanted cotton brown from a neutral or alkaline bath. |
| Primuline and *m*-sulphanilic acid. | *m*-Phenylene diamine-di-sulphonic acid. | 1893. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $21753^{93}$.<br>Am. Pat. $524261^{94}$.<br>Ger. Pat. $76118^{93}$.<br>Fr. Pat. 231694. | **Appearance of dyestuff**: brown powder.—**In water**: orange red solution.—**On addition of hydrochloric acid**: reddish precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: bright red solution; reddish precipitate on dilution.—**Dyes**: unmordanted cotton orange from a boiling bath. |
| *m*-Xylidine and sulphanilic acid. | Resorcin. | 1881. | O. Wallach.<br>Actiengesellsch. f. Anil. Fabrikn.<br>Am. Pat. 269359.<br>Ger. Pat. $18861^{81}$. | **Appearance of dyestuff**: brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: scarcely any change.—**In conc. sulphuric acid**: brown solution; brown precipitate on dilution with water.—**Dyes**: wool brown from an acid bath. |
| 2 mols. of sulphanilic acid. | 1 mol. of *a*-naphthol. | 1882. | C. Krohn.<br>Ber. (1888) 21, 3241. | **Appearance of dyestuff**: brown powder.—**In water**: reddish brown solution.—**On addition of hydrochloric acid to aqueous solution**: violet precipitate.—**On addition of caustic soda to aqueous solution**: cherry red colour.—**In conc. sulphuric acid**: violet solution; yellowish brown on dilution.—**Dyes**: wool brown from an acid bath. |

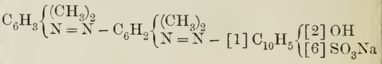
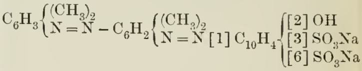
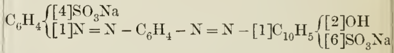
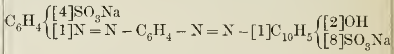
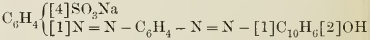
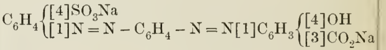
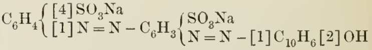
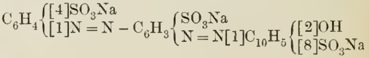
**and Fast Sulphone Violet 4 R** [*K. S*].

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 139 | **Fast Brown.** [*By.*] | Sodium salt of bi-sulphonaphthalene-disazo-resorcinol. | $C_{26}H_{16}N_4O_8S_2Na_2$ | $\left.\begin{array}{l}C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N\,[2]\end{array}\right.\\ C_{10}H_6\left\{\begin{array}{l}{[1]}\,N=N\,[4]\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right\}C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right.$ |
| 140 | **Fast Brown ONT yellow shade.** [*M.*] | Sodium salt of bi-sulpho-xylene-disazo-α-naphthol. | $C_{26}H_{22}N_4S_2O_7Na_2$ | $\left.\begin{array}{l}C_6H_2(CH_3)_2(SO_3Na)-N=N\,[2]\\ C_6H_2(CH_3)_2(SO_3Na)-N=N\,[4]\end{array}\right\}C_{10}H_5\,[1]\,OH$ |
| 141 | **Palatine Black.** [*B.*]<br>**Wool Black 4 B & 6 B.** [*A.*] | Sodium salt of *p*-sulpho-benzene-azo-disulpho-amido-naphthol-azo-naphthalene. | $C_{26}H_{16}N_5S_3O_{10}Na_2$ | $\left.\begin{array}{l}C_6H_4\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,N=N\,[2]\end{array}\right.\\ C_{10}H_7\,[\alpha]\,N=N\,[7]\end{array}\right\}C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.$ |
| 142 | **Naphthol Blue Black.** [*C.*]<br>**Naphthol Black 12 B.** | Sodium salt of *p*-nitro-benzene-azo-disulpho-amido-naphthol-azo-benzene. | $C_{22}H_{14}N_6O_9S_2Na_2$ | $\left.\begin{array}{l}C_6H_4\left\{\begin{array}{l}{[4]}\,NO_2\\ {[1]}\,-N=N\,[2]\end{array}\right.\\ C_6H_5-N=N\,[7]\end{array}\right\}C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.$ |
| 143 | **Sudan III.** [*A.*] [*Ib.*] [*Fi.*]<br>**Cerasine Red.** [*C.*] | Benzene-azo-benzene-azo-β-naphthol. | $C_{22}H_{16}N_4O$ | $C_6H_5-N=N-C_6H_4-N=N-C_{10}H_6\cdot OH\beta$ |
| 144 | **Cloth Red G.** [*By.*]<br>**Cloth Red R.** [*D.*]<br>**Fast Red 7 B.** [*N. I.*] | Sodium salt of benzene-azo-benzene-azo-α-naphthol-*p*-sulphonic acid. | $C_{22}H_{15}N_4O_4SNa$ | $C_6H_5-N=N-C_6H_4-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right.$ |
| 145 | **Croceïne B.** [*Sch.*] | Sodium salt of benzene-azo-benzene-azo-α-naphthol-disulphonic acid. | $C_{22}H_{14}N_4O_7S_2Na_2$ | $C_6H_5-N=N-C_6H_4-N=N-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\\ {[8]}\,SO_3Na\end{array}\right.$ |
| 146 | **Brilliant Croceïne M.** [*C.*] [*By.*] [*M.*]<br>**Cotton Scarlet.** [*B.*]<br>**Cotton Scarlet 3 B conc.** [*K.*]<br>**Ponceau BO extra.** [*A.*] | Sodium salt of benzene-azo-benzene-azo-β-naphthol-disulphonic acid. | $C_{22}H_{14}N_4O_7S_2Na_2$ | $C_6H_5-N=N-C_6H_4-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[6]}\,SO_3Na\\ {[8]}\,SO_3Na\end{array}\right.$ |
| 147 | **Ponceau S S extra.** [*A.*] | Sodium salt of benzene-azo-benzene-azo-β-naphthol-disulphonic acid. | $C_{22}H_{14}N_4O_7S_2Na_2$ | $C_6H_5-N=N-C_6H_4-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| 2 mols. of naphthionic acid. | 1 mol. resorcinol. | 1881. | Wallach.<br>Actiengesellsch. f. Anil. Fabrikn.<br>Ger. Pat. 18861. | **Appearance of dyestuff**: brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid**: red brown soluble precipitate.—**On addition of caustic soda**: cherry red solution.—**In conc. sulphuric acid**: currant red.—**Dyes**: wool brown from an acid bath, fast to light and alkalies. |
| 2 mols. of xylidine sulphonic acid. | 1 mol. of α-naphthol. | 1879. | Limpach. | **Appearance of dyestuff**: dark brown powder.—**In water**: brown solution.—**In alcohol**: ruby red solution.—**On addition of hydrochloric acid to aqueous solution**: violet red precipitate.—**On addition of caustic soda**: reddish yellow solution.—**In conc. sulphuric acid**: violet solution; red on dilution.—**Dyes**: wool and silk fairly level shades of brownish red; also employed for lakes. |
| 1 mol. sulphanilic acid (in acid solution) and 1 mol. α-naphthylamine (in alkaline solution). | 1 mol. 1 : 8-amido-naphthol-disulphonic acid H. | 1891. | Bülow.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $7713^{91}$.<br>Am. Pat. 590088.<br>Ger. Pat. $91855^{91}$.<br>Fr. Pat. 213232. | **Appearance of dyestuff**: brownish bronzy powder.—**In water**: dark blue solution.—**On addition of hydrochloric acid**: solution becomes bluish green.—**On addition of caustic soda**: solution becomes pure blue.—**In conc. sulphuric acid**: blue solution; granular blue precipitate on dilution.—**Dyes**: wool and silk black. |
| 1 mol. *p*-nitraniline (in acid solution) and 1 mol. aniline (in alkaline solution). | 1 mol. (1 : 8)-amido-naphthol-di-sulphonic acid H. | 1891. | M. Hoffmann.<br>L. Cassella & Co.<br>Eng. Pat. $6972^{91}$. | **Appearance of dyestuff**: dark powder.—**In water**: dark blue solution.—**In alcohol**: tolerably soluble.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**On addition of caustic soda**: no change.—**After reduction with zinc dust**: the colour returns on paper.—**In conc. sulphuric acid**: green solution: blue precipitate on dilution.—**Dyes**: wool a fast black from an alkaline bath. |
| Amido-azo-benzene. | β-Naphthol. | 1879. | Fr. Graessler.<br>Ger. Pat. $16483^{79}$.<br>R. Nietzki.<br>Ber. (1880) 13, 1838. | **Appearance of dyestuff**: brown powder.—**In water**: insoluble.—**In conc. sulphuric acid**: bluish green solution; on dilution with water blue solution and then a red precipitate.—**In alcohol**: red solution.—**Employment**: for colouring oils, varnishes, etc. |
| Amido-azo-benzene. | α-Naphthol-monosulphonic acid NW. | 1883. | O. N. Witt.<br>Verein Chem. Fabriken.<br>Eng. Pat. $2237^{83}$.<br>Ger. Pat. $26012^{83}$. | **Appearance of dyestuff**: brown powder.—**In water**: sparingly soluble with magenta red colour.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate.—**On addition of caustic soda to the aqueous solution**: reddish violet precipitate soluble in water.—**In conc. sulphuric acid**: bluish violet solution; brownish red precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| Amido-azo-benzene. | α-Naphthol-disulphonic acid Sch. | 1884. | Mensching.<br>The Schöllkopf Anil. & Chem. Co.<br>Eng. Pats. $15775^{85}$ and $15781^{85}$.<br>Am. Pat. 333037.<br>Ger. Pat. $40571^{85}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: sparingly soluble with magenta red colour.—**On addition of hydrochloric acid to aqueous solution**: violet precipitate.—**On addition of caustic soda**: solution violet.—**In conc. sulphuric acid**: violet solution; reddish violet precipitate on dilution.—**Dyes**: wool red from an acid bath. |
| Amido-azo-benzene. | β-Naphthol-disulphonic acid G (γ). | 1882.<br>1883. | L. Limpach.<br>Meinhard Hoffman.<br>Meister, Lucius, and Brüning.<br>Ger. Pat. 36491.<br>L. Cassella & Co.<br>Eng. Pat. $816^{84}$.<br>Am. Pat. $314939^{85}$.<br>Fr. Pat. 159998. | **Appearance of dyestuff**: light brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: brown solution.—**In conc. sulphuric acid**: reddish violet solution; on dilution with water, blue and then a brown precipitate.—**Dyes**: wool and silk red from an acid bath, fast to light and acids but not to washing. Also employed in paper staining and in the preparation of lakes. |
| Amido-azo-benzene. | β-Naphthol-disulphonic acid R. | 1879. | Fr. Bayer & Co.<br>Eng. Pats. $5003^{79}$ & $536^{80}$.<br>Am. Pat. 233465.<br>Ger. Pat. $16482^{79}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**On addition of caustic soda**: solution becomes reddish violet.—**In conc. sulphuric acid**: violet solution; violet precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 148 | **Ponceau 5 R.** [*M.*]<br>**Erythrine X.** [*B.*] | Sodium salt of benzene-azo-benzene-azo-β-naphthol-trisulphonic acid. | $C_{22}H_{13}N_4O_{10}S_3Na_3$ | $C_6H_5-N=N-C_6H_4-N=N-C_{10}H_3\left\{\begin{matrix}OH\beta\\(SO_3Na)_3\end{matrix}\right.$ |
| 149 | **Janus Red.**<br>[*M.*] | Chloride of trimethyl-amido-benzene-azo-*m*-toluene-azo-β-naphthol. | $C_{26}H_{26}N_5OCl$ | $C_6H_4\left\{\begin{matrix}[3]\,N(CH_3)_3Cl\\ [1]\,N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-C_{10}H_6\cdot OH\beta\end{matrix}\right.\end{matrix}\right.$ |
| 150 | **Oil Scarlet.**<br>[*M.*] [*K.*] [*W.*]<br>**Red B oil-soluble extra conc.**<br>[*Remy.*]<br>**Ponceau 3 B.** [*C. J.*] | Toluene-azo-toluene-azo-β-naphthol. | $C_{24}H_{20}N_4O$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-[1]\,C_{10}H_6[2]\,OH\end{matrix}\right.\end{matrix}\right.$ |
| 151 | **Croceïne 3 B.**<br>[*Sch.*] | Sodium salt of toluene-azo-toluene-azo-α-naphthol-disulphonic acid. | $C_{24}H_{18}N_4O_7S_2Na_2$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-C_{10}H_4\left\{\begin{matrix}OH\alpha\\(SO_3Na)_2\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 152 | **Cloth Red B.**<br>[*By.*] [*D.*] | Sodium salt of toluene-azo-toluene-azo-α-naphthol-monosulphonic acid. | $C_{24}H_{19}N_4O_4SNa$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-[2]\,C_{10}H_5\left\{\begin{matrix}[1]\,OH\\ [4]\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 153 | **Cloth Red G.** [*O.*]<br>**Cloth Red G extra.**<br>[*By.*] | Sodium salt of toluene-azo-toluene-azo-β-naphthol-monosulphonic acid. | $C_{24}H_{19}N_4O_4SNa$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-[1]\,C_{10}H_5\left\{\begin{matrix}[2]\,OH\\ [6]\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 154 | **Cloth Red B.** [*O.*]<br>**Cloth Red O.** [*M.*]<br>**Fast Bordeaux O.**<br>[*M.*]<br>**Cloth Red BA.** [*A.*]<br>**Fast Milling Red B.** [*Lev.*] | Sodium salt of toluene-azo-toluene-azo-β-naphthol-disulphonic acid. | $C_{24}H_{18}N_4O_7S_2Na_2$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-[1]\,C_{10}H_4\left\{\begin{matrix}[2]\,OH\\ [3]\,SO_3Na\\ [6]\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 155 | **Cloth Red 3 G extra.** [*By.*]<br>**Cloth Red 3 GA.**<br>[*A.*] | Sodium salt of toluene-azo-toluene-azo-β-naphthylamine-monosulphonic acid. | $C_{24}H_{20}N_5O_3SNa$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-[1]\,C_{10}H_5\left\{\begin{matrix}[2]\,NH_2\\ [6]\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 156 | **Cloth Red 3 B extra.** [*By.*] | Sodium salt of toluene-azo-toluene-azo-ethyl-β-naphthylamine sulphonic acid. | $C_{26}H_{24}N_5SO_3Na$ | $C_6H_4\left\{\begin{matrix}CH_3\\ N=N-C_6H_3\left\{\begin{matrix}CH_3\\ N=N-C_{10}H_5\left\{\begin{matrix}NH(C_2H_5)\\ SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Amido-azo-benzene. | $\beta$-Naphthol-trisulphonic acid. | 1881. | L. LIMPACH.<br>MEISTER, LUCIUS, and BRÜNING.<br>Eng. Pat. $2544^{82}$ (lapsed).<br>Am. Pat. 268507.<br>Ger. Pat. $22038^{82}$. | **Appearance of dyestuff**: brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown flocculent precipitate.—**On addition of caustic soda**: solution becomes brown.—**In conc. sulphuric acid**: reddish violet solution, becoming first blue and then red on dilution with water.—**Dyes**: wool bluish red from an acid bath. |
| *m*-Amido-phenyl-trimethyl ammonium chloride (diazotised) + *m*-toluidine. | $\beta$-Naphthol. | 1896. | KÖNIG.<br>MEISTER, LUCIUS, & BRÜNING.<br>*Dyeing process:*<br>Eng. Pat. $5119^{97}$ &<br>Fr. Pat. 264579.<br>Jour. Soc. Dyers, 1898, 222. | **Appearance of dyestuff**: red brown powder.—**In water**: red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to aqueous solution**: brownish red flocculent precipitate.—**On addition of caustic soda**: bluish violet precipitate.—**In conc. sulphuric acid**: green solution; red precipitate on dilution.—**Dyes**: cotton direct from an acid bath, and is employed for one-bath dyeing of mixed cotton and wool. |
| *o*-Amido-azo-toluene. | $\beta$-Naphthol. | | | **Appearance of dyestuff**: dark reddish brown powder.—**In water**: insoluble.—**In alcohol or benzene**: bluish red solution.—**On addition of caustic soda to alcoholic solution**: reddish violet colour.—**In conc. sulphuric acid**: blue solution; red precipitate on dilution.—**Employment**: for colouring oils and varnishes. Also produced as an insoluble colour upon the cotton fibre ("FAST AZO GARNET"). |
| Amido-azo-toluene. | $\alpha$-Naphthol-disulphonic acid Sch. | 1884. | MENSCHING.<br>THE SCHÖLLKOPF ANIL. & CHEM. CO.<br>Eng. Pats. $15775^{85}$ & $15781^{85}$.<br>Am. Pat. 333037.<br>Ger. Pat. $40571^{85}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**On addition of caustic soda**: solution becomes violet.—**In conc. sulphuric acid**: blue solution; on dilution with water, first a violet precipitate then a red solution.—**Dyes**: wool red from an acid bath. |
| Amido-azo-toluene. | $\alpha$-Naphthol-monosulphonic acid NW. | 1879. | K. OEHLER.<br>FR. BAYER & CO.<br>Ger. Pat. $16482^{79}$.<br>Eng. Pat. $5003^{79}$. | **Appearance of dyestuff**: dark brownish red powder.—**In water**: red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: red precipitate.—**On addition of caustic soda**: solution becomes violet.—**In conc. sulphuric acid**: blackish blue solution.—**Dyes**: chromed wool red. |
| Amido-azo-toluene. | $\beta$-Naphthol-monosulphonic acid S. | 1879. | K. OEHLER.<br>Ger. Pat. $16482^{79}$.<br>FR. BAYER & CO.<br>Eng. Pat. $5003^{79}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: sparingly soluble, with a brownish red colour.—**On addition of hydrochloric acid to aqueous solution**: brownish red precipitate.—**In conc. sulphuric acid**: blue solution; brownish red precipitate on dilution.—**Dyes**: chromed wool dark red from an acid bath. |
| Amido-azo-toluene. | $\beta$-Naphthol-disulphonic acid R. | 1879. | K. OEHLER.<br>Ger. Pat. $16482^{79}$.<br>FR. BAYER & CO.<br>Eng. Pats. $5003^{79}$ & $536^{80}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid**: the solution becomes browner.—**In conc. sulphuric acid**: blue solution; brownish red precipitate on dilution.—**Dyes**: chromed wool brownish red from an acid bath. Fast to washing and very fast to light. |
| Amido-azo-toluene. | $\beta$-Naphthyl-amine-sulphonic acid Br. | 1888. | C. DUISBERG. | **Appearance of dyestuff**: brownish red powder.—**In water**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: dark reddish brown precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: dark greenish blue solution; brownish red precipitate on dilution with water.—**Dyes**: chromed wool red. |
| Amido-azo-toluene. | Ethyl-$\beta$-naphthyl-amine-sulphonic acid $\delta$. | 1886. | HASSENCAMP & DUISBERG. | **Appearance of dyestuff**: dark brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid**: dull brown precipitate, greenish blue colour with large excess.—**In conc. sulphuric acid**: greenish blue solution; dull red precipitate on dilution.—**Dyes**: wool and silk bluish red from acid bath or upon chrome bottom. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 157 | **Bordeaux BX.** [*By.*] | Sodium salt of xylene-azo-xylene-azo-β-naphthol-β-monosulphonic acid. | $C_{26}H_{23}N_4O_4SNa$ |  $C_6H_3\left\{\begin{matrix}(CH_3)_2\\ N=N-C_6H_2\left\{\begin{matrix}(CH_3)_2\\ N=N-[1]\,C_{10}H_5\left\{\begin{matrix}{[2]}\,OH\\ {[6]}\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 158 | **Orchil Red A.** [*B.*]<br>**Union Fast Claret.** [*Lev.*] | Sodium salt of xylene-azo-xylene-azo-β-naphthol-disulphonic acid. | $C_{26}H_{22}N_4O_7S_2Na_2$ |  $C_6H_3\left\{\begin{matrix}(CH_3)_2\\ N=N-C_6H_2\left\{\begin{matrix}(CH_3)_2\\ N=N\,[1]\,C_{10}H_4\left\{\begin{matrix}{[2]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |
| 159 | **Fast Scarlet B.** [*K.*] | Sodium salt of sulphobenzene-azo-benzene-azo-β-naphthol-mono-sulphonic acid. | $C_{22}H_{14}N_4O_7S_2Na_2$ |  $C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N-C_6H_4-N=N-[1]C_{10}H_5\left\{\begin{matrix}{[2]}OH\\ {[6]}SO_3Na\end{matrix}\right.\end{matrix}\right.$ |
| 160 | **Croceïne Scarlet*** **3 B.** [*By.*]<br>**Ponceau 4 RB.** [*A.*] | Sodium salt of sulphobenzene-azo-benzene-azo-β-naphthol-mono-sulphonic acid. | $C_{22}H_{14}N_4O_7S_2Na_2$ |  $C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N-C_6H_4-N=N-[1]C_{10}H_5\left\{\begin{matrix}{[2]}OH\\ {[8]}SO_3Na\end{matrix}\right.\end{matrix}\right.$ |
| 161 | **Cloth Scarlet G.** [*K.*] | Sodium salt of sulphobenzene-azo-benzene-azo-β-naphthol. | $C_{22}H_{15}N_4O_4SNa$ |  $C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N-C_6H_4-N=N-[1]C_{10}H_6[2]OH\end{matrix}\right.$ |
| 162 | **Milling Orange.** [*D.*] | Sodium salt of sulphobenzene-azo-benzene-azo-salicylic acid. | $C_{19}H_{12}N_4SO_6Na_2$ |  $C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N-C_6H_4-N=N[1]C_6H_3\left\{\begin{matrix}{[4]}OH\\ {[3]}CO_2Na\end{matrix}\right.\end{matrix}\right.$ |
| 163 | **Biebrich Scarlet.**<br>**Ponceau 3 RB.** [*A.*]<br>**Ponceau B.** [*M.*]<br>**Fast Ponceau B.** [*B.*]<br>**New Red L.** [*K.*]<br>**Imperial Scarlet.** [*By.*] | Sodium salt of sulphobenzene-azo-sulphobenzene-azo-β-naphthol. | $C_{22}H_{14}N_4O_7S_2Na_2$ |  $C_6H_4\left\{\begin{matrix}{[4]}\,SO_3Na\\ {[1]}\,N=N-C_6H_3\left\{\begin{matrix}SO_3Na\\ N=N-[1]\,C_{10}H_6\,[2]\,OH\end{matrix}\right.\end{matrix}\right.$ |
| 164 | **Croceïne Scarlet O extra.** [*K.*] | Sodium salt of sulphobenzene-azo-sulphobenzene-azo-β-naphthol-sulphonic acid. | $C_{22}H_{13}N_4S_3O_{10}Na_3$ |  $C_6H_4\left\{\begin{matrix}{[4]}SO_3Na\\ {[1]}N=N-C_6H_3\left\{\begin{matrix}SO_3Na\\ N=N[1]C_{10}H_5\left\{\begin{matrix}{[2]}OH\\ {[8]}SO_3Na\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.$ |

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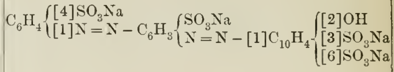
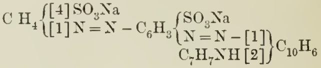
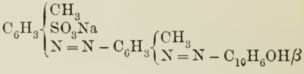
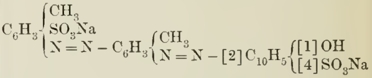
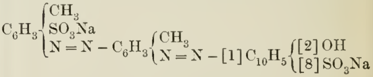
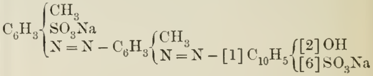
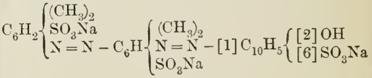
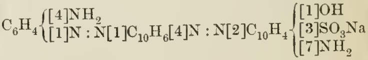
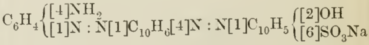
* Croceïne Scarlets R, B, and 2 B are mixtures

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Amido-azo-xylene. | β-Naphthol-monosulphonic acid S. | 1879. | Rübel.<br>Fr. Bayer & Co.<br>Eng. Pat. $5003^{79}$.<br>R. Krügener.<br>Ger. Pat. $16482^{79}$. | **Appearance of dyestuff**: greenish brown powder.—**In water**: brownish red solution.—**In alcohol**: bordeaux red solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate.—**On addition of caustic soda to the conc. aqueous solution**: brownish red precipitate.—**In conc. sulphuric acid**: brown solution; reddish brown precipitate on dilution with water.—**Dyes**: wool red from an acid bath. |
| Amido-azo-xylene. | β-Naphthol-disulphonic acid R. | 1879.<br>1880. | L. Limpach.<br>Meister, Lucius, & Brüning.<br>Eng. Pats. $5003^{79}$; $5021^{79}$; $536^{80}$.<br>Ger. Pat. $22010^{82}$; add. to $16482^{79}$.<br>Schuncke.<br>Am. Pat. 246221.<br>Badische Anil. & Soda Fabrik. | **Appearance of dyestuff**: dark brown powder.—**In water**: bluish red solution.—**On addition of hydrochloric acid to aqueous solution**: brownish red flocks.—**On addition of caustic soda to aqueous solution**: brown precipitate.—**In conc. sulphuric acid**: dark blue solution; reddish brown flocks on dilution with water.—**Dyes**: wool archil red from an acid bath. Fast to light and washing, fairly fast to acids and alkalies. |
| Amido-azo-benzene-monosulphonic acid. | β-Naphthol-sulphonic acid S. | 1879. | R. Nietzki. | **Appearance of dyestuff**; reddish brown powder.—**In water**: ponceau red solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: red violet solution.—**In conc. sulphuric acid**: blue solution; on dilution with water becomes red.—**Dyes**: wool scarlet from an acid bath. |
| Amido-azo-benzene-monosulphonic acid. | β-Naphthol-monosulphonic acid B. | 1881. | E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pats. $1225^{81}$; $2030^{81}$; $2411^{83}$; $8390^{84}$.<br>Am. Pat. 256381.<br>Ger. Pat. $18027^{81}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: scarlet red solution.—**On addition of hydrochloric acid to aqueous solution**: yellowish brown flocculent precipitate.—**On addition of caustic soda to the aqueous solution**: dull violet red colour.—**In conc. sulphuric acid**: pure blue solution; on dilution a yellowish brown precipitate, then a red solution.—**Dyes**: wool scarlet from an acid bath, cotton from an alum bath. |
| Amido-azo-benzene-sulphonic acid. | β-Naphthol. | 1878.<br>1878. | R. Nietzki.<br>R. Krügener.<br>Eng. Pat. $5003^{79}$.<br>Ger. Pat. $16482^{79}$. | **Appearance of dyestuff**: reddish brown crystalline powder.—**In water**: scarlet solution.—**On addition of hydrochloric acid**: yellower; when concentrated a light red flocculent precipitate.—**On addition of caustic soda**: brown flocks.—**In conc. sulphuric acid**: green solution; on dilution becomes blue red and finally scarlet.—**Dyes**: wool red from an acid bath or upon a chrome bottom. Very fast to washing. |
| Amido-azo-benzene-sulphonic acid. | Salicylic acid. | | | **Appearance of dyestuff**: red brown powder.—**In water**: orange red solution.—**On addition of hydrochloric acid**: grayish yellow gelatinous precipitate.—**On addition of caustic soda**: dark red solution and precipitate.—**In conc. sulphuric acid**: violet solution; grayish yellow precipitate on dilution.—**Dyes**: chrome wool from an acid bath orange red, fast to acids, alkalies, and light. |
| Amido-azo-benzene-disulphonic acid. | β-Naphthol. | 1878. | R. Nietzki.<br>Ber. (1880) **13**, 800, 1838.<br>R. Krügener.<br>Eng. Pats. $5003^{79}$ and $529^{80}$.<br>Ger. Pat. $16482^{79}$.<br>W. v. Miller.<br>Ber. (1880) **13**, 542, 803, 980.<br>Köhler.<br>Bad. Anil. & Soda Fabrik.<br>Am. Pats. $224927^{80}$ & $224928^{80}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: orange red solution.—**On addition of hydrochloric acid**: red flocks if the solution is strong.—**On addition of caustic soda to the aqueous solution**: brownish red precipitate.—**In conc. sulphuric acid**: green solution; on dilution with water, a blue solution and finally brownish red flocks.—**Dyes**: wool scarlet from an acid bath; fast to washing, acids, and alkalies, tolerably fast to light but not to stoving. Employed in preparation of lake colours. |
| Amido-azo-benzene-disulphonic acid. | β-Naphthol-monosulphonic acid B. | 1888. | Reinhardt. | **Appearance of dyestuff**: scarlet red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid or caustic soda**: violet coloration.—**In conc. sulphuric acid**: blue solution; on dilution yellowish red.—**Dyes**: wool and silk scarlet red. |

of 3 B with the oranges 5 B, 3 B, and 7 B.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 165 | **Fast Ponceau 2 B.** [*B.*] | Sodium salt of sulphobenzene-azo-sulphobenzene-azo-β-naphthol-disulphonic acid. | $C_{22}H_{12}N_4O_{13}S_4Na_4$ |  $C_6H_4\left\{\begin{array}{l}[4]SO_3Na\\ [1]N=N-C_6H_3\left\{\begin{array}{l}SO_3Na\\ N=N-[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ [3]SO_3Na\\ [6]SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 166 | **Wool Black.** [*A.*] [*B.*] | Sodium salt of sulphobenzene-azo-sulphobenzene-azo-*p*-tolyl-β-naphthylamine. | $C_{29}H_{21}N_5O_6S_2Na_2$ |  $C\,H_4\left\{\begin{array}{l}[4]SO_3Na\\ [1]N=N-C_6H_3\left\{\begin{array}{l}SO_3Na\\ \left.\begin{array}{r}N=N-[1]\\ C_7H_7NH\,[2]\end{array}\right\}C_{10}H_6\end{array}\right.\end{array}\right.$ |
| 167 | **Cloth Scarlet R.** [*K.*] | Sodium salt of sulphotoluene-azo-toluene-β-naphthol. | $C_{24}H_{19}N_4SO_4Na$ |  $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3Na\\ N=N-C_6H_3\left\{\begin{array}{l}CH_3\\ N=N-C_{10}H_6OH\beta\end{array}\right.\end{array}\right.$ |
| 168 | **Orseilline BB.** [*By.*] | Sodium salt of sulphotoluene-azo-toluene-azo-α-naphthol-*p*-sulphonic acid. | $C_{24}H_{18}N_4O_7S_2Na_2$ |  $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3Na\\ N=N-C_6H_3\left\{\begin{array}{l}CH_3\\ N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,OH\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 169 | **Croceïne Scarlet 7 B.**<br>**Ponceau 6 RB.** [*A.*]<br>**Croceïne Scarlet 8 B.** [*K.*] [*By.*] | Sodium salt of sulphotoluene-azo-toluene-azo-β-naphthol-α-sulphonic acid. | $C_{24}H_{18}N_4O_7S_2Na_2$ |  $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3Na\\ N=N-C_6H_3\left\{\begin{array}{l}CH_3\\ N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,OH\\ [8]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 170 | **Bordeaux G.** [*By.*] | Sodium salt of sulphotoluene-azo-toluene-azo-β-naphthol-β-sulphonic acid. | $C_{24}H_{18}N_4O_7S_2Na_2$ |  $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3Na\\ N=N-C_6H_3\left\{\begin{array}{l}CH_3\\ N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,OH\\ [6]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 171 | **Bordeaux BX.** [*By.*] | Sodium salt of sulphoxylene-azo-xylene-azo-β-naphthol-β-sulphonic acid. | $C_{26}H_{22}N_4O_7S_2Na_2$ |  $C_6H_2\left\{\begin{array}{l}(CH_3)_2\\ SO_3Na\\ N=N-C_6H\left\{\begin{array}{l}(CH_3)_2\\ N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,OH\\ [6]\,SO_3Na\end{array}\right.\\ SO_3Na\end{array}\right.\end{array}\right.$ |
| 172 | **Nyanza Black B.** [*A.*] | Sodium salt of amidobenzene-azo-naphthalene-azo-γ-amidonaphthol-sulphonic acid. | $C_{26}H_{19}N_6SO_4Na$ |  $C_6H_4\left\{\begin{array}{l}[4]NH_2\\ [1]N:N[1]C_{10}H_6[4]N:N[2]C_{10}H_4\left\{\begin{array}{l}[1]OH\\ [3]SO_3Na\\ [7]NH_2\end{array}\right.\end{array}\right.$ |
| 173 | **Coomassie Wool Black R.** [*Lev.*] | Sodium salt of amidobenzene-azo-naphthalene-azo-β-naphtholmono-sulphonic acid S. | $C_{26}H_{18}N_5SO_4Na$ |  $C_6H_4\left\{\begin{array}{l}[4]NH_2\\ [1]N:N[1]C_{10}H_6[4]N:N[1]C_{10}H_5\left\{\begin{array}{l}[2]OH\\ [6]SO_3Na\end{array}\right.\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Amidoazo-benzene-disulphonic acid. | *β*-Naphthol-disulphonic acid R. | 1880. | S. Pfaff.<br>W. v. Miller.<br>Ber. (1880) **13**, 542, 803.<br>Chem. Ind. (1880) **3**, 173, 203.<br>R. Nietzki.<br>Ber. (1880) **13**, 980, 1838.<br>Chem. Ind. (1880) **3**, 203, 388. | **Appearance of dyestuff:** brown powder.—**In water:** magenta red solution.—**On addition of hydrochloric acid to aqueous solution:** scarcely any change.—**On addition of caustic soda:** violet precipitate if the solution is strong.—**In conc. sulphuric acid:** blue solution; orange red on dilution with water.—**Dyes:** wool scarlet from an acid bath. |
| Amidoazo-benzene-disulphonic acid. | *p*-Tolyl-*β*-naphthylamine. | 1885. | L. Schad.<br>Actiengesellsch. f. Anil. Fabrikn.<br>Eng. Pat. 9754$^{86}$.<br>Am. Pat. 354746.<br>Ger. Pat. 38425$^{86}$. | **Appearance of dyestuff:** bluish black powder.—**In water:** violet solution.—**On addition of hydrochloric acid to the aqueous solution:** reddish violet precipitate.—**On addition of caustic soda:** violet precipitate.—**In conc. sulphuric acid:** blue solution; on dilution with water, brown precipitate; on boiling, decomposition with formation of tolunaphthazine and amidoazobenzene-disulphonic acid.—**Dyes:** wool bluish black from an acid bath. |
| Amidoazo-toluene-sulphonic acid. | *β*-Naphthol. | 1878. | R. Nietzki.<br>Krügener.<br>Ger. Pat. 16482. | **Appearance of dyestuff:** dark brown paste.—**In water:** red solution. **On addition of hydrochloric acid:** red precipitate.—**On addition of caustic soda:** yellowish brown precipitate.—**In conc. sulphuric acid:** green solution; on dilution blue and finally red.—**Dyes:** chromed wool and silk red from a neutral bath. |
| Amidoazo-toluene-monosulphonic acid. | *α*-Naphthol-monosulphonic acid NW. | 1883. | Verein Chem. Fabriken.<br>Eng. Pats. 2237$^{83}$ and 4237$^{83}$.<br>Ger. Pat. 26012$^{83}$. | **Appearance of dyestuff:** brown powder.—**In water:** magenta red solution.—**On addition of caustic soda:** solution becomes yellower.—**On addition of hydrochloric acid:** solution becomes reddish violet.—**In conc. sulphuric acid:** blue solution; magenta red on dilution.—**Dyes:** wool archil red from an acid bath. |
| Amidoazo-toluene-monosulphonic acid. | *β*-Naphthol-monosulphonic acid B. | 1881. | E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pats. 1225$^{81}$, 2030$^{81}$, 2411$^{83}$.<br>Am. Pat. 256375.<br>Ger. Pat. 18027$^{81}$. | **Appearance of dyestuff:** reddish brown powder.—**In water:** scarlet red solution.—**On addition of hydrochloric acid:** magenta red coloration and precipitate.—**On addition of caustic soda to aqueous solution:** dirty violet coloration and (if strong) precipitate.—**In conc. sulphuric acid:** blue solution; violet red on dilution.—**Dyes:** wool red from an acid bath. |
| Amidoazo-toluene-monosulphonic acid. | *β*-Naphthol-monosulphonic acid S. | 1879. | E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pat. 5003$^{79}$. | **Appearance of dyestuff:** brownish red powder.—**In water:** red solution.—**In alcohol:** slightly soluble.—**On addition of hydrochloric acid to the aqueous solution:** red precipitate.—**On addition of caustic soda:** solution becomes violet.—**In conc. sulphuric acid:** dark blue solution; red precipitate on dilution with water.—**Dyes:** wool red from an acid bath. |
| Amidoazo-xylene-disulphonic acid. | *β*-Naphthol-monosulphonic acid S. | 1879. | E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pat. 5003$^{79}$. | **Appearance of dyestuff:** dark brown powder.—**In water or alcohol:** red solution.—**On addition of hydrochloric acid to the aqueous solution:** dark reddish brown precipitate.—**On addition of caustic soda:** solution slightly browner.—**In conc. sulphuric acid:** dark green solution; blue solution and then brownish red precipitate on dilution with water.—**Dyes:** wool red from an acid bath. |
| *p*-Amido-benzene-azo-*α*-naphthylamine. | *γ*-Amido-naphthol-sulphonic acid. | 1892. | Diehl.<br>Berlin Aniline Co.<br>Eng. Pats. 227$^{92}$ & 6630$^{92}$.<br>Am. Pat. 491410.<br>Ger. Pat. 72394$^{92}$.<br>Fr. Pat. 221378.<br>L. Paul.<br>J. Soc. Chem. Ind. 1896, 707. | **Appearance of dyestuff:** brownish black powder.—**In water:** dark violet solution.—**On addition of hydrochloric acid:** dark violet precipitate.—**On addition of caustic soda.** soluble violet precipitate.—**In conc. sulphuric acid:** blue solution; violet precipitate on dilution.—**Dyes:** wool and unmordanted cotton direct from a neutral bath; silk from a slightly acid bath. Can be diazotised and developed on the fibre, and gives shades fast to rubbing, washing, and milling. |
| *p*-Acetamido-benzene-azo-*α*-naphthyl-amine and saponified. | *β*-Naphthol-sulphonic acid S | 1899. | C. Mensching.<br>Levinstein Ltd.<br>Eng. Pat. 24980$^{99}$.<br>Am. Appl. 1764$^{00}$.<br>Ger. Pat. 122457. | **Appearance of dyestuff:** black powder.—**In water:** dark violet solution.—**On addition of hydrochloric acid:** precipitate.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** green, changing to wine red on dilution.—**Dyes:** wool fast violet black. |

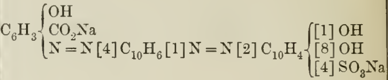
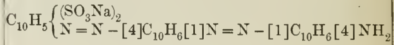
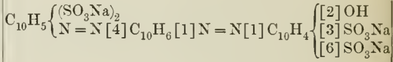
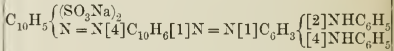
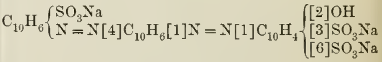
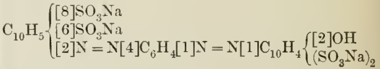
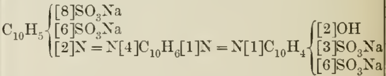
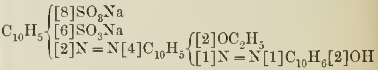
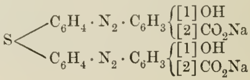
| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 174 | **Coomassie Wool Black S.** [*Lev.*] | Sodium salt of amidobenzene-azo-naphthalene-azo-β-naphthol-disulphonic acid R. | $C_{26}H_{17}N_5S_2O_7Na_2$ | $C_6H_4\left\{\begin{array}{l}{[4]}NH_2\\ {[1]}N:N[1]C_{10}H_6[4]N:N[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[6]}SO_3Na\\ {[7]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 175 | **Diaminogen.*** [*C.*] | Sodium salt of sulphoamido-naphthalene-azo-naphthalene-azo-β-naphthol-sulphonic acid. | $C_{30}H_{19}N_5S_2O_7Na_2$ | $C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[6\ \&\ 7]}SO_3Na\\ {[4]}N:N[4]C_{10}H_6[1]N=N[1]C_{10}H_5\left\{\begin{array}{l}{[2]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 176 | **Fast Violet R.** [*By.*] | Sodium salt of sulphobenzene-azo-α-naphthalene-azo-β-naphthol-β-sulphonic acid. | $C_{26}H_{16}N_4O_7S_2Na_2$ | $C_6H_4\left\{\begin{array}{l}{[4]}SO_3Na\\ {[1]}N:N[4]C_{10}H_6[1]N:N[1]C_{10}H_5\left\{\begin{array}{l}{[2]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 177 | **Victoria Black B.†** [*By.*] | Sodium salt of sulphobenzene-azo-naphthalene-azo-dioxy-naphthalene-sulphonic acid. | $C_{26}H_{16}N_4S_2O_8Na_2$ | $C_6H_4\left\{\begin{array}{l}{[4]}SO_3Na\\ {[1]}N:N[1]C_{10}H_6[4]N:N[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 178 | **Jet Black R.** [*By.*] | Sodium salt of disulphobenzene-azo-α-naphthalene-azo-phenyl-α-naphthylamine. | $C_{32}H_{21}N_5S_2O_6Na_2$ | $C_6H_3\left\{\begin{array}{l}(SO_3Na)_2\\ N=N[4]C_{10}H_6[1]N=N[1]C_{10}H_6[4]NHC_6H_5\end{array}\right.$ |
| 179 | **Fast Violet B.** [*By.*] | Sodium salt of sulpho-*p*-toluene-azo-α-naphthalene-azo-β-naphthol-β-sulphonic acid. | $C_{27}H_{18}N_4O_7S_2Na_2$ | $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3Na\\ N=N[4]C_{10}H_6[1]N=N[1]C_{10}H_5\left\{\begin{array}{l}{[2]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 180 | **Diamond Black F.** [*By.*] | Sodium salt of carboxy-phenol-azo-α-naphthalene-azo-α-naphthol-*p*-sulphonic acid. | $C_{27}H_{16}N_4O_7SNa_2$ | $C_6H_3\left\{\begin{array}{l}OH\\ CO_2Na\\ N=N[4]C_{10}H_6[1]N=N[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 181 | **Chrome Black I.** [*H.*] | Sodium salt of sulphocarboxyphenol azo-α-naphthalene-azo-α-naphthol-*p*-sulphonic acid. | $C_{27}H_{15}N_4S_2O_{10}Na_3$ | $C_6H_2\left\{\begin{array}{l}OH\\ CO_2Na\\ SO_3Na\\ N=N[4]C_{10}H_6[1]N=N[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |

* **Diazo Indigo Blue** [*By.*] is an analogous product. **Zambesi Sky Blue 4 B** [*A.*]

† **Victoria Black G** and **5 G** [*By.*] belong to the same class,

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| *p*-Acetamido-benzene-azo-α-naphthylamine<br>and saponified. | β-Naphthol-disulphonic acid R | 1899. | C. MENSCHING.<br>LEVINSTEIN LTD.<br>Eng. Pat. $24980^{99}$.<br>Am. Appl. $1763^{00}$.<br>Ger. Pat. 122457. | **Appearance of dyestuff:** black powder.—**In water:** blue black solution.—**On addition of hydrochloric acid:** redder.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** green, changing to red on dilution.—**Dyes:** wool a level black. |
| Acetyl-1 : 4-naphthylenediamine-6 & 7-sulphonic acid (diaz.)<br>↓<br>α-Naphthylamine<br>The end product saponified. | β-Naphthol-sulphonic acid S | | L. CASSELLA & Co.<br>J. Soc. Dyers, 1896, 66. | **Dyes:** unmordanted cotton a dark blue, which by diazotisation on the fibre and combination with β-naphthol gives fast indigo blue shades, with metadiamines fast blacks. |
| *p*-Sulpho-benzene-azo-α-naphthylamine. | β-Naphthol-sulphonic acid S. | 1882. | FR. BAYER & Co.<br>L. CASSELLA & Co.<br>Ger. Pat. $40977^{86}$. | **Appearance of dyestuff:** dark green bronzy powder.—**In water or alcohol:** reddish violet solution.—**On addition of hydrochloric acid to the aqueous solution:** reddish violet precipitate.—**On addition of caustic soda:** the solution becomes bluer with separation of a brownish precipitate.—**In conc. sulphuric acid:** dull greenish blue solution, on dilution becoming first gray and then giving a reddish violet precipitate.—**Dyes:** wool from an acid bath or mordanted with chrome, reddish violet, tolerably fast to light and milling. |
| *p*-Sulpho-benzene-azo-α-naphthylamine. | Dioxy-naphthalene-sulphonic acid S. | 1889. | ULRICH & DUISBERG.<br>FR. BAYER & Co.<br>Eng. Pat. $13665^{89}$.<br>Am. Pat. $466202^{89}$.<br>Fr. Pat. $200520^{89}$.<br>Ger. Pats. 61707 & 62945. | **Appearance of dyestuff:** black powder.—**In water:** dark reddish violet solution.—**On addition of hydrochloric acid:** redder solution and bordeaux red precipitate.—**On addition of caustic soda:** dark blue violet solution.—**In conc. sulphuric acid:** moss-green solution; on dilution changing to sea green and then to bluish red.—**Dyes:** wool from an acid bath bluish black, fairly level shades fast to light, alkalies, acids, and sulphur, but not to milling. Fastness to milling increased by after-chroming. |
| Disulpho-benzene-azo-α-naphthylamine. | Phenyl-α-naphthylamine. | 1888. | M. KAHN.<br>FR. BAYER & Co.<br>Eng. Pat. $14442^{88}$.<br>Am. Pat. 425885.<br>Ger. Pat. $48924^{88}$.<br>J. Soc. Dyers and Colorists, 1889, 106. | **Appearance of dyestuff:** black powder.—**In water:** bluish violet solution.—**In alcohol:** violet solution.—**On addition of hydrochloric acid to the aqueous solution:** bluish black precipitate.—**On addition of caustic soda to the aqueous solution:** soluble violet precipitate.—**In conc. sulphuric acid:** blue solution; greenish blue precipitate on dilution with water.—**Dyes:** wool bluish black from an acetic acid bath or a neutral bath containing salt. |
| Sulpho-*p*-toluene-azo-α-naphthylamine. | β-Naphthol-β-sulphonic acid. | 1882.<br>1886. | FR. BAYER & Co.<br>L. CASSELLA & Co.<br>Ger. Pat. $40977^{86}$. | **Appearance of dyestuff:** greenish brown powder.—**In water or alcohol:** violet solution.—**On addition of hydrochloric acid to the aqueous solution:** violet precipitate.—**On addition of caustic soda to the aqueous solution:** violet precipitate if the solution is strong—**In conc. sulphuric acid:** dull green solution; violet precipitate on dilution.—**Dyes:** wool violet from an acid bath. |
| Salicylic-acid-azo-α-naphthylamine. | α-Naphthol-monosulphonic acid NW. | 1889. | R. LAUCH & K. KREKELER.<br>FR. BAYER & Co.<br>Eng. Pat. $8299^{89}$.<br>Am. Pat. 438438.<br>Ger. Pat. $51504^{89}$. | **Appearance of dyestuff:** blackish blue powder.—**In water or alcohol:** bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution:** violet precipitate.—**On addition of caustic soda:** solution becomes blue.—**In conc. sulphuric acid:** greenish solution; violet precipitate on dilution with water.—**Dyes:** chrome mordanted wool bluish black, the shades being very fast to light, milling, stoving, acids, and alkalies. |
| Amidosalicylic-sulphonic-acid-azo-α-naphthylamine. | α-Naphthol-*p*-sulphonic acid. | 1899. | TURNER, DEAN, & TURNER.<br>READ HOLLIDAY & SONS.<br>Eng. Pat. $2468^{99}$.<br>Ger. Pat. $123115^{99}$.<br>Fr. Pat. $293923^{99}$. | **Appearance of dyestuff:** blue black powder.—**In water:** red violet solution.—**On addition of hydrochloric acid:** crimson.—**On addition of caustic soda:** blue solution.—**In conc. sulphuric acid:** bluish green solution, changing to violet on dilution.—**Dyes:** fast shades on chromed wool. |

contains as a component amidocresol ether (Zeit. f. Farben & Textil Chemie, 1902, 224).
and contain equivalent components in place of sulphanilic acid.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 182 | **Diamond Green.**<br>[*By.*] | Sodium salt of carboxyphenol-azo-α-naphthalene-azo-dioxynaphthalene-sulphonic acid. | $C_{27}H_{16}N_4SO_8Na$ |  $C_6H_3\left\{\begin{array}{l}OH\\CO_2Na\\N=N[4]C_{10}H_6[1]N=N[2]C_{10}H_4\left\{\begin{array}{l}[1]OH\\ [8]OH\\ [4]SO_3Na\end{array}\right.\end{array}\right.$ |
| 183 | **Naphthylamine Black D.**<br>[*C.*] | Sodium salt of disulphonaphthalene-azo-α-naphthalene-azo-α-naphthylamine. | $C_{30}H_{19}N_5O_6S_2Na_2$ |  $C_{10}H_5\left\{\begin{array}{l}(SO_3Na)_2\\N=N-[4]C_{10}H_6[1]N=N-[1]C_{10}H_6[4]NH_2\end{array}\right.$ |
| 184 | **Naphthol Black 6 B.** [*C.*] [*D.*]<br>**Acid Black 6 B.**<br>[*H.*] | Sodium salt of disulphonaphthalene-azo-α-naphthalene-azo-β-naphthol-disulphonic acid R. | $C_{30}H_{16}N_4O_{13}S_4Na_4$ |  $C_{10}H_5\left\{\begin{array}{l}(SO_3Na)_2\\N=N[4]C_{10}H_6[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ [3]SO_3Na\\ [6]SO_3Na\end{array}\right.\end{array}\right.$ |
| 185 | **Anthracite Black* B.** [*C.*]<br>**Phenylene Black.**<br>[*P.*] | Sodium salt of disulphonaphthalene-azo-α-naphthalene-azo-diphenyl-*m*-phenylene diamine. | $C_{38}H_{26}N_6O_6S_2Na_2$ |  $C_{10}H_5\left\{\begin{array}{l}(SO_3Na)_2\\N=N[4]C_{10}H_6[1]N=N[1]C_6H_3\left\{\begin{array}{l}[2]NHC_6H_5\\ [4]NHC_6H_5\end{array}\right.\end{array}\right.$ |
| 186 | **Blue Black B.**†<br>[*B.*]<br>**Azo Black O.**<br>[*M.*] | Sodium salt of sulpho-β-naphthalene-azo-α-naphthalene-azo-β-naphthol-disulphonic acid. | $C_{30}H_{17}N_4O_{10}S_3Na_3$ |  $C_{10}H_6\left\{\begin{array}{l}SO_3Na\\N=N[4]C_{10}H_6[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ [3]SO_3Na\\ [6]SO_3Na\end{array}\right.\end{array}\right.$ |
| 187 | **Brilliant Croceïne 9 B.** [*C.*] | Sodium salt of disulpho-β-naphthalene-azo-benzene-azo-β-naphthol-disulphonic acid. | $C_{26}H_{14}N_4S_4O_{13}Na_4$ |  $C_{10}H_5\left\{\begin{array}{l}[8]SO_3Na\\ [6]SO_3Na\\ [2]N=N[4]C_6H_4[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\(SO_3Na)_2\end{array}\right.\end{array}\right.$ |
| 188 | **Naphthol Black B.**<br>[*C.*]<br>**Brilliant Black B.**<br>[*B.*] | Sodium salt of disulpho-β-naphthalene-azo-α-naphthalene-azo-β-naphthol-disulphonic acid. | $C_{30}H_{16}N_4S_4O_{13}Na_4$ |  $C_{10}H_5\left\{\begin{array}{l}[8]SO_3Na\\ [6]SO_3Na\\ [2]N=N[4]C_{10}H_6[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ [3]SO_3Na\\ [6]SO_3Na\end{array}\right.\end{array}\right.$ |
| 189 | **Diamine Blue 6 G.**<br>[*C.*] | Sodium salt of disulpho-β-naphthalene-azo-ethoxy-α-naphthalene-azo-β-naphthol. | $C_{32}H_{22}N_4S_2O_8Na_2$ |  $C_{10}H_5\left\{\begin{array}{l}[8]SO_3Na\\ [6]SO_3Na\\ [2]N=N[4]C_{10}H_5\left\{\begin{array}{l}[2]OC_2H_5\\ [1]N=N[1]C_{10}H_6[2]OH\end{array}\right.\end{array}\right.$ |
| 190 | **Anthracene Yellow C.**<br>[*C.*] | Sodium salt of thio-di-benzene-disazo-di-salicylic acid. | $C_{26}H_{16}N_4SO_6Na_2$ |  |

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* **Anthracite Black** is derived from the α-naphthylamine-3 : 6-disulphonic acid, **Phenylene**

† **Blue Black B** is derived from the mixture of mono-sulphonic acids, **Azo Black O** from the mixture of mono- and

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| Amidosalicylic-acid-azo-α-naphthylamine. | Dioxy-naphthalene-monosulphonic acid S. | 1890. | LAUCH, KREKELER, & ULRICH.<br>FR. BAYER & CO.<br>Ger. Pats. $51504^{89}$ & $62003^{90}$. | **Appearance of dyestuff:** black powder.—**In water:** blackish violet solution.—**In alcohol:** blue solution.—**On addition of hydrochloric acid to aqueous solution:** dark reddish violet precipitate.—**On addition of caustic soda:** dark blue solution.—**In conc. sulphuric acid:** bluish green solution; on dilution first greenish blue and then blackish violet precipitate.—**Dyes:** chrome mordanted wool dark bluish green, fast to light, milling, acids, and alkalies. |
| Disulpho-naphthalene-azo-α-naphthyl-amine. | α-Naphthyl-amine. | 1888. | A. WEINBERG.<br>L. CASSELLA & CO.<br>Eng. Pat. $18425^{88}$.<br>Am. Pat. 412440.<br>Ger. Pat. 50907; addn. to 39029. | **Appearance of dyestuff:** black powder.—**In water:** violet black solution.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** black precipitate.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** bluish black solution; on dilution with water, first green, then a black precipitate.—**Dyes:** wool and silk black from an acid bath or from a neutral bath containing salt. |
| Disulpho-naphthalene-azo-α-naphthyl-amine. | β-Naphthol-disulphonic acid R. | 1885. | M. HOFFMANN & A. WEINBERG.<br>L. CASSELLA & CO.<br>Eng. Pat. $9214^{85}$ (amended).<br>Am. Pat. 345901.<br>Ger. Pat. $39029^{85}$.<br>Fr. Pat. 170342. | **Appearance of dyestuff:** black powder.—**In water:** easily soluble with a violet colour.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda to the aqueous solution:** blackish blue colour.—**In conc. sulphuric acid:** greenish black solution; on dilution with water, first greenish blue, then a violet precipitate.—**Dyes:** wool bluish black from an acid bath. |
| *Disulpho-naphthalene-azo-α-naphthyl-amine. | Diphenyl-*m*-phenylene-diamine. | 1889.<br>1889. | ROSENSTIEHL.<br>SOC. ANON. DES MAT. COL. DE ST. DENIS.<br>Fr. Pat. $196793^{89}$.<br>Am. Pat. $502912^{93}$.<br>Ger. Pat. $52616^{89}$.<br>L. CASSELLA & CO.<br>Eng. Pat. $7977^{89}$.<br>Ger. Pat. $61202^{89}$.<br>Fr. Pat. $197963^{89}$. | **Appearance of dyestuff:** blackish powder.—**In water:** dull violet solution.—**On addition of hydrochloric acid to the aqueous solution:** violet precipitate.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** black solution; greenish black precipitate on dilution.—**Dyes:** wool from an acid bath a black fast to milling. |
| †Mono- (or di-) sulpho-β-naphthalene-azo-α-naphthyl-amine. | β-Naphthol-disulphonic acid R. | 1882.<br>1882. | BAD. ANIL. & SODA FABRIK.<br>L. LIMPACH.<br>MEISTER, LUCIUS, & BRÜNING. | **Appearance of dyestuff:** bluish black powder.—**In water:** bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution:** blue precipitate.—**On addition of caustic soda to the aqueous solution:** blue precipitate, soluble in water.—**In conc. sulphuric acid:** bluish green solution; on dilution with water, blue solution and then a blue precipitate.—**Dyes:** wool bluish violet from an acid bath. |
| Diazotised β-naphthylamine-γ-disulphonic acid combined with aniline, again diazotised and combined with β-naphthol-disulphonic acid R and G (mixed). | | 1886. | A. WEINBERG.<br>L. CASSELLA & CO. | **Appearance of dyestuff:** brownish red powder.—**In water:** bluish red solution.—**On addition of hydrochloric acid:** darker and bluer, with excess violet.—**On addition of caustic soda:** brownish coloration.—**In conc. sulphuric acid:** blue solution, changing to bluish red on dilution.—**Dyes:** wool red from an acid bath. |
| Diazotised β-naphthylamine-γ-disulphonic acid combined with α-naphthylamine, again diazotised and combined with β-naphthol-disulphonic acid R. | | 1885. | A. WEINBERG.<br>L. CASSELLA & CO.<br>Eng. Pat. $9214^{85}$.<br>Am. Pat. 345901.<br>Ger. Pat. 39029.<br>Fr. Pat. 170342. | **Appearance of dyestuff:** blue black powder.—**In water:** violet solution.—**On addition of hydrochloric acid:** reddish violet precipitate.—**On addition of caustic soda:** blue soluble precipitate.—**In conc. sulphuric acid:** green solution, on dilution becoming bluer and then giving a reddish violet precipitate.—**Dyes:** wool blue black from an acid bath. Employed in garment dyeing and for wool printing. |
| Diazotised β-naphthylamine-γ-disulphonic acid combined with 1:2-amidonaphthol ether, again diazotised and combined with β-naphthol. | | 1889. | A. WEINBERG.<br>L. CASSELLA & CO. | **Appearance of dyestuff:** dark violet powder.—**In water:** dark blue solution.—**On addition of hydrochloric acid:** violet precipitate.—**On addition of caustic soda:** solution duller.—**In conc. sulphuric acid:** bluish green solution; violet precipitate on dilution.—**Dyes:** cotton direct. |
| Combination of diazotised thio-aniline with salicylic acid (2 mols.). | | | L. CASSELLA & CO. | **Appearance of dyestuff:** brownish yellow powder.—**In water:** sparingly soluble, with light yellowish brown colour.—**On addition of hydrochloric acid:** greenish brown precipitate.—**In conc. sulphuric acid:** dark reddish violet solution; yellowish gray precipitate on dilution.—**Dyes:** chromed wool fast to milling and light. |

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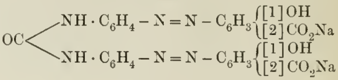
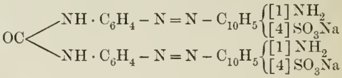
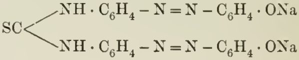
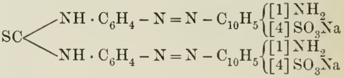
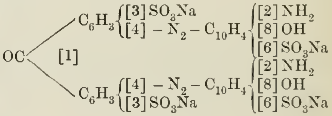
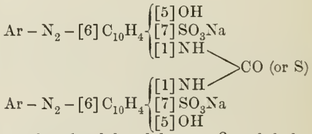
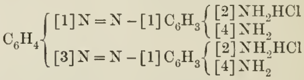
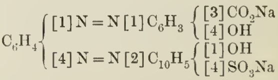
**Black** from the disulphonic acids obtained by direct sulphonation of α-naphthylamine.

di-sulphonic acids, which are formed by direct sulphonation of β-naphthylamine nnder different conditions.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 191 | **Cotton Yellow G.** [*B.*] | Sodium salt of diphenylurea-disazo-bi-salicylic acid. | $C_{27}H_{18}N_6O_7Na_2$ |  $OC\begin{cases}NH\cdot C_6H_4-N=N-C_6H_3\begin{cases}[1]OH\\ [2]CO_2Na\end{cases}\\ NH\cdot C_6H_4-N=N-C_6H_3\begin{cases}[1]OH\\ [2]CO_2Na\end{cases}\end{cases}$ |
| 192 | **Salmon Red.** [*B.*] | Sodium salt of diphenylurea-disazo-bi-naphthionic acid. | $C_{33}H_{24}N_8O_7S_2Na_2$ |  $OC\begin{cases}NH\cdot C_6H_4-N=N-C_{10}H_5\begin{cases}[1]NH_2\\ [4]SO_3Na\end{cases}\\ NH\cdot C_6H_4-N=N-C_{10}H_5\begin{cases}[1]NH_2\\ [4]SO_3Na\end{cases}\end{cases}$ |
| 193 | **Heligoland Yellow.** [*N. I.*] | Sodium salt of diphenyl-thiourea-disazo-bi-phenol. | $C_{25}H_{18}N_6SO_2Na_2$ |  $SC\begin{cases}NH\cdot C_6H_4-N=N-C_6H_4\cdot ONa\\ NH\cdot C_6H_4-N=N-C_6H_4\cdot ONa\end{cases}$ |
| 194 | **Salmon Red.** [*N. I.*] | Sodium salt of diphenyl-thiourea-disazo-bi-naphthionic acid. | $C_{33}H_{24}N_8S_3O_6Na_2$ |  $SC\begin{cases}NH\cdot C_6H_4-N=N-C_{10}H_5\begin{cases}[1]NH_2\\ [4]SO_3Na\end{cases}\\ NH\cdot C_6H_4-N=N-C_{10}H_5\begin{cases}[1]NH_2\\ [4]SO_3Na\end{cases}\end{cases}$ |
| 195 | **Benzo Fast Pink 2 BL.** [*By.*] | Sodium salt of diphenyl-urea-disulphonic acid-disazo-bi-amido-naphthol-sulphonic acid. | $C_{33}H_{20}N_6S_4O_{14}Na_4$ |  $OC\begin{cases}C_6H_3\begin{cases}[3]SO_3Na\\ [4]-N_2-C_{10}H_4\begin{cases}[2]NH_2\\ [8]OH\\ [6]SO_3Na\end{cases}\end{cases}\\ [1]\\ C_6H_3\begin{cases}[4]-N_2-C_{10}H_4\begin{cases}[2]NH_2\\ [8]OH\\ [6]SO_3Na\end{cases}\\ [3]SO_3Na\end{cases}\end{cases}$ |
| 196 | **Benzo Fast Scarlets GS, 4 BS, & 8 BS.** [*By.*]<br>**Benzo Fast Orange S.** [*By.*]<br>**Benzo Fast Red.** | Sodium salts of bi-benzene- (or homologue) disazo-di-oxynaphthyl-urea-di-sulphonic acid. | |  $\left.\begin{matrix}Ar-N_2-[6]C_{10}H_4\begin{cases}[5]OH\\ [7]SO_3Na\\ [1]NH\end{cases}\\ Ar-N_2-[6]C_{10}H_4\begin{cases}[1]NH\\ [7]SO_3Na\\ [5]OH\end{cases}\end{matrix}\right\rangle CO\text{ (or S)}$<br>(Ar = phenyl, tolyl, xylyl, α- or β-naphthyl, or $C_6H_5\cdot N_2\cdot C_6H_4'$). |
| 197 | **Bismarck Brown.**<br>**Manchester Brown.**<br>**Phenylene Brown.**<br>**Vesuvine.**<br>**Leather Brown.**<br>**Cinnamon Brown.**<br>**English Brown.** | Hydrochloride of benzene-disazo-phenylene-diamine. | $C_{18}H_{20}N_8Cl_2$ |  $C_6H_4\begin{cases}[1]N=N-[1]C_6H_3\begin{cases}[2]NH_2HCl\\ [4]NH_2\end{cases}\\ [3]N=N-[1]C_6H_3\begin{cases}[2]NH_2HCl\\ [4]NH_2\end{cases}\end{cases}$ |
| 198 | **Azoalizarine Bordeaux W.** [*D. H.*] | Sodium salt of benzene-disazo-salicylic-acid-α-naphthol-sulphonic acid. | $C_{23}H_{14}N_4SO_7Na_2$ |  $C_6H_4\begin{cases}[1]N=N[1]C_6H_3\begin{cases}[3]CO_2Na\\ [4]OH\end{cases}\\ [4]N=N[2]C_{10}H_5\begin{cases}[1]OH\\ [4]SO_3Na\end{cases}\end{cases}$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Combination of diazotised *p*-amidoacetanilide with salicylic acid, saponification of the product and treatment with carbonyl chloride. | | 1888. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 15258$^{88}$.<br>Am. Pat. 430535$^{90}$.<br>Ger. Pats. 4673$7^{88}$ and 47902$^{89}$.<br>J. Soc. Dyers and Colorists, 1889, 106. | **Appearance of dyestuff**: yellowish powder. — **In water**: yellow solution. — **On addition of hydrochloric acid to the aqueous solution**: brown precipitate. — **On addition of caustic soda**: solution becomes rather more orange.—**In conc. sulphuric acid**: orange red solution; bluish violet precipitate on dilution with water.—**Dyes**: unmordanted cotton yellow from a boiling alkaline bath. |
| Combination of diazotised *p*-amidoacetanilide with naphthionic acid, saponification of the product, and treatment with carbonyl chloride. | | 1888. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 14222$^{89}$.<br>Am. Pat. 430534$^{90}$.<br>Ger. Pat. 50852$^{89}$. | **Appearance of dyestuff**: brownish powder. — **In water**: orange yellow solution. — **On addition of hydrochloric acid**: bluish violet precipitate.—**On addition of caustic soda**: no change.— **In conc. sulphuric acid**: magenta red solution; bluish violet precipitate on dilution with water.—**Dyes**: unmordanted cotton from a boiling alkaline bath shades ranging from flesh colour to brownish orange. |
| Di-*p*-amido-diphenyl-thiourea. | Phenol (2 mols.) | 1890. | Prager & Istel.<br>Ger. Pats. 58204 & 60152$^{90}$. | **Appearance of dyestuff**: brown powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: brown precipitate.— **On addition of caustic soda**: rather redder.—**In conc. sulphuric acid**: orange red solution; brown precipitate on dilution.—**Dyes**: unmordanted cotton yellow. |
| Di-*p*-amido-diphenyl-thiourea. | Naphthionic acid (2 mols.) | 1890. | Prager & Istel.<br>Eng. Pat. 3731$^{91}$.<br>Ger. Pats. 58204 & 60152$^{90}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: orange red solution.—**On addition of hydrochloric acid**: bluish violet precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: magenta red solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton orange red. |
| Di-*p*-amido-diphenyl-urea-disulphonic acid. | 2 mols. Amidonaphthol sulphonic acid $\gamma$ (neutral or acid solution). | 1900. | Fr. Bayer & Co.<br>Ger. Pats. 129388 & 131513.<br>Z. Farb. Chem. 1902, 192; Chem. Zeit. 1902, 485. | **Dyes**: unmordanted cotton direct bright pink shades of remarkable fastness to light and good fastness to alkalies. Also employed in calico printing. |
| Combination of 2 mols. of a diazotised monamine (or 1 mol. of each of two monamines) with the urea obtained by the action of phosgene gas upon 2 mols. of amidonaphthol-sulphonic acid J ($NH_2:OH:SO_3H=1:5:7$). | | 1899. | Fr. Bayer & Co.<br>Eng. Pat. 3615$^{00}$.<br>Ger. Pats. 122904; 126133; 126801; 128195; 129464; and 132511.<br>Z. Farb. Chem. 1902, 101; J. Soc. Dyers, 1900, 220; 1901, **16**, 255 | Direct dyeing cotton colours of very good fastness to light and acid. They dye bright shades, but are somewhat difficult to discharge by tin salts. |
| *m*-Phenylene-diamine. | *m*-Phenylene-diamine (2 mols.) | 1863. | Martius.<br>Dale & Caro.<br>Eng. Pat. 3307$^{63}$.<br>Caro & P. Griess.<br>Zeit. f. Chem. (1867) **3**, 287.<br>Cf. Ber. **30**, 2111, 2203, 2899. | **Appearance of dyestuff**: dark brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: brown precipitate.—**In conc. sulphuric acid**: brown solution; red on dilution with water.—**Dyes**: wool, leather, and tannined cotton reddish brown. Not fast to light, soap, or milling. |
| *p*-Phenylene-diamine (diazotised in steps). | Salicylic acid and $\alpha$-naphthol-1:4-sulphonic acid. | | C. O. Müller.<br>Am. Pat. 631089$^{99}$.<br>Fr. Pat. 284775$^{99}$. | **Solution in water**: red.—**In conc. sulphuric acid**: blue solution.— **Dyes**: chromed wool fast bordeaux; also suitable for wool printing. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 199 | **Azoalizarine Black.** [*D. H.*] | Sodium salt of benzene-disazo-salicylic-acid-dioxy-naphthalene-di- (or mono-) sulphonic acid. | $C_{23}H_{13}N_4S_2O_{11}Na_3$ | $C_6H_4\left\{\begin{array}{l}{[1]}N=N{[1]}C_6H_3\left\{\begin{array}{l}{[3]}CO_2Na\\ {[4]}OH\end{array}\right.\\ {[4]}N=N{[2]}C_{10}H_3\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 200 | **Violet Black.** [*B.*] | Sodium salt of benzene-disazo-α-naphthylamine-α-naphthol-sulphonic acid. | $C_{26}H_{18}N_5O_4SNa$ | $C_6H_4\left\{\begin{array}{l}{[1]}N=N-{[1]}C_{10}H_6{[4]}NH_2\\ {[4]}N=N-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 201 | **Manchester Brown E E.** [*C.*] [*Lev.*]<br>**Bismarck Brown R.** [*H.*] [*W.*] [*I.*]<br>**Vesuvine B.** [*B.*] | Hydrochloride of toluene-disazo-*m*-tolylene-diamine. | $C_{21}H_{26}N_8Cl_2$ | $C_6H_3\left\{\begin{array}{l}{[3]}N=N{[1]}C_6H_2\left\{\begin{array}{l}{[2]}NH_2HCl\\ {[4]}NH_2\\ {[5]}CH_3\end{array}\right.\\ {[4]}CH_3\\ {[1]}N=N{[1]}C_6H_2\left\{\begin{array}{l}{[2]}NH_2HCl\\ {[4]}NH_2\\ {[5]}CH_3\end{array}\right.\end{array}\right.$ |
| 202 | **Toluylene Brown G.** [*O.*] [*By.*] | Sodium salt of sulphotoluene-disazo-*m*-phenylene-diamine. | $C_{13}H_{11}N_6SO_3Na$ | $C_6H_2\left\{\begin{array}{l}{[1]}N=N\\ {[2]}CH_3\\ {[5]}SO_3Na\\ {[3]}N=N\end{array}\right\rangle C_6H_2(NH_2)_2{[1:3]}$ |
| 203 | **Toluylene Yellow.** [*O.*] | Sulphotoluene-disazo-bi-nitro-*m*-phenylene-diamine. | $C_{19}H_{17}N_{10}O_7SNa$ | $C_6H_2\left\{\begin{array}{l}{[1]}N=N{[4]}C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}NO_2\end{array}\right.\\ {[2]}CH_3\\ {[5]}SO_3Na\\ {[3]}N=N{[4]}C_6H_2\left\{\begin{array}{l}{[6]}NO_2\\ {[3]}NH_2\\ {[1]}NH_2\end{array}\right.\end{array}\right.$ |
| 204 | **Toluylene Orange R R.** [*O.*] | Sodium salt of sulphotoluene-disazo-bi-β-naphthylamine. | $C_{27}H_{21}N_6O_3SNa$ | $C_6H_2\left\{\begin{array}{l}{[1]}N=N{[1]}C_{10}H_6{[2]}NH_2\\ {[2]}CH_3\\ {[5]}SO_3Na\\ {[3]}N=N{[1]}C_{10}H_6{[2]}NH_2\end{array}\right.$ |
| 205 | **Naphthylene Red.** [*B.*] | Sodium salt of naphthalene-disazo-bi-naphthionic acid. | $C_{30}H_{20}N_6O_6S_2Na_2$ | $C_{10}H_6\left\{\begin{array}{l}{[1]}N=N{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\\ {[5]}N=N{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 206 | **Diamine Gold.** [*C.*] | Sodium salt of disulphonaphthalene disazo-phenetol-phenol. | $C_{24}H_{18}N_4O_8S_2Na_2$ | $C_{10}H_4\left\{\begin{array}{l}{[1]}N=N{[1]}C_6H_4{[4]}OC_2H_5\\ {[3]}SO_3Na\\ {[7]}SO_3Na\\ {[5]}N=N{[1]}C_6H_4{[4]}OH\end{array}\right.$ |
| 207 | **Naphthylene Violet.** [*C.*] (for production of **Diamine Cutch** on the fibre). | Sodium salt of disulphonaphthalene-disazo-bi-α-naphthyl-amine. | $C_{30}H_{20}N_6S_2O_6Na_2$ | $C_{10}H_4\left\{\begin{array}{l}{[1]}N=N{[4]}C_{10}H_6{[1]}NH_2\\ {[3]}SO_3Na\\ {[7]}SO_3Na\\ {[5]}N=N{[4]}C_{10}H_6{[1]}NH_2\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| *p*-Phenylene-diamine (diazotised in steps). | Salicylic acid and 1 : 8-dioxynaphthalene-3 : 6-di- (or 4-mono-) sulphonic acid. | | Durand & Huguenin.<br>C. O. Müller.<br>Am. Pats. $640010^{89}$ & $628721^{89}$.<br>Fr. Pat. $284775^{89}$. | **Solution in water**: violet.—**In conc. sulphuric acid**: blue.—**Dyes**: chromed wool fast black. |
| *p*-Phenylene-diamine (diazotised in steps). | α-Naphthol-1 : 4-sulphonic acid and α-naphthylamine. | 1887. | Bülow.<br>Bad. Anil. & Soda Fabrik.<br>Ger. Pat. $42814^{87}$, addn. to $42011^{87}$. | **Appearance of dyestuff**: bronzy powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: solution becomes reddish violet.—**On addition of caustic soda**: solution becomes reddish violet.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: cotton and wool violet black. |
| *m*-Tolylene-diamine (1 mol.) | *m*-Tolylene-diamine (2 mols.) | 1878. | P. Griess.<br>Ber. (1878) 11, 627. | **Appearance of dyestuff**: dark brown powder.—**In water**: reddish brown solution.—**In alcohol**: reddish brown solution.—**On addition of hydrochloric acid to the aqueous solution**: yellowish brown colour.—**On addition of caustic soda**: light brown precipitate.—**In conc. sulphuric acid**: dark brown solution; on dilution becoming red and then brown.—**Dyes**: wool, leather, and tannin mordanted cotton reddish brown. |
| *c*-Tolylene-diamine-sulphonic acid (1 mol.) | *m*-Phenylene-diamine (1 mol.) | 1890. | Rudolph & Voges.<br>K. Oehler.<br>Eng. Pat. $17456^{92}$.<br>Am. Pat. 516380.<br>Ger. Pat. $65863^{91}$.<br>Cf. Chem. Ztg. 1890, 1731. | **Appearance of dyestuff**: blackish brown powder.—**In water**: brown solution.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: brownish red solution.—**Dyes**: cotton direct yellowish brown, very fast to soap. |
| *c*-Tolylene-diamine-sulphonic acid (1 mol.) | Nitro-*m*-phenylene-diamine (2 mols.) | 1894. | Rudolph & Voges.<br>K. Oehler.<br>Ger. Pat. $86940^{94}$. | **Appearance of dyestuff**: light yellow powder.—**In water**: yellowish brown solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: soluble brown precipitate.—**In conc. sulphuric acid**: brown solution.—**Dyes**: unmordanted cotton direct from a neutral bath yellow shades of good fastness to washing, acids, and chlorine. |
| *c*-Tolylene-diamine-sulphonic acid (1 mol.) | β-Naphthyl-amine (2 mols.) | 1891. | Rudolph & Voges.<br>K. Oehler.<br>Ger. Pat. 70147.<br>Am. Pat. 497032. | **Appearance of dyestuff**: red powder.—**In water**: yellowish red solution.—**In 94 per cent alcohol**: orange solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate. **On addition of caustic soda**: yellowish red precipitate.—**In conc. sulphuric acid**: blue gray solution.—**Dyes**: unmordanted cotton reddish orange from a soap bath. |
| (1 : 5)-Diamido-naphthalene. | Naphthionic acid (2 mols.) | 1886. | A. Römer.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $14625^{86}$.<br>Am. Pat. $359576^{87}$.<br>Ger. Pat. $39954^{86}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet black precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution; bluish black precipitate on dilution with water.—**Dyes**: unmordanted cotton red from a boiling alkaline bath. |
| (1 : 5 : 3 : 7)-Diamido-naphthalene-disulphonic acid.<br>And ethylation of the product. | Phenol (2 mols.) | 1890. | M. Hoffmann.<br>L. Cassella & Co.<br>Eng. Pat. $15346^{90}$.<br>Am. Pat. $472121^{92}$.<br>Ger. Pat. $61174^{90}$.<br>Fr. Pat. $182063^{91}$. | **Appearance of dyestuff**: bright orange yellow powder.—**In water**: insoluble in cold, yellow solution in hot.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow precipitate, turned black by a large excess.—**On addition of caustic soda**: gelatinous yellow precipitate.—**In conc. sulphuric acid**: reddish violet solution; on dilution dull green and then yellow.—**Dyes**: unmordanted cotton yellow from a salt bath. Fast to light, acids, alkalies, and chlorine. |
| (1 : 5 : 3 : 7)-Diamido-naphthalene-disulphonic acid. | α-Naphthyl-amine (2 mols.) | 1890. | M. Hoffmann.<br>L. Cassella & Co.<br>Eng. Pat. $15346^{90}$.<br>Am. Pat. $464566^{91}$.<br>Ger. Pat. $62075^{90}$.<br>Fr. Pat. $208526^{90}$. | **Appearance of dyestuff**: brown powder.—**In water**: bordeaux red solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: soluble red precipitate.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: cotton and silk direct and by treatment on the fibre with nitrous acid and heating is converted into a fast cutch brown. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 208 | **Coomassie Black B.** [*Lev.*] | Sodium salt of sulphonaphthalene-disazo-β-naphthylamine-β-naphthol-disulphonic acid. | $C_{30}H_{18}N_5S_3O_{10}Na_3$ | $C_{10}H_5\left\{\begin{array}{l}[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[2]}SO_3Na\\ {[4]}N=N[1]C_{10}H_6[2]NH_2\end{array}\right.$ |
| 209 | **Coomassie Navy Blue.** [*Lev.*] | Sodium salt of sulphonaphthalene-disazo-β-naphthol-β-naphthol-disulphonic acid. | $C_{30}H_{17}N_4S_3O_{11}Na_3$ | $C_{10}H_5\left\{\begin{array}{l}[1]N=N[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[2]}SO_3Na\\ {[4]}N=N[1]C_{10}H_6[2]OH\end{array}\right.$ |
| 210 | **Diphenyl Fast Black.*** [*G.*] | Sodium salt of ditolylamine-disazo-*m*-tolylene-diamine-amido-naphthol-sulphonic acid. | $C_{31}H_{29}N_8SO_4Na$ | $HN\left<\begin{array}{l}C_6H_3(CH_3)-N_2-[2]C_{10}H_4\left\{\begin{array}{l}[1]OH\\ {[3]}SO_3Na\\ {[7]}NH_2\end{array}\right.\\ C_6H_3(CH_3)-N_2-[4]C_6H_2\left\{\begin{array}{l}[1]NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\end{array}\right.$ |
| 211 | **Cotton Scarlet.** [*B. K.*]<br>**Cinnabar Red.** [*B. K.*] | Sodium salt of phenyl-dixylyl-methane-disazo-bi-β-naphthol-disulphonic acid. | $C_{43}H_{32}N_4O_{14}S_4Na_4$ | $CH\left\{\begin{array}{l}C_6H_2(CH_3)_2-N=N-C_{10}H_4(OH)(SO_3Na)_2\\ C_6H_5\\ C_6H_2(CH_3)_2-N=N-C_{10}H_4(OH)(SO_3Na)_2\end{array}\right.$ |
| 212 | **Rock Scarlet YS.** [*B.S.S.*] | Sodium salt of azoxytoluene-disazo-β-naphthol-α-naphthol-monosulphonic acid. | $C_{34}H_{25}N_6O_6SNa$ | $O\left<\begin{array}{l}N-C_6H_3(CH_3)-N=N-[2]C_{10}H_5\left\{\begin{array}{l}[1]OH\\ {[4]}SO_3Na\end{array}\right.\\ \vert\\ N-C_6H_3(CH_3)-N=N-[1]C_{10}H_6[2]OH\end{array}\right.$ |
| 213 | **St. Denis Red.** [*P.*]<br>**Dianthine.** [*B.S.S.*]<br>**Rosophenine 4 B.** [*Cl. Co.*]<br>**Trona Red.** [*By.*]<br>**Rock Scarlet BS.** [*B.S.S.*] | Sodium salt of azoxytoluene-disazo-bi-α-naphthol-sulphonic acid. | $C_{34}H_{24}N_6O_9S_2Na_2$ | $O\left<\begin{array}{l}N-C_6H_3(CH_3)-N=N-[2]C_{10}H_5\left\{\begin{array}{l}[1]OH\\ {[4]}SO_3Na\end{array}\right.\\ \vert\\ N-C_6H_3(CH_3)-N=N-[2]C_{10}H_5\left\{\begin{array}{l}[4]SO_3Na\\ {[1]}OH\end{array}\right.\end{array}\right.$ |
| 214 | **Acid Milling Scarlet.** [*B.S.S.*] | Sodium salt of azoxytoluene-disazo-α-naphthol-monosulphonic-β-naphthol-disulphonic acid. | $C_{34}H_{23}N_6O_{12}S_3Na_3$ | $O\left<\begin{array}{l}N-C_6H_3(CH_3)-N=N-[2]C_{10}H_5\left\{\begin{array}{l}[1]OH\\ {[4]}SO_3Na\end{array}\right.\\ \vert\\ N-C_6H_3(CH_3)-N=N-[1]C_{10}H_4\left\{\begin{array}{l}[2]OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 215 | **Congo G R.** [*A.*] [*By.*] | Sodium salt of diphenyl-disazo-*m*-amidobenzene-sulphonic-acid-naphthionic acid. | $C_{22}H_{20}N_6S_2O_6Na_2$ | $\begin{array}{ll} & C_6H_4[4]-N_2-NH\cdot C_6H_4\cdot SO_3Na[1:3]\\ {[1]} & \vert\\ & C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}[1]NH_2\\ {[4]}SO_3Na\end{array}\right.\end{array}$ |

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* Diamine Deep Black [*C.*] is derived from di-*p*-amido-

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| (1 : 4 : 2)-Diamido-naphthalene-sulphonic acid (diazotised and coupled in steps). | β-Naphthol-disulphonic acid R + β-naphthylamine. | 1895. | R. Herz.<br>Levinstein Limd.<br>Eng. Pat. $2946^{96}$.<br>Am. Pat. 639748.<br>Ger. Pat. $102160^{96}$.<br>Fr. Pat. 256862. | **Appearance of dyestuff:** black powder.—**In water:** blue black solution.—**On addition of hydrochloric acid:** violet solution.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** green blue solution; dull red on dilution.—**Dyes:** wool deep black. |
| (1 : 4 : 2)-Diamido-naphthalene-sulphonic acid (diazotised and coupled in steps). | β-Naphthol-disulphonic acid R + β-naphthol. | 1896. | R. Herz.<br>Levinstein Limd.<br>Eng. Pat. $2946^{96}$.<br>Am. Pat. 619194.<br>Ger. Pat. 102160.<br>Fr. Pat. 256862. | **Appearance of dyestuff:** blackish blue powder.—**In water:** dark blue solution: **On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** solution becomes violet.—**In conc. sulphuric acid:** blue green solution; dark blue on dilution.—**Dyes:** wool navy blue. |
| *p*-Diamido-ditolylamine. | Amido-naphthol-sulphonic acid γ (combined alkaline) + *m*-tolylene diamine. | 1896. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $16582^{96}$.<br>Am. Pat. 575904.<br>Fr. Pat. 258521. | **Appearance of dyestuff:** black powder.—**In water:** violet black solution when hot, sparingly cold.—**In alcohol:** dark violet solution.—**On addition of hydrochloric acid:** bluish black precipitate.—**On addition of caustic soda:** black precipitate.—**In conc. sulphuric acid:** dark blue solution; black precipitate on dilution.—**Dyes:** unmordanted cotton black. |
| Diamido-di-xylyl-phenyl-methane. | β-Naphthol-disulphonic acid R (2 mols.) | 1887. | Hoffmann.<br>Leipziger Anil. Fabrik.<br>Beyer & Kegel.<br>Ger. Pat. $43644^{87}$. | **Appearance of dyestuff:** reddish brown powder.—**In water:** red solution.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda:** solution becomes a deeper red.—**In conc. sulphuric acid:** brownish red solution; yellowish red on dilution with water.—**Dyes:** unmordanted cotton red from a boiling alkaline bath. Employed for preparing lakes. |
| Di-*m*-amido-azoxytoluene. | α-Naphthol-monosulphonic acid NW + β-naphthol. | 1892. | A. G. Green.<br>Brooke, Simpson, & Spiller, Limd.<br>Eng. Pat. $19891^{92}$. | **Appearance of dyestuff:** red powder.—**In water:** very sparingly soluble.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** scarlet precipitate.—**On addition of caustic soda:** orange red solution.—**In conc. sulphuric acid:** bluish red solution; scarlet precipitate on addition of water.—**Dyes:** wool a bright scarlet from an acid bath, and is extremely fast to milling and scouring. |
| Diamidoazoxy-toluene. | α-Naphthol-monosulphonic acid NW (2 mols.) | 1887. | Nölting & Rosenstiehl.<br>Soc. Anom. des Mat. Color. et Produits chimiques.<br>Ger. Pat. $44045^{87}$.<br>Eng. Pats. $9315^{87}$ and $5736^{90}$.<br>Färberzeitung, 1, 106. | **Appearance of dyestuff:** red powder.—**In water:** red solution.—**In alcohol:** slightly soluble.—**On addition of hydrochloric acid to the aqueous solution:** red precipitate.—**On addition of caustic soda to the aqueous solution:** brick red precipitate.—**In conc. sulphuric acid:** red solution; red precipitate on dilution.—**Dyes:** cotton red from an alkaline bath. |
| Diamido-azoxy-toluene. | α-Naphthol-monosulphonic acid NW + β-naphthol-disulphonic acid R. | 1889. | A. F. Poirrier, and D. A. Rosenstiehl.<br>Ger. Pat. $51363^{89}$.<br>Brooke, Simpson, & Spiller, Limd.<br>Eng. Pat. $10915^{92}$. | **Appearance of dyestuff:** dark red powder.—**In water:** easily soluble to a scarlet solution.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda:** orange red solution.—**In conc. sulphuric acid:** bluish red solution; scarlet on dilution with water.—**Dyes:** wool from an iron bath a bright scarlet, which is very fast to milling and scouring. |
| Benzidine. | *m*-Sulphanilic acid + naphthionic acid. | 1885. | S. Pfaff.<br>The Berlin Aniline Co.<br>Eng. Pat. $2213^{86}$.<br>Am. Pats. 344971 & 358865.<br>Ger. Pat. 40954.<br>Fr. Pats. 160722 & 163172. | **Appearance of dyestuff:** brown powder.—**In water:** brownish red solution.—**On addition of hydrochloric acid:** blue precipitate.—**On addition of caustic soda:** no change of colour.—**In conc. sulphuric acid:** blue solution; blue precipitate on dilution.—**Dyes:** cotton direct from a soap bath red. |

diphenylamine; **Pluto Black** [*By.*] also belongs to the same class.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 216 | **Alkali Yellow R.** [*D.*] | Sodium salt of diphenyl-disazo-salicylic-dehydro-thio-toluidine-sulphonic acid. | $C_{33}H_{22}N_6S_2O_6Na_2$ | $\begin{array}{ll} & C_6H_4[4]-N_2-NH\cdot C_6H_4\cdot C{<}\begin{smallmatrix}N\\S\end{smallmatrix}{>}C_6H_2\left\{\begin{array}{l}CH_3\\SO_3Na\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CO_2Na\end{array}\right.\end{array}$ |
| 217 | **Congo Orange G.** [*A.*] | Sodium salt of diphenyl-disazo-phenetol-$\beta$-naphthyl-amine-disulphonic acid. | $C_{30}H_{23}N_5S_2O_7Na_2$ | $\begin{array}{ll} & C_6H_4[4]-N_2-[4]C_6H_4[1]OC_2H_5 \\ {[1]} & \vert \\ & C_6H_4[4]-N_2-[1]C_{10}H_4\left\{\begin{array}{l}[2]\,NH_2\\{[3]}\,SO_3Na\\{[6]}\,SO_3Na\end{array}\right.\end{array}$ |
| 218 | **Oxamine Orange G.** [*Remy.*] | Sodium salt of diphenyl-disazo-phenol-*m*-tolylene-diamine-oxamic acid. | $C_{27}H_{21}N_6O_4Na$ | $\begin{array}{ll} & C_6H_4[4]-N_2-[4]C_6H_4[1]OH \\ {[1]} & \vert \\ & C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}[1]\,NH_2\\{[3]}\,NH\cdot CO\cdot CO_2Na\\{[6]}\,CH_3\end{array}\right.\end{array}$ |
| 219 | **Pyramidol Brown BG.** [*Pick Lange.*] | Sodium salt of diphenyl-disazo-bi-resorcin. | $C_{24}H_{18}N_4O_4$ | $\begin{array}{ll} & C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[3]}\,OH\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[3]}\,OH\end{array}\right.\end{array}$ |
| 220 | **Chrysamine G.** [*By.*] [*A.*] | Sodium salt of diphenyl-disazo-bi-salicylic acid. | $C_{26}H_{16}N_4O_6Na_2$ | $\begin{array}{ll} & C_6H_4[4]-N=N-[4]C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CO_2H\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N=N-[4]C_6H_3\left\{\begin{array}{l}[2]\,CO_2H\\{[1]}\,OH\end{array}\right.\end{array}$ |
| 221 | **Cresotine Yellow G.** [*A.*] [*By.*] [*O.*] | Sodium salt of diphenyl-disazo-bi-*o*-cresol-carboxylic acid. | $C_{28}H_{20}N_4O_6Na_2$ | $\begin{array}{ll} & C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CH_3\\{[6]}\,CO_2Na\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CH_3\\{[6]}\,CO_2Na\end{array}\right.\end{array}$ |
| 222 | **Cloth Orange.** [*By.*] | Sodium salt of diphenyl-disazo-resorcinol-salicylic acid. | $C_{25}H_{17}N_4O_5Na$ | $\begin{array}{ll} & C_6H_4[4]-N=N-C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CO_2H\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N=N-[4]C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[3]}\,OH\end{array}\right.\end{array}$ |
| 223 | **Cloth Brown R.** [*By.*] | Sodium salt of diphenyl-disazo-salicylic-naphthol-sulphonic acid. | $C_{29}N_{18}N_4O_7SNa_2$ | $\begin{array}{ll} & C_6H_4[4]-N=N-C_6H_3\left\{\begin{array}{l}[1]\,OH\\{[2]}\,CO_2Na\end{array}\right. \\ {[1]} & \vert \\ & C_6H_4[4]-N=N-C_{10}H_5\left\{\begin{array}{l}SO_3Na\\OH\end{array}\right.\end{array}$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Benzidine. | Dehydrothiotoluidinesulphonic acid + salicylic acid. | 1889. | DAHL & Co.<br>Ger. Pat. 57095. | **Appearance of dyestuff:** brownish powder.—**In water:** opalescent yellow solution.—**On addition of hydrochloric acid:** brownish yellow precipitate.—**On addition of caustic soda:** orange red precipitate.—**In conc. sulphuric acid:** brownish red solution; brownish yellow precipitate on dilution.—**Dyes:** unmordanted cotton yellow, moderately fast to washing and light, reddened by alkalies. |
| Benzidine. | $\beta$-Naphthylamine disulphonic acid R + phenol<br>And ethylation of the product. | 1889. | BORGMANN.<br>BERLIN ANILINE Co. | **Appearance of dyestuff:** brownish red powder.—**In water:** orange yellow solution.—**On addition of hydrochloric acid:** brown precipitate.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** blue solution; on dilution becoming reddish violet and finally giving a brown precipitate.—**Dyes:** unmordanted cotton orange. |
| Benzidine. | Phenol + *m*-tolylene diamine-oxamic acid. | 1894. | MARKFELDT.<br>Eng. Pat. 22114.<br>Fr. Pat. 252140. | **Appearance of dyestuff:** reddish brown powder.—**In water:** insoluble cold, soluble hot.—**In alcohol:** soluble.—**On addition of hydrochloric acid:** brownish red precipitate.—**On addition of caustic soda:** darker.—**In conc. sulphuric acid:** violet solution; reddish brown precipitate on dilution.—**Dyes:** unmordanted cotton from a salt bath orange, which can be diazotised and developed on the fibre. |
| Benzidine. | 2 mols. Resorcin. | 1898. | PICK LANGE & Co. | **Appearance of dyestuff:** dark brown powder.—**In water:** orange brown solution.—**In alcohol:** orange solution.—**On addition of hydrochloric acid to the aqueous solution:** brown precipitate.—**On addition of caustic soda:** bordeaux red solution.—**In conc. sulphuric acid:** reddish violet solution; brown precipitate on dilution.—**Dyes:** unmordanted cotton red, converted into a deep washing-fast brown by coupling with a diazo compound on the fibre. |
| Benzidine. | Salicylic acid (2 mols.) | 1884. | E. FRANK.<br>FR. BAYER & Co.<br>Eng. Pat. 9162$^{84}$.<br>Am. Pat. 329638.<br>Ger. Pat. 31658$^{84}$. | **Appearance of dyestuff:** yellowish brown powder.—**In water:** very sparingly soluble with brownish yellow colour.—**On addition of hydrochloric acid to the aqueous solution:** brown precipitate.—**Dilute acetic acid:** brown precipitate.—**On addition of caustic soda:** solution becomes reddish brown.—**In conc. sulphuric acid:** reddish violet solution; brown precipitate on dilution with water.—**Dyes:** unmordanted cotton yellow from a soap bath. |
| Benzidine. | *o*-Cresol-carboxylic acid (2 mols.) | 1888. | RUDOLPH & PRIEBS.<br>K. OEHLER & Co.<br>Eng. Pat. 7997$^{88}$.<br>FR. BAYER & Co.<br>Am. Pat. 394841$^{88}$. | **Appearance of dyestuff:** yellowish brown powder.—**In water:** yellow solution.—**On addition of hydrochloric acid:** flocculent brownish yellow precipitate.—**On addition of caustic soda:** yellowish red solution.—**In conc. sulphuric acid:** reddish violet solution; on dilution violet precipitate becoming greenish yellow. **Dyes:** unmordanted cotton yellow, fast to light. |
| 1 mol. benzidine. | 1 mol. salicylic acid + 1 mol. resorcinol. | 1887. | E. FRANK & C. DUISBERG.<br>G. SCHULTZ.<br>FR. BAYER & Co.<br>Eng. Pats. 2213$^{86}$ and 6687$^{87}$ (amended).<br>Ger. Pat. 44797$^{87}$.<br>*Employment:*<br>Ger. Pat. 52183$^{89}$.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff:** reddish brown powder.—**In water:** yellowish brown solution.—**In alcohol:** yellowish brown solution.—**On addition of hydrochloric acid to the aqueous solution:** brown precipitate.—**On addition of caustic soda:** solution becomes red and (if concentrated) gives a red precipitate.—**In conc. sulphuric acid:** reddish violet solution; brown precipitate on dilution with water.—**Dyes:** chrome mordanted wool brownish orange. |
| 1 mol. benzidine. | 1 mol. salicylic acid + 1 mol. naphthol-monosulphonic acid. | 1887. | E. FRANK & C. DUISBERG.<br>G. SCHULTZ.<br>FR. BAYER & Co.<br>Eng. Pats. 2213$^{86}$ and 6687$^{87}$ (amended).<br>Ger. Pat. 44797$^{87}$.<br>*Employment:*<br>Ger. Pat. 52183$^{89}$.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff:** dark brownish red powder.—**In water:** reddish brown solution.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** brown precipitate.—**In conc. sulphuric acid:** bluish violet solution; reddish brown precipitate on dilution with water.—**Dyes:** chrome mordanted wool brownish red. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 224 | **Cloth Brown G.** [*By.*] | Sodium salt of diphenyl-disazo-dioxy-naphthalene-salicylic acid. | $C_{29}H_{19}N_4O_5Na$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N=N-C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2H\end{array}\right. \\ C_6H_4\,[4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[7]}\,OH\end{array}\right.\end{array}\right.$ |
| 225 | **Benzo Orange R.** [*By.*] [*A.*] | Sodium salt of diphenyl-disazo-salicylic-naphthionic-acid. | $C_{29}H_{19}N_5O_6SNa_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N=N-C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,NH_2\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 226 | **Diamine Fast Red.** [*C.*] | Sodium salt of diphenyl-disazo-salicylic-amido-naphthol-sulphonic-acid. | $C_{29}H_{19}N_5O_7SNa_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right. \\ C_6H_4\,[4]-N=N-C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right.\end{array}\right.$ |
| 227 | **Diamine Brown M.** [*C.*] | Sodium salt of diphenyl-disazo-salicylic acid-amido-naphthol-sulphonic acid $\gamma$. | $C_{29}H_{19}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2H\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[7]}\,NH_2\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 228 | **Diphenyl Brown RN.** [*G.*] | Sodium salt of diphenyl-disazo-salicylic acid-methyl-amidonaphthol-sulphonic acid $\gamma$. | $C_{30}H_{21}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[7]}\,NH\,(CH_3)\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 229 | **Diphenyl Brown BN.** [*G.*] | Sodium salt of diphenyl-disazo-salicylic acid-dimethylamido-naphthol-sulphonic acid $\gamma$. | $C_{31}H_{23}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[7]}\,N(CH_3)_2\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 230 | **Diamine Brown B.** [*C.*] | Sodium salt of diphenyl-disazo-salicylic acid-phenyl-amidonaphthol-sulphonic acid $\gamma$. | $C_{35}H_{23}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[7]}\,NHC_6H_5\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 231 | **Oxamine Maroon.** [*B.*] | Sodium salt of diphenyl-disazo-salicylic acid-1 : 5-amidonaphthol-sulphonic acid. | $C_{29}H_{19}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[5]}\,NH_2\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 232 | **Oxamine Red.** [*B.*] | Sodium salt of diphenyl-disazo-salicylic acid-2 : 5-amidonaphthol-sulphonic acid. | $C_{29}H_{19}N_5SO_7Na_2$ | $[1]\left\lvert\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ C_6H_4\,[4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[6]}\,NH_2\\ {[3]}\,SO_3Na\end{array}\right.\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| 1 mol. benzidine. | 1 mol. salicylic acid + 1 mol. dioxynaphthalene (2 : 7). | 1887. | E. Frank & C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. 6687$^{87}$ (amended).<br>Ger. Pat. 44797$^{87}$.<br>*Employment :*<br>Ger. Pat. 52183$^{89}$.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff** : dark brownish powder.—**In water** : brown solution.—**In alcohol** : slightly soluble.—**On addition of hydrochloric acid to the aqueous solution** : brown precipitate.—**On addition of caustic soda** : solution becomes reddish brown.—**In conc. sulphuric acid** : reddish violet solution ; brown precipitate on dilution.—**Dyes** : chrome mordanted wool brownish yellow. |
| 1 mol. benzidine. | 1 mol. salicylic acid + 1 mol. naphthionic acid. | 1887. | C. Duisberg & G. Schultz.<br>Fr. Bayer & Co.<br>Eng. Pat. 2213$^{86}$ (amended).<br>Ger. Pat. 44797$^{87}$.<br>Am. Pat. 447303$^{91}$. | **Appearance of dyestuff** : brownish red crystalline powder.—**In water** : orange yellow solution.—**In alcohol** : nearly insoluble.—**On addition of hydrochloric acid to the aqueous solution** : reddish violet.—**On addition of caustic soda to the strong aqueous solution** : reddish yellow precipitate.—**In conc. sulphuric acid** : violet blue solution ; grayish violet precipitate on dilution with water.—**Dyes** : unmordanted cotton orange from an alkaline bath. Also dyes chromed wool. |
| 1 mol. benzidine. | 1 mol. amidonaphthol-sulphonic acid G (or $\gamma$) in acid solution + 1 mol. salicylic acid. | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. 16699$^{89}$.<br>Ger. Pat. 55648$^{89}$. | **Appearance of dyestuff** : brownish red powder.—**In water** : red solution.—**In alcohol** : soluble.—**On addition of hydrochloric acid to the aqueous solution** : brown precipitate.—**On addition of caustic soda to the aqueous solution** : no change.—**In conc. sulphuric acid** : reddish blue solution ; on dilution with water brown precipitate.—**Dyes** : unmordanted cotton and chromed wool a fast red. |
| Benzidine. | Salicylic acid + amidonaphthol-sulphonic acid $\gamma$ (coupled alkaline). | 1889. | L. Gans.<br>Ger. Pat. 57857$^{89}$.<br>Fr. Pat. 201770. | **Appearance of dyestuff** : brown powder.—**In water** : reddish brown solution.—**On addition of hydrochloric acid** : brown precipitate.—**On addition of caustic soda** : soluble reddish brown precipitate.—**In conc. sulphuric acid** : violet, changing to brown on dilution.—**Dyes** : unmordanted cotton direct deep brown. By treatment with copper salts it becomes fairly fast to light and washing. |
| Benzidine. | Salicylic acid + methyl-amido-naphthol-sulphonic acid $\gamma$. | 1895. | C. Ris.<br>J. R. Geigy & Co.<br>Am. Pat. 567413.<br>Ger. Pat. 103149$^{95}$.<br>Fr. Pat. 250697. | **Appearance of dyestuff** : blackish brown powder.—**In water** : dark red brown solution.—**On addition of hydrochloric acid** : brown red precipitate.—**In conc. sulphuric acid** : blue violet solution : brown red precipitate on dilution.—**Dyes** : unmordanted cotton dark reddish brown. |
| Benzidine. | Salicylic acid + dimethyl-amido-naphthol-sulphonic acid $\gamma$. | 1895. | C. Ris.<br>J. R. Geigy & Co.<br>Am. Pat. 567413.<br>Ger. Pat. 103149$^{95}$.<br>Fr. Pat. 250697. | **Appearance of dyestuff** : blackish brown powder.—**In water** : dark brown solution.—**On addition of hydrochloric acid** : bordeaux red precipitate.—**In conc. sulphuric acid** : bluish violet solution ; bordeaux red precipitate on dilution.—**Dyes** : unmordanted cotton dark brown. |
| Benzidine. | Salicylic acid + phenyl-amidonaphthol-sulphonic acid $\gamma$. | 1894. | A. Weinberg.<br>L. Cassella & Co. | **Appearance of dyestuff** : black brown powder.—**In water** : dark brown solution.—**On addition of hydrochloric acid** : bordeaux brown precipitate.—**On addition of caustic soda** : redder solution.—**In conc. sulphuric acid** : violet solution ; brown solution and precipitate on addition of water.—**Dyes** : unmordanted cotton dark brown, fast to acids and alkalies, tolerably fast to light and washing. |
| Benzidine. | Salicylic acid + 1 : 5-amido-naphthol-7-sulphonic acid. | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 2370$^{93}$.<br>Ger. Pat. 82572$^{93}$.<br>Fr. Pat. 229263. | **Appearance of dyestuff** : blackish brown powder.—**In water** : ruby red solution.—**In alcohol** : easily soluble, reddish violet solution.—**On addition of hydrochloric acid or caustic soda** : no change. **In conc. sulphuric acid** : dark violet solution, changed on dilution to wine red.—**Dyes** : unmordanted cotton dark brownish red, fairly fast to acids and washing, moderately fast to light. Fastness increased by coppering. |
| Benzidine. | Salicylic acid + 2 : 5-amido-naphthol-7-sulphonic acid. | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 2614$^{93}$.<br>Am. Pat. 555359.<br>Ger. Pat. 93276$^{93}$.<br>Fr. Pat. 227892. | **Appearance of dyestuff** : dark brown powder.—**In water** : red solution.—**In alcohol** : slightly soluble.—**On addition of hydrochloric acid to the aqueous solution** : no change.—**On addition of caustic soda** : slightly more violet.—**In conc. sulphuric acid** : blue solution, changed on dilution to wine red.—**Dyes** : unmordanted cotton dark red, same fastness as preceding. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 233 | **Oxamine Red B.** [*Remy.*] | Sodium salt of diphenyl-disazo-α-naphthol-sulphonic acid-*m*-phenylene-diamine-oxamic acid. | $C_{30}H_{20}N_6SO_7Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH\cdot CO\cdot CO_2Na\end{array}\right.\end{array}$ |
| 234 | **Diamine Scarlet B.**[*] [*C.*] | Sodium salt of diphenyl-disazo-phenetol-β-naphthol-γ-disulphonic acid. | $C_{30}H_{22}N_4O_8S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N-[1]C_6H_4[4]OC_2H_5\\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[6]}SO_3Na\\ {[8]}SO_3Na\end{array}\right.\end{array}$ |
| 235 | **Pyramine Orange 2 R.** [*B.*] | Sodium salt of diphenyl-disazo-nitro-*m*-phenylene-diamine-β-naphthyl-amine-disulphonic acid. | $C_{28}H_{20}N_8S_2O_8Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}NO_2\end{array}\right.\end{array}$ |
| 236 | **Pyramine Orange 3 G.** [*B.*] | Sodium salt of diphenyl-disazo-nitro-*m*-phenylene-diamine-*m*-phenylene-diamine-disulphonic acid. | $C_{24}H_{19}N_9S_2O_8Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}NO_2\end{array}\right.\\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[2]C_6H\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[4]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}$ |
| 237 | **Oxamine Scarlet B.** [*Remy.*] | Sodium salt of diphenyl-disazo-naphthionic-*m*-phenylene-diamine-oxamic acid. | $C_{30}H_{21}N_7SO_6Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\\ \vert \\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH\cdot CO\cdot CO_2Na\end{array}\right.\end{array}$ |
| 238 | **Glycine Corinth.** [*Ki.*] | Sodium salt of diphenyl-disazo-bi-α-naphthyl-glycine. | $C_{36}H_{26}N_6O_4Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[4]C_{10}H_6[1]NH\cdot CH_2\cdot CO_2Na\\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[4]C_{10}H_6[1]NH\cdot CH_2\cdot CO_2Na\end{array}$ |
| 239 | **Glycine Red.** [*Ki.*] | Sodium salt of diphenyl-disazo-α-naphthyl-glycine-naphthionic acid. | $C_{34}H_{24}N_6SO_5Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[4]C_{10}H_6[1]NH\cdot CH_2\cdot CO_2Na\\ \vert \\ C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\end{array}$ |
| 240 | **Congo Red.** [*A.*] [*By.*] | Sodium salt of diphenyl-disazo-bi-naphthionic acid. | $C_{32}H_{22}N_6O_6S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[2]C_{10}H_5\left\{\begin{array}{l}{[4]}SO_3Na\\ {[1]}NH_2\end{array}\right.\end{array}$ |
| 241 | **Brilliant Congo G.** [*A.*] [*By.*] | Sodium salt of diphenyl-disazo-β-naphthylamine-sulphonic-β-naphthylamine-disulphonic acid. | $C_{32}H_{21}N_6O_9S_3Na_3$ | $\begin{array}{l} C_6H_4[4]-N=N-[1]C_{10}H_5\left\{\begin{array}{l}{[2]}NH_2\\ {[6]}SO_3Na\end{array}\right.\\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[1]C_{10}H_4\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[2]}NH_2\end{array}\right.\end{array}$ |

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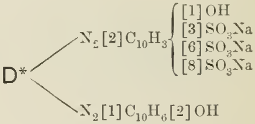
[*] **Diamine Scarlet 3 B** [*C.*] belongs to the same group, but is bluer. Allied products are also **Diamine Bordeaux B** [*C.*] and **Diamine**

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Benzidine. | α-Naphthol-sulphonic acid (1 : 4) + *m*-phenylene-diamine-oxamic acid. | 1894. | Markfeldt.<br>Eng. Pat. 22114.<br>Fr. Pat. 252140. | **Appearance of dyestuff**: black powder.—**In water**: red solution.—**In alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate.—**On addition of caustic soda**: cherry red solution.—**In conc. sulphuric acid**: pure blue solution; bluish red precipitate on dilution.—**Dyes**: unmordanted cotton direct bluish red, which can be diazotised and developed on the fibre, giving dark shades. |
| Ethylation of the dyestuff from tetrazotised benzidine, β-naphthol-disulphonic acid G, and phenol. | | 1889. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $12560^{89}$.<br>Am. Pat. 426345.<br>Ger. Pat. $54084^{89}$, dependent on 40954.<br>Fr. Pat. 200152. | **Appearance of dyestuff**: reddish crystalline powder.—**In water**: red solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: brownish red.—**On addition of caustic soda to the aqueous solution**: no change. **In conc. sulphuric acid**: violet solution; brown on dilution.—**Dyes**: wool and silk scarlet from an acid or neutral bath, cotton from an alkaline bath. |
| Benzidine. | β-Naphthyl-amine-disulphonic acid R + nitro-*m*-phenylene-diamine. | 1899. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $6827^{99}$.<br>Am. Pat. 631611.<br>Ger. Pat. $107731^{99}$.<br>Fr. Pat. 280914. | **Appearance of dyestuff**: reddish brown powder.—**In water**: sparingly soluble with a yellow colour and brownish red fluorescence.—**On addition of hydrochloric acid or caustic soda**: no change.—**In conc. sulphuric acid**: blue solution; yellowish red on dilution.—**Dyes**: unmordanted cotton reddish orange of good fastness to washing, heat, alkalies, and sulphur. |
| Benzidine. | Nitro-*m*-phenylene-diamine + *m*-phenylene-diamine-disulphonic acid. | 1898. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $18506^{98}$.<br>Am. Pat. 631610.<br>Ger. Pat. $105349^{98}$.<br>Fr. Pat. 280914. | **Appearance of dyestuff**: reddish brown powder.—**In water**: sparingly soluble with yellowish red colour.—**In alcohol**: sparingly soluble with yellowish green colour and slight brownish red fluorescence.—**On addition of hydrochloric acid or caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: yellowish red solution; brownish yellow on dilution.—**Dyes**: unmordanted cotton yellowish orange. |
| Benzidine. | Naphthionic acid + *m*-phenylene-diamine-oxamic acid. | 1894. | Markfeldt.<br>Eng. Pat. 22114.<br>Fr. Pat. 252140. | **Appearance of dyestuff**: reddish brown powder.—**In water**: red solution.—**On addition of hydrochloric acid**: violet black precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: pure blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton scarlet red from a salt bath. Diazotisable on the fibre. |
| Benzidine. | α-Naphthyl-glycine (2 mols.). | 1891. | Kinzlberger & Co.<br>Ger. Pat. 74775. | **Appearance of dyestuff**: brown powder.—**In water**: bluish red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**On addition of caustic soda**: red precipitate.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: cotton currant red from a soap bath. |
| Benzidine. | α-Naphthyl-glycine + naphthionic acid. | 1891. | Kinzlberger & Co.<br>Ger. Pat. 74775. | **Appearance of dyestuff**: reddish brown powder.—**In water**: yellowish red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid**: violet precipitate.—**On addition of caustic soda**: yellowish red precipitate.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: cotton red from a soap bath. |
| Benzidine. | Naphthionic acid (2 mols.). | 1884. | P. Böttiger.<br>Eng. Pat. $4415^{84}$ (amended).<br>Ger. Pat. $28753^{84}$.<br>O. N. Witt.<br>Ber. (1886) 19, 1719. | **Appearance of dyestuff**: reddish brown powder.—**In water**: reddish brown solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**Dilute acetic acid**: bluish violet precipitate.—**On addition of caustic soda to the aqueous solution**: reddish brown precipitate, soluble in water.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution.—**Dyes**: wool or unmordanted cotton red from a neutral or alkaline bath; very sensitive to acids, even organic acids. |
| Benzidine. | 1 mol. each β-naphthylamine monosulphonic acid β and di-sulphonic acid R. | 1886. | R. Krügener.<br>Berlin Aniline Co.<br>Eng. Pat. $6687^{87}$ (amended).<br>Ger. Pat. $41095^{87}$; third addn. to 28753.<br>Fr. Pat. $160722^{87}$. | **Appearance of dyestuff**: brown powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish violet precipitate.—**Dilute acetic acid**: solution rather bluer.—**On addition of caustic soda to the aqueous solution**: little change.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: cotton red from a soap bath; faster to light and acids than Congo Red. Also used for mixed wool and cotton goods. |

**Bordeaux S** [*C.*], which dye unmordanted cotton bordeaux shades fairly fast to washing and light; the S-mark also dyes wool in fast shades.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 242 | **Congo Corinth G.** [*A.*] [*By.*]<br>**Cotton Corinth G.** [*B.*] | Sodium salt of diphenyl-disazo-naphthionic-α-naphthol-sulphonic acid. | $C_{32}H_{21}N_5O_7S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[2]C_{10}H_5\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,NH_2\end{array}\right.\end{array}$ |
| 243 | **Congo Rubine.** [*A.*] | Sodium salt of diphenyl-disazo-naphthionic acid-β-naphthol-sulphonic acid. | $C_{32}H_{21}N_5S_2O_7Na_2$ | $\begin{array}{l} C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}\,NH_2\\ {[4]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[1]C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[8]}\,SO_3Na\end{array}\right.\end{array}$ |
| 244 | **Congo Violet.** [*A.*]<br>**Bordeaux COV.** [*A.*]<br>**Bordeaux Extra.** [*By.*] | Sodium salt of diphenyl-disazo-bi-β-naphthol-β-sulphonic acid. | $C_{32}H_{20}N_4O_8S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N-[1]C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[6]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[1]C_{10}H_5\left\{\begin{array}{l}{[6]}\,SO_3Na\\ {[2]}\,OH\end{array}\right.\end{array}$ |
| 245 | **Heliotrope 2 B.** [*By.*] [*A.*] [*L.*] | Sodium salt of diphenyl-disazo-α-naphthol-4 : 8-di-sulphonic-β-naphthol-8-sulphonic acid. | $C_{32}H_{19}N_4S_3O_{11}Na_3$ | $\begin{array}{l} C_6H_4[4]-N_2-[1]C_{10}H_5\left\{\begin{array}{l}{[2]}\,OH\\ {[8]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\\ {[8]}\,SO_3Na\end{array}\right.\end{array}$ |
| 246 | **Trisulphone Violet B.** [*K. S.*]<br>**Trisulphone Blue R.** [*K. S.*]<br>**Trisulphone Blue B.** [*K. S.*] | | |  |
| 247 | **Chicago Blue 4 R.** [*A.*]<br>**Columbia Blue R.** [*A.*] | Mixed disazo compounds from benzidine, amido-naphthol-sulphonic acid (1 : 8 : 4) or disulphonic acid (1 : 8 : 2 : 4), and a naphthol-sulphonic acid. | | For instance— $\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[2]}\,SO_3Na\\ {[4]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right.\end{array}$ |
| 248 | **Diamine Violet N.** [*C.*] | Sodium salt of diphenyl-disazo-bi-amido-naphthol-sulphonic acid. | $C_{32}H_{22}N_6O_8S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N=N-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right.\end{array}$ |
| 249 | **Diamine Black RO.** [*C.*] | Sodium salt of diphenyl-disazo-bi-amidonaphthol-sulphonic acid. | $C_{32}H_{22}N_6O_8S_2Na_2$ | $\begin{array}{l} C_6H_4[4]-N=N[7]C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4[4]-N=N[7]C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right.\end{array}$ |

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* D = residue of paradiamine, which for Trisulphone Violet is benzidine, for

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Benzidine. | Naphthionic acid + α-naphthol-monosulphonic acid NW. | 1886. | S. Pfaff.<br>Berlin Aniline Co.<br>Eng. Pats. $15296^{85}$, $2213^{86}$, $6687^{86}$.<br>Am. Pats. 344971 & 358865.<br>Ger. Pat. $39096^{86}$.<br>Fr. Pats. 160722 & 163172. | **Appearance of dyestuff**: greenish black powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: solution becomes violet.—**On addition of caustic soda**: solution becomes cherry red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: cotton brownish violet from a soap bath; moderately fast to washing, but not to light, alkalies, or acids. |
| Benzidine. | β-Naphthol-sulphonic acid B + naphthionic acid. | 1891. | G. Schultz.<br>Berlin Aniline Co.<br>Ger. Pat. 62659. | **Appearance of dyestuff**: greenish crystalline powder.—**In water** cherry red solution.—**On addition of hydrochloric acid**: pure blue precipitate.—**On addition of caustic soda**: violet red precipitate.—**In conc. sulphuric acid**: pure blue solution; blue precipitate on dilution.—**Dyes**: cotton direct bluish red. |
| Benzidine. | β-Naphthol-sulphonic acid B (2 mols.). | 1883.<br>1884. | G. Schultz.<br>Ber. (1884) 17, 462.<br>E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pats. $1225^{81}$ and $8495^{84}$.<br>Ger. Pat. $30077^{84}$; fourth addn. to 18027. | **Appearance of dyestuff**: brown powder.—**In water**: bordeaux red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: no change.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: violet solution; violet precipitate on dilution with water.—**Dyes**: wool bordeaux red from an acid bath; cotton violet from a salt bath. |
| Benzidine. | α-Naphthol-disulphonic acid S + β-naphthol sulphonic acid B. | 1892. | Kahn.<br>Fr. Bayer & Co.<br>Eng. Pat. 1346.<br>Ger. Pat. 45342. | **Appearance of dyestuff**: dark gray powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid**: bluish violet precipitate.—**On addition of caustic soda**: redder solution.—**In conc. sulphuric acid**: blue solution; on dilution reddish violet solution and finally violet precipitate.—**Dyes**: unmordanted cotton violet. |
| Benzidine, tolidine, or dianisidine. | α-Naphthol-trisulphonic acid + β-naphthol. | 1896. | Böninger.<br>Sandoz & Co.<br>Eng. Pat. $4703^{97}$.<br>Am. Pat. 584981.<br>Fr. Pat. 264279. | **Appearance of dyestuffs**: dark bronzy or blue powders.—**In water**: violet to pure blue solutions.—**On addition of hydrochloric acid**: bluish violet to blue precipitates.—**On addition of caustic soda**: reddish violet solutions.—**In conc. sulphuric acid**: greenish blue solutions; violet precipitates on dilution.—**Dye**: cotton and mixed fabrics violet to pure blue shades fast to alkalies. |
| Benzidine. | (1 : 8)-Amido-naphthol-monosulphonic acid S or di-sulphonic acid SS + naphthol-sulphonic acid. | 1894. | Möller.<br>Berlin Aniline Co. | **Appearance of dyestuffs**: violet powders.—**In water**: Chicago Blue 4 R gives a violet blue, Columbia Blue R a pure blue, solution.—**On addition of hydrochloric acid**: blue flocculent precipitates.—**On addition of caustic soda**: Chicago Blue 4 R becomes reddish violet, Columbia Blue R blue.—**In conc. sulphuric acid**: corn-flower blue solutions; violet precipitates on dilution.—**Dye**: cotton direct blue. |
| Benzidine. | Amido-naphthol-sulphonic acid G (or γ) in acid solution (2 mols.). | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. $16699^{89}$.<br>Ger. Pat. $55648^{89}$. | **Appearance of dyestuff**: blackish brown powder.—**In water**: reddish violet solution.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: violet black precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: greenish blue solution; reddish violet precipitate on dilution.—**Dyes**: unmordanted cotton violet, fairly fast to light, washing, and acids; wool and silk from neutral baths very fast shades. Employed also for mixed materials. |
| Benzidine. | Amido-naphthol-sulphonic acid G (or γ) in alkaline solution (2 mols.). | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. $16699^{89}$.<br>Ger. Pat. $55648^{89}$. | **Appearance of dyestuff**: black powder.—**In water**: violet black solution.—**In alcohol**: sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**On addition of caustic soda to the aqueous solution**: violet solution.—**In conc. sulphuric acid**: blue solution; reddish blue precipitate on dilution with water.—**Dyes**: unmordanted cotton grayish violet; after diazotisation on the fibre can be developed to a black fast to washing, light, acids, and alkalies. |

Trisulphone Blue R is tolidine, and for Trisulphone Blue B is dianisidine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 250 | **Diamine Brown V.** [*C.*] | Sodium salt of diphenyl-disazo-phenylene-diamine-amidonaphthol-sulphonic acid. | $C_{28}H_{22}N_7O_4SNa$ | $[1]\begin{array}{l} C_6H_4[4]-N=N[7]C_{10}H_4\left\{\begin{array}{l}[2]NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N=N-[4]C_6H_3\left\{\begin{array}{l}[1]NH_2\\ {[3]}NH_2\end{array}\right.\end{array}$ |
| 251 | **Diamine Black BH.** [*C.*] | Sodium salt of diphenyl-disazo-amidonaphthol-sulphonic acid-amidonaphthol-disulphonic acid. | $C_{32}H_{21}N_6S_3O_{11}Na_3$ | $[1]\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}[2]NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}[1]NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}$ |
| 252 | **Oxamine Violet.** [*B.*] | Sodium salt of diphenyl-disazo-bi-amidonaphthol-sulphonic acid. | $C_{32}H_{22}N_6S_2O_8Na_2$ | $[1]\begin{array}{l} C_6H_4[4]-N_2-[6]C_{10}H_4\left\{\begin{array}{l}[2]NH_2\\ {[5]}OH\\ {[7]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[6]C_{10}H_4\left\{\begin{array}{l}[2]NH_2\\ {[5]}OH\\ {[7]}SO_3Na\end{array}\right.\end{array}$ |
| 253 | **Diphenyl Blue Black.** [*G.*] | Sodium salt of diphenyl-disazo-ethyl-amidonaphthol-sulphonic-amido-naphthol-disulphonic acid. | $C_{22}H_{25}N_6S_3O_{11}Na_3$ | $[1]\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}[2]NHC_2H_5\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}[1]NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}$ |
| 254 | **Diamine Blue BB.** [*C.*]<br>**Benzo Blue BB.** [*By.*] [*Lev.*]<br>**Congo Blue 2 BX.** [*A.*] | Sodium salt of diphenyl-disazo-bi-amidonaphthol-disulphonic acid. | $C_{32}H_{20}N_6O_{14}S_4Na_4$ | $[1]\begin{array}{l} C_6H_4[4]-N=N[7]C_{10}H_3\left\{\begin{array}{l}[1]NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N=N[7]C_{10}H_3\left\{\begin{array}{l}[1]NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}$ |
| 255 | **Direct Gray R.** [*I.*] | Sodium salt of diphenyl-disazo-bi-dioxynaphthoic-sulphonic acid. | $C_{34}H_{18}N_4O_{14}S_2Na_2$ | $[1]\begin{array}{l} C_6H_4[4]-N=N-C_{10}H_3(OH)_2(CO_2Na)(SO_3Na)\\ \vert\\ C_6H_4[4]-N=N-C_{10}H_3(OH)_2(CO_2Na)(SO_3Na)\end{array}$ |
| 256 | **Direct Violet R.** [*Bl.*] | Sodium salt of diphenyl-disazo-*m*-tolylene-diamine-dioxynaphthoic-sulphonic acid. | $C_{30}H_{22}N_6SO_7Na$ | $[1]\begin{array}{l} C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}[1]NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[8]C_{10}H_3\left\{\begin{array}{l}[1]OH\\ {[7]}OH\\ {[2]}CO_2Na\\ {[4]}SO_3Na\end{array}\right.\end{array}$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Benzidine. | Amido-naphthol-sulphonic acid G (or $\gamma$) + *m*-phenylene-diamine. | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. $16699^{89}$. | **Appearance of dyestuff**: blackish powder.—**In water**: insoluble cold, sparingly hot to a brown red solution.—**In alcohol**; brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: chocolate brown precipitate.—**On addition of caustic soda to the aqueous solution**: purplish brown precipitate.—**In conc. sulphuric acid**: bluish violet solution; purplish brown precipitate on dilution.—**Dyes**: unmordanted cotton dark violet brown, tolerably fast to light, washing, alkalies, and acids. Can be developed to faster shades on the fibre. |
| Benzidine. | Amido-naphthol-sulphonic acid $\gamma$ + 1 : 8-amido-naphthol-disulphonic acid H. | 1890. | Gans & Hoffmann.<br>Ger. Pat. $68462^{91}$.<br>Fr. Pat. 233032. | **Appearance of dyestuff**: grayish blue powder.—**In water**: reddish blue solution.—**On addition of hydrochloric acid**: violet coloration.—**On addition of caustic soda**: reddish violet coloration.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: black blue on unmordanted cotton; on diazotisation and development it gives dark blue and black shades. |
| Benzidine. | 2 mols. of 2 : 5-Amido-naphthol-7-sulphonic acid (in alkaline solution). | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $2614^{93}$.<br>Am. Pat. 521096.<br>Fr. Pat. 227892.<br>Ger. Pat. 75469. | **Appearance of dyestuff**: dark glistening powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid or caustic soda**: violet precipitate.—**In conc. sulphuric acid**: pure blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton reddish violet; moderately fast to washing but not to light. Can be diazotised and developed on the fibre. |
| Benzidine. | Ethyl-amido-naphthol-sulphonic acid $\gamma$ + 1 : 8-amido-naphthol-disulphonic acid H. | 1895. | C. Ris & C. Simon.<br>J. R. Geigy & Co.<br>Eng. Pat. $2771^{96}$.<br>Am. Pat. 556164.<br>Ger. Pat. $103149^{95}$.<br>Fr. Pat. 250697. | **Appearance of dyestuff**: dark gray powder.—**In water**: dark blue solution.—**On addition of hydrochloric acid**: dark violet precipitate.—**On addition of caustic soda**: dark violet solution.—**In conc. sulphuric acid**: blue solution; dark violet precipitate on dilution.—**Dyes**: unmordanted cotton black blue. |
| Benzidine. | 2 mols. Amido-naphthol-disulphonic acid H (in alkaline solution). | 1890.<br>1890.<br>1890. | Rudolph.<br>Bammann & Ulrich.<br>M. Hoffmann.<br>Fr. Bayer & Co.<br>Eng. Pat. $13443^{90}$.<br>Am. Pat. 464135.<br>Fr. Pat. 210033.<br>L. Cassella & Co.<br>Eng. Pat. $1742^{91}$.<br>Ger. Pat. 74593. | **Appearance of dyestuff**: slate gray powder.—**In water**: reddish blue solution.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: no change of colour.—**In conc. sulphuric acid**: blue solution; violet on dilution with water.—**Dyes**: unmordanted cotton blue. |
| Benzidine. | 2 mols. Dioxy-naphthoic-sulphonic acid (from $\beta$-oxy-naphthoic acid of m.p. 216° by disulphonation and soda fusion). | 1891. | J. Schmid.<br>Société pour l'Industrie Chimique á Bâle.<br>Eng. Pat. $14253^{92}$.<br>Am. Pat. $493564^{93}$.<br>Fr. Pat. $220468^{92}$.<br>Ger. Pat. 75258. | **Appearance of dyestuff**: grayish black powder.—**In water**: sparingly soluble cold, easily hot with a violet colour.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: bluish gray precipitate.—**On addition of caustic soda to the warm aqueous solution**: dull violet red.—**In conc. sulphuric acid**: blue solution; bluish gray precipitate on dilution with water.—**Dyes**: unmordanted cotton reddish gray to bluish black shades fast to light. |
| Benzidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + *m*-tolylene-diamine. | 1894. | Müller.<br>Am. Pat. $524070^{94}$. | **Appearance of dyestuff**: black powder.—**In water**: violet solution.—**On addition of caustic soda**: solution redder.—**On addition of hydrochloric acid**: solution bluer.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton reddish violet. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 257 | **Direct Indigo Blue BN.** [*I.*] | Sodium salt of diphenyl-disazo-dioxynaphthoic-sulphonic-amido-naphthol-disulphonic acid. | $C_{33}H_{19}N_5S_3O_{14}Na_4$ | $\begin{array}{l} C_6H_4{[4]}-N_2-{[8]}C_{10}H_3\left\{\begin{array}{l}{[1]}OH\\ {[7]}OH\\ {[2]}CO_2Na\\ {[4]}SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4{[4]}-N_2-C_{10}H_3\left\{\begin{array}{l}NH_2\\ OH\\ (SO_3Na)_2\end{array}\right.\end{array}$ |
| 258 | **Alkali Dark Brown G & V.** [*D.*]<br>**Alkali Red Brown 3 R.** [*D.*] | | | Mixed disazo compounds from benzidine, tolidine, or dianisidine, and 1 mol. of the bisulphite derivative of nitroso-$\beta$-naphthol + 1 mol. of an amido-naphthol-sulphonic acid. |
| 259 | **Dianol Red 2 B.** [*Lev.*] | Sodium salt of dichlorodiphenyl-disazo-bi-naphthionic acid. | $C_{32}H_{20}N_6S_2O_6Na_2Cl_2$ | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\\ {[3]}Cl\end{array}\right. \\ {[1]}\,\vert \\ C_6H_3\left\{\begin{array}{l}{[3]}Cl\\ {[4]}-N_2-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 260 | **Dianol Red B.** [*Lev.*] | Sodium salt of dichlorodiphenyl-disazo-bi-$\beta$-naphthyl-amine-sulphonic acid. | $C_{32}H_{20}N_6S_2O_6Na_2Cl_2$ | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[1]}C_{10}H_5\left\{\begin{array}{l}{[2]}NH_2\\ {[6]}SO_3Na\end{array}\right.\\ {[3]}Cl\end{array}\right. \\ {[1]}\,\vert \\ C_6H_3\left\{\begin{array}{l}{[3]}Cl\\ {[4]}-N_2-{[1]}C_{10}H_5\left\{\begin{array}{l}{[2]}NH_2\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 261 | **Dianol Brilliant Red.** [*Lev.*]<br>**Toluylene Red.** [*O.*] | Sodium salt of dichlorobenzidine-disazo-bi-$\beta$-naphthyl-amine-disulphonic acid. | $C_{32}H_{18}N_6S_4O_{12}Na_4Cl_2$ | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[1]}C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[3]}Cl\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}Cl\\ {[4]}-N_2-{[1]}C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 262 | **Anthracene Red.*** [*I.*] [*By.*] | Sodium salt of nitrodiphenyl-disazo-salicylic-$\alpha$-naphthol-sulphonic acid. | $C_{28}H_{17}N_5SO_9Na_2$ | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\\ {[3]}NO_2\end{array}\right. \\ {[1]}\,\vert \\ C_6H_4{[4]}-N_2-{[4]}C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |
| 263 | **Glycine Blue.** [*Ki.*] | Sodium salt of diphenylsulphone-disazo-bi-$\alpha$-naphthyl-glycine. | | $O_2S\left\langle\begin{array}{l}C_6H_3{[4]}-N_2-{[4]}C_{10}H_6\cdot NH\cdot CH_2\cdot CO_2Na\\ \vert\\ C_6H_3{[4]}-N_2-{[4]}C_{10}H_6\cdot NH\cdot CH_2\cdot CO_2Na\end{array}\right.$ |
| 264 | **Sulphone Azurine.** [*By.*] | Sodium salt of disulpho-diphenyl-sulphone-disazo-bi-phenyl-$\beta$-naphthylamine. | $C_{44}H_{28}N_6O_8S_3Na_2$ | $O_2S\left\langle\begin{array}{l}C_6H_2(SO_3Na)-N=N-{[1]}C_{10}H_6{[2]}NHC_6H_5\\ \vert\\ C_6H_2(SO_3Na)-N=N-{[1]}C_{10}H_6{[2]}NHC_6H_5\end{array}\right.$ |
| 265 | **Pyramine Orange R.** [*B.*] | Sodium salt of disulphodiphenyl-disazo-bi-nitro-*m*-phenylene-diamine. | $C_{24}H_{18}N_{10}O_{10}S_2Na_2$ | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[4]}C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}NO_2\end{array}\right.\\ SO_3Na\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}SO_3Na\\ {[4]}-N_2-{[4]}C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}NO_2\end{array}\right.\end{array}\right.\end{array}$ |

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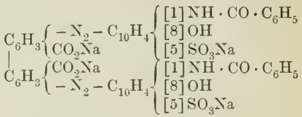
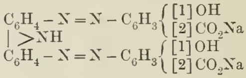
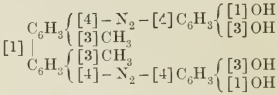
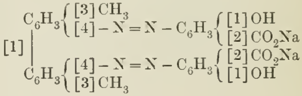
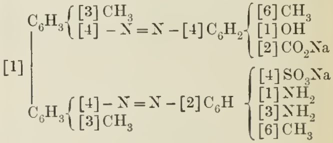
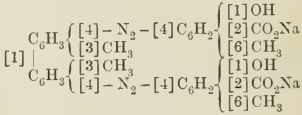
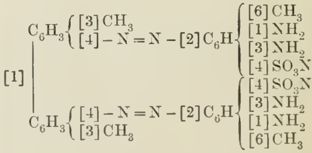
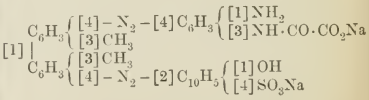
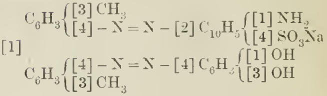
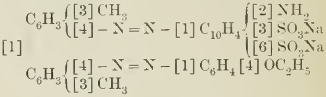
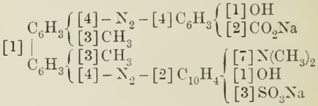
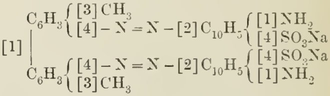
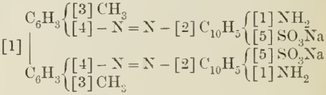
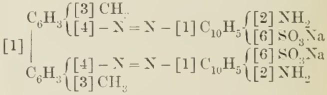
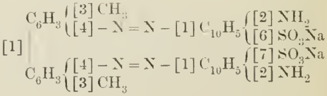
* Other colours derived from nitrobenzidine are **Salicine Red** [*K.*] (= nitrobenzidine, salicylic

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Benzidine. | Dioxy-naphthoic-sulphonic acid + amido-naphthol-disulphonic acid. | | Société pour l'Industrie Chimique à Bâsle.<br>Ger. Pat. 83244.<br>Fr. Pat. 233901. | **Dyes** : cotton direct from a slightly alkaline, mixed fabrics from a slightly acid bath, indigo blue. Fairly fast to light, acids, and alkalies. |
| | | 1897. | Elsässer.<br>Dahl & Co.<br>Am. Pat. 611111.<br>Ger. Pat. 95758. | Alkali Dark Brown G is a dark brown powder.—**In water** : violet red solution.—**On addition of hydrochloric acid** : the aqueous solution becomes bluer and gives a brown precipitate.—**On addition of caustic soda** : solution becomes yellower.—**In conc. sulphuric acid** : blue solution ; brown precipitate on dilution. —**Dyes** : cotton and half-wool direct dark brown. |
| Dichloro-benzidine. | 2 mols. of Naphthionic acid. | 1896. | H. Pfeiffer.<br>Levinstein Limd.<br>Eng. Pat. $25725^{96}$.<br>Am. Pat. 640743.<br>Fr. Pat. 265135. | **Appearance of dyestuff** : brownish red powder. —**In water** : red solution. —**In alcohol** : red solution. —**On addition of hydrochloric acid to the aqueous solution** : becomes violet.—**On addition of caustic soda** : red solution.—**In conc. sulphuric acid** : blue solution, changing to violet on dilution. —**Dyes** : cotton bluish red. |
| Dichloro-benzidine. | 2 mols. of β-Naphthyl-amine-sulphonic acid Br. | 1896. | H. Pfeiffer.<br>Levinstein Limd.<br>Eng. Pat. $25725^{96}$.<br>Am. Pat. $625174^{99}$.<br>Fr. Pat. 265135.<br>Ger. Pats. 94410 & 97101. | **Appearance of dyestuff** : dark red powder.—**In water or alcohol** : yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution** : violet red.—**On addition of caustic soda** : no change.—**In conc. sulphuric acid** : blue solution ; brown on dilution. —**Dyes** : unmordanted cotton yellowish red, fast to organic acids. |
| Dichloro-benzidine. | 2 mols. of β-Naphthyl-amine-disulphonic acid R. | 1896. | H. Pfeiffer.<br>Levinstein Limd.<br>Eng. Pat. $25725^{96}$.<br>Am. Pat. $625174^{99}$.<br>Fr. Pat. 265135.<br>Ger. Pats. 94410 & 97101. | **Appearance of dyestuff** : red powder.—**In water** : bluish red solution.—**In alcohol** : insoluble.—**On addition of hydrochloric acid to the aqueous solution** : slightly darker.—**On addition of caustic soda** : no change.—**In conc. sulphuric acid** : blue solution ; red on dilution. —**Dyes** : unmordanted cotton brilliant bluish red, fast to acids. |
| Nitro-benzidine. | 1 : 4-Naphthol-sulphonic acid + salicylic acid. | 1892. | Gnehm & Schmid.<br>Société pour l'Industrie Chimique à Bâsle.<br>Fr. Pat. $223176^{92}$.<br>Ger. Pat. $72867^{92}$. | **Appearance of dyestuff** : brownish red powder. —**In water** : red solution. —**On addition of hydrochloric acid** : red flocculent precipitate.—**On addition of caustic soda** : no change.—**In conc. sulphuric acid** : carmine red solution ; brownish red precipitate on dilution.—**Dyes** : wool from an acid bath a tolerably fast red. By subsequent chroming the shades become a bluish scarlet of good fastness to light, acids, and alkalies, and very fast to milling. |
| Benzidine-sulphone. | 2 mols. of α-Naphthyl-glycine. | 1891. | Kinzlberger & Co.<br>Ger. Pat. 74775. | **Appearance of dyestuff** : dark powder.— **In water** : bordeaux red solution. —**In alcohol** : bluish red solution. —**On addition of hydrochloric acid to the aqueous solution** : violet precipitate.—**On addition of caustic soda** : red precipitate.—**In conc. sulphuric acid** : blue solution ; violet precipitate on dilution.—**Dyes** : unmordanted cotton from a soap bath blue. |
| Benzidine-sulphone-disulphonic acid. | 2 mols. Phenyl-β-naphthyl-amine. | 1883.<br>-<br>1885. | P. Griess.<br>Eng. Pat. $1099^{84}$.<br>C. Duisberg.<br>Ber. **22**, 2459.<br>Fr. Bayer & Co.<br>Ger. Pats. $27954^{83}$ & $33088^{85}$.<br>J. Soc. Chem. Ind. 1890, 51, 55.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff** : dark grayish blue powder. - **In water** : blue solution.—**In alcohol** : dark blue solution.— **On addition of hydrochloric acid to the aqueous solution** : blue precipitate.—**On addition of caustic soda** : slow separation of a blue precipitate.—**In conc. sulphuric acid** : violet solution ; blackish violet precipitate on dilution with water. —**Dyes** : wool blue from a neutral bath containing sodium sulphate, unmordanted cotton blue from a neutral or soap bath. |
| Benzidine-disulphonic acid. | 2 mols. of Nitro-*m*-phenylene-diamine. | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $8564^{94}$.<br>Am. Pat 545333.<br>Ger. Pat. $80973^{93}$.<br>Fr. Pat. 238940. | **Appearance of dyestuff** : reddish powder.—**In water** : orange red solution. —**On addition of hydrochloric acid or caustic soda** : yellowish red precipitate.—**In conc. sulphuric acid** : yellow solution ; yellowish red precipitate on dilution.—**Dyes** : unmordanted cotton direct bright orange red, of good fastness to washing, acids, and alkalies. |

acid, and β-naphthol) and **Salicine Yellow** [*K.*] (nitrobenzidine and 2 mols. salicylic acid).

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 266 | **Naphthyl Blue 2 B.** [*B.*] | Sodium salt of dicarboxy-diphenyl-disazo-bi-benzoyl-amidonaphthol-sulphonic acid. | $C_{48}H_{28}N_6S_2O_{14}Na_4$ |  $\begin{array}{l} C_6H_3\left\{\begin{array}{l} -N_2-C_{10}H_4\left\{\begin{array}{l}{[1]}NH\cdot CO\cdot C_6H_5\\ {[8]}OH\\ {[5]}SO_3Na\end{array}\right.\\ CO_2Na\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l} CO_2Na\\ -N_2-C_{10}H_4\left\{\begin{array}{l}{[1]}NH\cdot CO\cdot C_6H_5\\ {[8]}OH\\ {[5]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 267 | **Carbazol Yellow.** [*B.*] | Sodium salt of carbazol-disazo-bi-salicylic acid. | $C_{26}H_{15}N_5O_6Na_2$ |  $\begin{array}{l} C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\\ \vert>NH\\ C_6H_4-N=N-C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |
| 268 | **Pyramidol Brown T.** [*P. L.*] | Sodium salt of ditolyl-disazo-bi-resorcin. | $C_{26}H_{22}N_4O_4$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[3]}OH\end{array}\right.\\ {[3]}CH_3\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}OH\\ {[1]}OH\end{array}\right.\end{array}\right.\end{array}$ |
| 269 | **Chrysamine R** [*By.*] [*A.*] | Sodium salt of ditolyl-disazo-bi-salicylic acid. | $C_{28}H_{20}N_4O_6Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N=N-C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-C_6H_3\left\{\begin{array}{l}{[2]}CO_2Na\\ {[1]}OH\end{array}\right.\\ {[3]}CH_3\end{array}\right.\end{array}$ |
| 270 | **Toluylene Orange G.** [*O.*] [*By.*] [*A.*]<br>**Kanthosine J.** | Sodium salt of ditolyl-disazo-*o*-cresol-carboxylic-*m*-tolylene-diamine-sulphonic acid. | $C_{29}H_{26}N_6O_6SNa_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N=N-[4]C_6H_2\left\{\begin{array}{l}{[6]}CH_3\\ {[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]C_6H\left\{\begin{array}{l}{[4]}SO_3Na\\ {[1]}NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\\ {[3]}CH_3\end{array}\right.\end{array}$ |
| 271 | **Cresotine Yellow R.** [*A.*] [*By.*] [*O.*] | Sodium salt of ditolyl-disazo-bi-*o*-cresol-carboxylic acid. | $C_{30}H_{24}N_4O_6Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\\ {[6]}CH_3\end{array}\right.\\ {[3]}CH_3\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\\ {[6]}CH_3\end{array}\right.\end{array}\right.\end{array}$ |
| 272 | **Toluylene Orange R.** [*O.*]<br>**Kanthosine R.** | Sodium salt of ditolyl-disazo-bi-*m*-tolylene-diamine-sulphonic acid. | $C_{28}H_{28}N_8S_2O_6Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N=N-[2]C_6H\left\{\begin{array}{l}{[6]}CH_3\\ {[1]}NH_2\\ {[3]}NH_2\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]C_6H\left\{\begin{array}{l}{[4]}SO_3Na\\ {[3]}NH_2\\ {[1]}NH_2\\ {[6]}CH_3\end{array}\right.\\ {[3]}CH_3\end{array}\right.\end{array}$ |
| 273 | **Oxamine Violet GR.** [*Remy.*] | Sodium salt of ditolyl-disazo-*m*-phenylene-diamine-oxamic-α-naphthol-sulphonic acid. | $C_{32}H_{24}N_6SO_7Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH\cdot CO\cdot CO_2Na\end{array}\right.\\ {[3]}CH_3\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Diamido-diphenic acid. | 2 mols. Benzoyl-1 : 8-amidonaphthol-5-sulphonic acid. | 1890. | Schraube.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $9676^{90}$.<br>Am. Pat. $524220^{94}$.<br>Ger. Pat. $54662^{90}$.<br>Fr. Pat. $206501^{90}$. | **Appearance of dyestuff**: dark blue powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: bluish violet precipitate.—**On addition of caustic soda**: magenta red solution.—**In conc. sulphuric acid**: pure blue solution; violet precipitate on dilution. **Dyes**: unmordanted cotton from a salt bath pure blue; not fast to light or alkalies, and not very fast to washing. |
| Diamido-carbazol. | 2 mols. Salicylic acid. | 1888. | R. Bohn.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $14478^{88}$ & $14479^{88}$.<br>Am. Pat. $401634^{89}$.<br>Ger. Pat. $46438^{88}$.<br>Fr. Pat. $193212^{88}$.<br>J. Soc. Dyers & Colorists, 1889, 106. | **Appearance of dyestuff**: brownish yellow powder.—**In water**: brownish yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: orange yellow solution.—**In conc. sulphuric acid**: violet blue solution; brown precipitate on dilution with water.—**Dyes**: unmordanted cotton from a boiling alkaline bath. |
| Tolidine. | 2 mols. of Resorcin. | 1898. | Pick Lange & Co. | **Appearance of dyestuff**: dark brown powder.—**In water**: reddish brown solution.—**In alcohol**: orange solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: brownish red solution.—**In conc. sulphuric acid**: violet solution; blackish brown precipitate on dilution.—**Dyes**: unmordanted cotton brownish red, developed to a deep brown by diazo solutions. |
| Tolidine. | 2 mols. Salicylic acid. | 1884. | E. Frank.<br>Fr. Bayer & Co.<br>Eng. Pat. $9606^{84}$.<br>Am. Pat. 329639.<br>Ger. Pat. $31658^{84}$. | **Appearance of dyestuff**: yellowish brown powder.—**In water**: brownish yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brown flocculent precipitate.—**Dilute acetic acid**: brown flocculent precipitate.—**On addition of caustic soda to the aqueous solution**: reddish brown colour.—**In conc. sulphuric acid**: reddish violet solution; brown flocculent precipitate on dilution with water.—**Dyes**: unmordanted cotton yellow from a soap bath; fast to light. |
| Tolidine. | *o*-Cresotic acid + *m*-tolylene diamine sulphonic acid. | 1888. | Chr. Rudolph and B. Priebs.<br>K. Oehler.<br>Eng. Pat. $7997^{88}$.<br>Ger. Pat. $47235^{88}$, dependent on 31658 and 44797.<br>Am. Pat. 396634. | **Appearance of dyestuff**: yellowish red powder with bluish cast.—**In water**: brownish yellow solution.—**Dilute acetic acid**: no change.—**On addition of hydrochloric acid to the aqueous solution**: yellowish brown flocculent precipitate.—**On addition of caustic soda**: solution becomes reddish orange.—**In conc. sulphuric acid**: magenta red solution; brown precipitate on dilution with water.—**Dyes**: unmordanted cotton orange; tolerably fast to light, washing, and acid. |
| Tolidine. | 2 mols. of *o*-Cresol-carboxylic acid. | 1888. | Rudolph & Priebs.<br>Fr. Bayer & Co.<br>Am. Pat. $394841^{88}$. | **Appearance of dyestuff**: light brown powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: brown yellow flocks.—**On addition of caustic soda**: orange solution or precipitate.—**In conc. sulphuric acid**: violet solution; on dilution a blue precipitate becoming green and finally yellow.—**Dyes**: unmordanted cotton yellow; fast to light. |
| Tolidine. | 2 mols. *m*-Tolylene-diamine-sulphonic acid. | 1886. | P. Friedländer.<br>B. Priebs.<br>K. Oehler.<br>Eng. Pat. $4492^{87}$.<br>Ger. Pat. $40905^{86}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: orange solution.—**Dilute acetic acid**: reddish opalescent solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish red flocculent precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: brown solution; reddish precipitate on dilution with water.—**Dyes**: unmordanted cotton reddish orange. Converted into a full fast reddish brown by development with diazotised paranitraniline. |
| Tolidine. | *m*-Phenylene-diamine-oxamic acid + α-naphthol-sulphonic acid (1 : 4). | 1894. | Markfeldt.<br>Eng. Pat. 22114.<br>Fr. Pat. 252140. | **Appearance of dyestuff**: dark bronzy powder.—**In water**: bluish red solution.—**On addition of hydrochloric acid**: violet precipitate.—**On addition of caustic soda**: solution becomes redder.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton dark reddish violet. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 274 | **Congo Red 4 R.**<br>[*A.*] [*By.*] | Sodium salt of ditolyl-disazo-resorcinol-naphthionic acid. | $C_{30}H_{24}N_5O_5SNa$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,OH\\ [3]\,OH\end{array}\right.\\ [3]\,CH_3\end{array}\right.\end{array}$ |
| 275 | **Congo Orange R.**<br>[*A.*] | Sodium salt of ditolyl-disazo-phenetol-β-naphthylamine-disulphonic acid. | $C_{32}H_{27}N_5O_7S_2Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}[2]\,NH_2\\ [3]\,SO_3Na\\ [6]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[1]\,C_6H_4\,[4]\,OC_2H_5\\ [3]\,CH_3\end{array}\right.\end{array}$ |
| 276 | **Diphenyl Brown 3 GN.** [*G.*] | Sodium salt of ditolyl-disazo-salicylic acid-dimethyl-amidonaphthol-sulphonic acid. | $C_{33}H_{27}N_5SO_7Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,OH\\ [2]\,CO_2Na\end{array}\right.\\ [3]\,CH_3\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N_2-[2]\,C_{10}H_4\left\{\begin{array}{l}[7]\,N(CH_3)_2\\ [1]\,OH\\ [3]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 277 | **Benzopurpurine 4 B.***<br>[*By.*] [*A.*] [*Lev.*]<br>**Cotton Red 4 B.**<br>[*B.*]<br>**Sultan Red 4 B.**<br>[*H.*] | Sodium salt of ditolyl-disazo-bi-naphthionic acid. | $C_{34}H_{26}N_6O_6S_2Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[4]\,SO_3Na\\ [1]\,NH_2\end{array}\right.\\ [3]\,CH_3\end{array}\right.\end{array}$ |
| 278 | **Benzopurpurine 6 B.**<br>[*A.*] [*By.*] | Sodium salt of ditolyl-disazo-bi-α-naphthylamine-sulphonic acid. | $C_{34}H_{26}N_6O_6S_2Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [5]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[5]\,SO_3Na\\ [1]\,NH_2\end{array}\right.\\ [3]\,CH_3\end{array}\right.\end{array}$ |
| 279 | **Benzopurpurine B.**<br>[*By.*] [*A.*] | Sodium salt of ditolyl-disazo-bi-β-naphthylamine-β-sulphonic acid. | $C_{34}H_{26}N_6O_6S_2Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,NH_2\\ [6]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[6]\,SO_3Na\\ [2]\,NH_2\end{array}\right.\\ [3]\,CH_3\end{array}\right.\end{array}$ |
| 280 | **Diamine Red B.**<br>[*A.*] [*By.*] [*L.*]<br>**Deltapurpurine 5 B.**<br>[*By.*] [*A.*] | Sodium salt of ditolyl-disazo-bi-β-naphthylamine-sulphonic acid. | $C_{34}H_{26}N_6O_6S_2Na_2$ |  $[1]\,\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,NH_2\\ [6]\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[7]\,SO_3Na\\ [2]\,NH_2\end{array}\right.\\ [3]\,CH_3\end{array}\right.\end{array}$ |

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* Benzopurpurine 4 B has also appeared in commerce under the following names:

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| 1 mol. tolidine. | 1 mol. naphthionic acid + 1 mol. resorcinol. | 1885. | S. Pfaff.<br>Actiengesellschaft für Anilinfabrikation.<br>Eng. Pats. $15296^{85}$ and $2213^{86}$ (amended).<br>Ger. Pat. $39096^{85}$, 2nd addn. to 28753. | **Appearance of dyestuff**: brown powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: scarcely altered.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton red from a soap bath. |
| Ethylation of the product obtained by combining 1 mol. of tetrazoditolyl with 1 mol. of β-naphthylamine-disulphonic acid R and 1 mol. of phenol. | | 1889. | Borgmann.<br>Actiengesellschaft für Anilinfabrikation.<br>Eng. Pat. $17957^{89}$.<br>Ger. Pat. 52328. | **Appearance of dyestuff**: yellowish red powder.—**In water**: yellowish red solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: dark brown precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: dark blue solution; dark brown precipitate on dilution with water.—**Dyes**: unmordanted cotton orange. |
| Tolidine. | Salicylic acid + dimethyl-amido-naphthol sulphonic acid γ. | 1895. | O. Ris.<br>Am. Pat. 567413.<br>Ger. Pat. $103149^{95}$.<br>Fr. Pat. 250697. | **Appearance of dyestuff**: dark brown powder.—**In water**: dark yellowish brown solution.—**On addition of hydrochloric acid**: brownish red precipitate.—**On addition of caustic soda**: brown solution.—**In conc. sulphuric acid**: violet blue solution; brownish red precipitate on dilution.—**Dyes**: unmordanted cotton dark yellowish brown. |
| 1 mol. Tolidine.<br>Also oxidation of toluene-azo-naphthionic acid (Badische). | 2 mols. Naphthionic acid. | 1884.<br>1885. | G. Schultz.<br>C. Duisberg.<br>Berlin Aniline Co.<br>Ger. Pat. $35615^{85}$, 1st addn. to 28753.<br>Am. Pat. 329632.<br>Fr. Bayer & Co.<br>Eng. Pat. $3803^{85}$.<br>Fr. Pat. 167876.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $6697^{95}$.<br>Fr. Pat. 248210.<br>Ger. Pat. 84893. | **Appearance of dyestuff**: brown powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**Dilute acetic acid**: brown precipitate.—**On addition of caustic soda**: no change of colour.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution with water.—**Dyes**: unmordanted cotton red from an alkaline bath, wool from a neutral bath. |
| 1 mol. tolidine. | 2 mols. α-naphthyl-amine-mono-sulphonic acid L. | 1885. | S. Pfaff. C. Duisberg.<br>Actiengesellschaft für Anilinfabrikation.<br>Ger. Pat. $35615^{85}$, 1st addn. to 28753.<br>Fr. Bayer & Co.<br>Eng. Pat. $3803^{85}$ (amended). | **Appearance of dyestuff**: red powder.—**In water**: orange red solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**Dilute acetic acid**: blue precipitate.—**On addition of caustic soda to the aqueous solution**: red solution.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution with water.—**Dyes**: unmordanted cotton red from an alkaline bath. |
| 1 mol. tolidine. | 2 mols. β-naphthyl-amine-mono-sulphonic acid Br. | 1885. | C. Duisberg.<br>Actiengesellschaft für Anilinfabrikation.<br>Ger. Pat. $35615^{85}$, 1st addn. to 28753.<br>Fr. Bayer & Co.<br>Eng. Pat. $3803^{85}$ (amended).<br>Am. Pat. 329633. | **Appearance of dyestuff**: brown powder.—**In water**: reddish brown solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**Dilute acetic acid**: solution becomes brown.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution; dark brown flocculent precipitate on dilution with water.—**Dyes**: unmordanted cotton red from an alkaline bath. |
| 1 mol. tolidine. | 1 mol. β-naphthyl-amine-δ-sulphonic acid + 1 mol. β-naphthyl-amine-sulphonic acid Br. | 1886. | Fr. Bayer and C. Duisberg.<br>Ber. 20, 1430.<br>Fr. Bayer & Co.<br>Eng. Pat. $5846^{86}$.<br>Ger. Pat. $42021^{86}$, dependent upon 28735.<br>Compare Ber. 20, 2910, 3160, & 3353. | **Appearance of dyestuff**: reddish brown powder.—**In water**: bright yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**Dilute acetic acid**: solution becomes brown.—**On addition of caustic soda to the aqueous solution**: red precipitate.—**In conc. sulphuric acid**: blue solution; brown precipitate on dilution.—**Dyes**: unmordanted cotton red from an alkaline bath. |

**Eclipse Red, Fast Scarlet, Azamine 4 B, Victoria Red, Imperial Red, etc.**

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 281 | **Brilliant Congo R.**<br>[*A.*] [*By.*] | Sodium salt of ditolyl-disazo-$\beta$-naphthylamine-monosulphonic-$\beta$-naphthylamine-disulphonic acid. | $C_{34}H_{25}N_6O_9S_3Na_3$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,NH_2\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 282 | **Diamine Red 3 B.**<br>[*C.*]<br>**Deltapurpurine 7 B.**<br>[*By.*] [*A.*] | Sodium salt of ditolyl-disazo-bi-$\beta$-naphthylamine-$\delta$-sulphonic acid. | $C_{34}H_{26}N_6O_6S_2Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,NH_2\\ {[7]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[7]}\,SO_3Na\\ {[2]}\,NH_2\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 283 | **Brilliant Purpurine R.**<br>[*A.*] [*By.*] | Sodium salt of ditolyl-disazo-naphthionic-$\beta$-naphthylamine-disulphonic acid. | $C_{34}H_{25}N_6O_9S_3Na_3$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[1]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,NH_2\\ {[4]}\,SO_3Na\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 234 | **Rosazurine G.**<br>[*By.*] | Sodium salt of ditolyl-disazo-ethyl-$\beta$-naphthylamine-sulphonic-$\beta$-naphthylamine-sulphonic acid. | $C_{36}H_{30}N_6O_6S_2Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,NHC_2H_5\\ {[7]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[7]}\,SO_3Na\\ {[2]}\,NH_2\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 285 | **Rosazurine B.**<br>[*By.*] | Sodium salt of ditolyl-disazo-bi-ethyl-$\beta$-naphthylamine-sulphonic acid. | $C_{38}H_{34}N_6O_6S_2Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,NHC_2H_5\\ {[7]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}{[7]}\,SO_3Na\\ {[2]}\,NHC_2H_5\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 286 | **Congo Corinth B.**<br>[*By.*] [*A.*] | Sodium salt of ditolyl-disazo-naphthionic-$\alpha$-naphthol-*p*-sulphonic acid. | $C_{34}H_{25}N_5O_7S_2Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,NH_2\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,OH\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 287 | **Azo Blue.**<br>[*By.*] [*A.*] | Sodium salt of ditolyl-disazo-bi-$\alpha$-naphthol-*p*-sulphonic acid. | $C_{34}H_{24}N_4O_8S_2Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,OH\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\end{array}$ |
| 288 | **Azo Black Blue.**<br>[*O.*]<br>**Azo Navy Blue.**<br>[*O.*] | Sodium salt of ditolyl-disazo-*m*-oxy-diphenylamine-amidonaphthol-di-sulphonic acid. | $C_{36}H_{28}N_6S_2O_8Na_2$ | $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,NHC_6H_5\end{array}\right.\\ {[3]}\,CH_3\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |

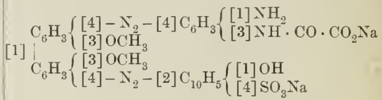
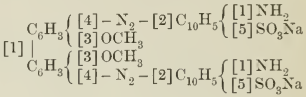
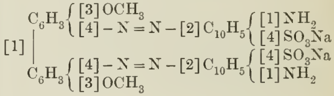
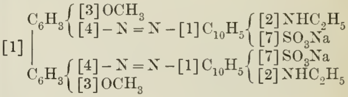
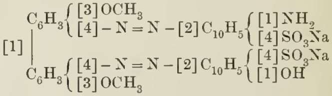
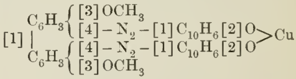
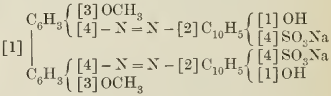
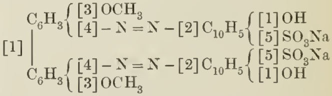
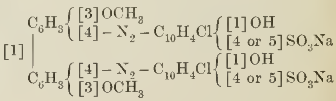
| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| 1 mol. tolidine. | 1 mol. β-naphthylamine monosulphonic acid Br. + 1 mol. β-naphthylamine disulphonic acid R. | 1886. | S. Pfaff and R. Krügener.<br>Actiengesellschaft für Anilinfabrikation.<br>Eng. Pat. $6687^{87}$ (amended).<br>Ger. Pat. $41095^{87}$, 3rd addn. to 28753. | **Appearance of dyestuff**: brown powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid to the aqueous solution**: reddish brown precipitate.—**Dilute acetic acid**: colour somewhat bluer.—**On addition of caustic soda to the aqueous solution**: reddish yellow precipitate soluble in much water.—**In conc. sulphuric acid**: blue solution; brownish black precipitate on dilution—**Dyes**: unmordanted cotton red from a soap bath. |
| 1 mol. tolidine. | 2 mols. β-naphthylamine-δ-sulphonic acid. | 1886. | Fr. Bayer and C. Duisberg.<br>Ber. **20**, 2910, 3160.<br>Fr. Bayer & Co.<br>Eng. Pat. $4846^{86}$.<br>Ger. Pat. $42021^{86}$, dependent upon 28753.<br>L. Cassella & Co.<br>Eng. Pat. $12908^{86}$.<br>Ger. Pat. 48074. | **Appearance of dyestuff**: reddish brown powder.—**In water**: sparingly soluble cold, easily on boiling.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**With acetic acid**: brownish violet precipitate.—**Magnesium sulphate**: precipitates the magnesium salt; sparingly soluble in water.—**On addition of caustic soda to the aqueous solution**: red precipitate.—**In conc. sulphuric acid**: blue solution; yellowish brown precipitate on dilution with water.—**Dyes**: unmordanted cotton red from an alkaline bath. |
| 1 mol. tolidine. | 1 mol. β-naphthylamine-disulphonic acid R + 1 mol. naphthionic acid. | 1887. | Actiengesellschaft für Anilinfabrikation.<br>Eng. Pat. $6687^{87}$.<br>Ger. Pat. $41095^{87}$.<br>Fr. Pat. $160722^{87}$. | **Appearance of dyestuff**: red powder.—**In water**: red solution.—**In alcohol**: yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution**: black precipitate.—**On addition of caustic soda to the aqueous solution**: red precipitate.—**In conc. sulphuric acid**: blue solution; blue black precipitate on dilution with water.—**Dyes**: unmordanted cotton red from an alkaline bath. |
| 1 mol. tolidine. | 1 mol. ethyl-β-naphthylamine-δ-sulphonic acid + 1 mol. β-naphthylamine-δ-sulphonic acid. | 1886. | E. Hassenkamp and C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $17083^{86}$.<br>Ger. Pat. $41761^{86}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: reddish violet precipitate.—**Dilute acetic acid**: no change.—**On addition of caustic soda to the aqueous solution**: scarcely altered.—**In conc. sulphuric acid**: blue; reddish violet precipitate on dilution with water.—**Dyes**: unmordanted cotton bluish red from an alkaline bath. |
| 1 mol. tolidine. | 2 mols. ethyl-β-naphthylamine-δ-sulphonic acid. | 1886. | E. Hassenkamp.<br>Fr. Bayer & Co.<br>Eng. Pat. $17083^{86}$.<br>Ger. Pat. $41761^{86}$. | **Appearance of dyestuff**: brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: reddish violet precipitate.—**Dilute acetic acid**: colour somewhat darker.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: cotton bluish red from an alkaline bath. |
| 1 mol. tolidine. | 1 mol. naphthionic acid + 1 mol. α-naphthol-monosulphonic acid NW. | 1885. | S. Pfaff.<br>Actiengesellschaft für Anilinfabrikation.<br>Eng. Pats. $15296^{85}$; $2213^{86}$; $6687^{86}$.<br>Am. Pat. 358865.<br>Ger. Pat. 39096, 2nd addn. to 28753. | **Appearance of dyestuff**: grayish black powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: solution rather bluer.—**On addition of caustic soda to the aqueous solution**: colour becomes cherry red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton brownish violet from a soap bath. |
| 1 mol. tolidine. | 2 mols. α-naphthol-monosulphonic acid NW. | 1885. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $9510^{85}$ (amended).<br>Am. Pat. 366078.<br>Ger. Pat. $35341^{85}$. | **Appearance of dyestuff**: bluish black powder.—**In water**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: no change.—**On addition of caustic soda**: the solution becomes magenta red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton grayish violet from a soap bath. |
| Tolidine. | *m*-Oxydiphenylamine + 1 : 8-amidonaphthol-3 : 6-disulphonic acid. | 1890. | Rudolph.<br>K. Oehler.<br>Eng. Pat. $10861^{91}$ | **Appearance of dyestuff**: grayish brown powder.—**In water**: brownish violet solution.—**In conc. sulphuric acid**: blue solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton gray to dark violet blue from a boiling salt bath. By subsequent chroming becomes very fast to washing, alkalies, and acids, but not to light or chlorine. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 289 | **Azo Mauve.**<br>[*O.*] | Sodium salt of ditolyl-disazo-α-naphthylamine-amido-naphthol-disulphonic acid. | $C_{34}H_{26}N_6O_7S_2Na_2$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N=N-C_{10}H_3(NH_2)(OH)(SO_3Na)_2\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[4]}-N=N-C_{10}H_6\cdot NH_2\\ {[3]}CH_3\end{cases}\end{array}$ |
| 290 | **Oxamine Blue 3 R.**<br>[*B.*] | Sodium salt of ditolyl-disazo-α-naphthol-sulphonic-amido-naphthol-sulphonic acid. | $C_{34}H_{25}N_5S_2O_8Na_2$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[4]}-N_2-[2]C_{10}H_5\begin{cases}{[1]}OH\\ {[4]}SO_3Na\end{cases}\\ {[3]}CH_3\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N_2-[6]C_{10}H_4\begin{cases}{[2]}NH_2\\ {[5]}OH\\ {[7]}SO_3Na\end{cases}\end{cases}\end{array}$ |
| 291 | **Columbia Blue G.**<br>[*A.*]<br>**Chicago Blue 2 R.**<br>[*A.*] | Mixed disazo dyestuffs from tolidine, amido-naphthol-sulphonic acids, and a third component. | | |
| 292 | **Chicago Blue R.**<br>[*A.*] | Sodium salt of ditolyl-disazo-bi-amidonaphthol-sulphonic acid. | $C_{34}H_{26}N_6S_2O_8Na_2$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[4]}-N_2-[7]C_{10}H_4\begin{cases}{[1]}NH_2\\ {[8]}OH\\ {[4]}SO_3Na\end{cases}\\ {[3]}CH_3\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N_2-[7]C_{10}H_4\begin{cases}{[1]}NH_2\\ {[8]}OH\\ {[4]}SO_3Na\end{cases}\end{cases}\end{array}$ |
| 293 | **Diamine Blue 3 B.**<br>[*C.*]<br>**Benzo Blue 3 B.**<br>[*By.*]<br>**Congo Blue 3 B.**<br>[*A.*] [*Lev.*] | Sodium salt of ditolyl-disazo-bi-amido-naphthol-disulphonic acid. | $C_{34}H_{24}N_6O_{14}S_4Na_4$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N=N[7]C_{10}H_3\begin{cases}{[1]}NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{cases}\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[4]}-N=N[7]C_{10}H_3\begin{cases}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[1]}NH_2\end{cases}\\ {[3]}CH_3\end{cases}\end{array}$ |
| 294 | **Diamine Blue BX.**<br>[*C.*]<br>**Benzo Blue BX.**<br>[*By.*]<br>**Congo Blue BX.**<br>[*A.*] [*Lev.*] | Sodium salt of ditolyl-disazo-α-naphthol-monosulphonic-amido-naphthol-disulphonic acid. | $C_{34}H_{24}N_5O_{11}S_3Na_3$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N=N-[2]C_{10}H_5\begin{cases}{[1]}OH\\ {[4]}SO_3Na\end{cases}\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[4]}-N=N-[7]C_{10}H_3\begin{cases}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[1]}NH_2\end{cases}\\ {[3]}CH_3\end{cases}\end{array}$ |
| 295 | **Direct Blue R.**<br>[*I.*] | Sodium salt of ditolyl-disazo-dioxy-naphthoic-sulphonic-α-naphthol-*p*-sulphonic acid. | $C_{35}H_{23}N_4O_{11}S_2Na_3$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N=N-C_{10}H_3(OH)_2(CO_2Na)(SO_3Na)\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[4]}-N=N-C_{10}H_5(OH)(SO_3Na)\\ {[3]}CH_3\end{cases}\end{array}$ |
| 296 | **Indazurine RM.**<br>[*Bl.*] | Sodium salt of ditolyl-disazo-dioxy-naphthoic-sulphonic-α-naphthol-*p*-sulphonic acid. | $C_{35}H_{23}N_4O_{11}S_2Na_3$ | $[1]\ \begin{array}{l} C_6H_3\begin{cases}{[4]}-N_2-[8]C_{10}H_3\begin{cases}{[1]}OH\\ {[7]}OH\\ {[2]}CO_2Na\\ {[4]}SO_3Na\end{cases}\\ {[3]}CH_3\end{cases}\\ \vert \\ C_6H_3\begin{cases}{[3]}CH_3\\ {[4]}-N_2-[2]C_{10}H_5\begin{cases}{[1]}OH\\ {[4]}SO_3Na\end{cases}\end{cases}\end{array}$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Tolidine. | Amido-naphthol-di-sulphonic acid + α-naphthylamine. | 1890. | Chr. Rudolph.<br>K. Oehler.<br>Ger. Pat. $1434^{90}$. | **Appearance of dyestuff**: blackish powder.—**In water**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: colour rather bluer.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution; violet on dilution with water.—**Dyes**: unmordanted cotton blackish blue violet from an alkaline bath. |
| Tolidine. | α-Naphthol-sulphonic acid (1 : 4) + 2 : 5-amido-naphthol-7-sulphonic acid. | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $2614^{93}$.<br>Am. Pat. $521095^{94}$.<br>Ger. Pat. $93276^{93}$.<br>Fr. Pat. $227892^{93}$. | **Appearance of dyestuff**: dark brownish violet powder.—**In water**: violet solution.—**On addition of hydrochloric acid**: violet precipitate, soluble in water.—**On addition of caustic soda**: violet solution or precipitate.—**In conc. sulphuric acid**: pure blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton direct from a salt bath violet blue, fairly fast to light and acids, moderately fast to washing, diazotisable on the fibre. |
| Tolidine. | 1 : 8-Amido-naphthol-sulphonic acid S + third component, *i.e.* a naphthol-sulphonic acid. | 1894. | Möller.<br>Berlin Aniline Co. | **Appearance of dyestuffs**: Columbia Blue G is a blue powder, Chicago Blue 2 R a brown powder.—**In water**: Columbia Blue G forms a pure blue solution, Chicago Blue 2 R a violet blue solution.—**On addition of hydrochloric acid**: Columbia Blue G gives blue flocks, Chicago Blue 2 R a pure blue solution.—**On addition of caustic soda**: both give a reddish violet solution.—**In conc. sulphuric acid**: Columbia Blue G gives a greenish blue solution, Chicago Blue 2 R a cornflower blue solution.—**On dilution with water**: Columbia Blue G throws down reddish violet flocks, Chicago Blue 2 R blue flocks.—**Dye**: unmordanted cotton direct blue. |
| Tolidine. | 2 mols. 1 : 8-Amido-naphthol-4-sulphonic acid. | 1893. | Möller.<br>Berlin Aniline Co. | **Appearance of dyestuff**: blue powder.—**In water**: violet blue solution.—**In alcohol**: blue solution.—**On addition of hydrochloric acid to the aqueous solution**: dark violet flocculent precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: cornflower blue solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton direct blue. |
| Tolidine. | 2 mols. Amido-naphthol-di-sulphonic acid H (in alkaline solution). | 1890.<br>1890. | Bammann & Ulrich.<br>M. Hoffmann.<br>Fr. Bayer & Co.<br>Ger. Pat. 74593.<br>Fr. Pat. $210033^{90}$.<br>Eng. Pat. $13443^{90}$.<br>L. Cassella & Co.<br>Eng. Pat. $1742^{91}$. | **Appearance of dyestuff**: slate gray powder.—**In water**: violet solution.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: bluer; violet precipitate with an excess.—**On addition of caustic soda**; no change.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton blue. |
| Tolidine. | α-Naphthol-monosulphonic acid NW. + amido-naphthol-di-sulphonic acid H (in alkaline solution). | 1890.<br>1890. | Bammann & Ulrich.<br>M. Hoffmann.<br>L. Cassella & Co.<br>Eng. Pat. $1742^{91}$.<br>Fr. Bayer & Co.<br>Ger. Pat. 74593. | **Appearance of dyestuff**: dark powder.—**In water**: bluish violet solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**On addition of caustic soda**: the solution becomes bluish red.—**In sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton a deep blue, moderately fast to light and washing. Can be diazotised and developed. |
| Tolidine. | Dioxy-naphthoic-sulphonic acid + α-naphthol-*p*-sulphonic acid. | 1891. | J. Schmid.<br>Société pour l'Industrie Chimique à Bâle.<br>Am. Pat. 493564.<br>Fr. Pat. 220468.<br>Ger. Pat. 75258. | **Appearance of dyestuff**: bluish black powder.—**In water**: violet solution.—**On addition of hydrochloric acid**: violet precipitate.—**On addition of caustic soda**: violet red solution.—**In conc. sulphuric acid**: blue solution.—**Dyes**: unmordanted cotton black violet. |
| Tolidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + α-naphthol-sulphonic acid (1 : 4). | 1894. | Müller.<br>Am. Pat. $524070^{94}$. | **Appearance of dyestuff**: blackish green powder.—**In water**: violet blue solution.—**On addition of hydrochloric acid**: bluer.—**On addition of caustic soda**: solution becomes red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes** unmordanted cotton reddish blue. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 297 | **Indazurine TS.** [*Bl.*] | Sodium salt of ditolyl-disazo-dioxy-naphthoic-sulphonic-amidonaphthol-sulphonic acid. | $C_{35}H_{24}N_5S_2O_{11}Na_3$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[8]}C_{10}H_3\left\{\begin{array}{l}{[1]}OH\\ {[7]}OH\\ {[2]}CO_2Na\\ {[4]}SO_3Na\end{array}\right.\\ {[3]}CH_3\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-{[7]}C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 298 | **Direct Gray B.** [*I.*] | Sodium salt of ditolyl-disazo-bi-dioxynaphthoic-sulphonic acid. | $C_{36}H_{22}N_4O_{14}S_2Na_2$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-C_{10}H_3(OH)_2(CO_2Na)\,(SO_3Na)\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-C_{10}H_3(OH)_2(CO_2Na)\,(SO_3Na)\\ {[3]}\,CH_3\end{array}\right.\end{array}\right.$ |
| 299 | **Diamine Yellow N.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-phenetol-salicylic acid. | $C_{29}H_{25}N_4O_5Na$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}OC_2H_5\\ {[4]}-N=N-C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[4]}\,C_6H_4\,{[1]}\,OC_2H_5\end{array}\right.$ |
| 300 | **Diamine Red NO.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-β-naphthylamine-β-sulphonic-β-naphthylamine-δ-sulphonic acid. | $C_{34}H_{26}N_6O_7S_2Na_2$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,OC_2H_5\\ {[4]}-N=N-{[1]}\,C_{10}H_5\left\{\begin{array}{l}{[2]}\,NH_2\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[1]}\,C_{10}H_5\left\{\begin{array}{l}{[7]}\,SO_3Na\\ {[2]}\,NH_2\end{array}\right.\end{array}\right.$ |
| 301 | **Diamine Blue 3 R.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-bi-α-naphthol-*p*-sulphonic acid. | $C_{34}H_{24}N_4O_9S_2Na_2$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,OC_2H_5\\ {[4]}-N=N-{[2]}\,C_{10}H_5\left\{\begin{array}{l}{[1]}\,OH\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[2]}\,C_{10}H_5\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,OH\end{array}\right.\end{array}\right.$ |
| 302 | **Diamine Blue B.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-β-naphthol-δ-disulphonic-α-naphthol-monosulphonic acid. | $C_{34}H_{23}N_4O_{12}S_3Na_3$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,OC_2H_5\\ {[4]}-N=N-{[1]}\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[3]}\,SO_3Na\\ {[7]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[2]}\,C_{10}H_5\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}\,OH\end{array}\right.\end{array}\right.$ |
| 303 | **Diamine Blue Black E.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-amido-naphthol-mono-sulphonic-β-naphthol-δ-disulphonic acid. | $C_{34}H_{24}N_5O_{12}S_3Na_3$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,OC_2H_5\\ {[4]}-N=N-{[1]}\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,OH\\ {[3]}\,SO_3Na\\ {[7]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[5]}\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.$ |
| 304 | **Diamine Black BO.** [*C.*] | Sodium salt of ethoxy-diphenyl-disazo-bi-amido-naphthol-sulphonic acid. | $C_{34}H_{26}N_6O_9S_2Na_2$ | $[1]\left\vert\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,OC_2H_5\\ {[4]}-N=N-{[5]}\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4\,{[4]}-N=N-{[5]}\,C_{10}H_4\left\{\begin{array}{l}{[6]}\,SO_3Na\\ {[8]}\,OH\\ {[2]}\,NH_2\end{array}\right.\end{array}\right.$ |

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Tolidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + 2 : 8-amidonaphthol-6-sulphonic acid. | 1894. | Müller.<br>Am. Pat. $524070^{94}$. | **Appearance of dyestuff** : blackish blue powder.—**In water** ; violet blue solution.—**On addition of hydrochloric acid or caustic soda** : solution redder.—**In conc. sulphuric acid** : blue solution ; violet precipitate on dilution.—**Dyes** : unmordanted cotton reddish blue. Diazotised and developed on the fibre it gives blacks and navy blues. |
| 1 mol. tolidine. | 2 mols. dioxynaphthoic-sulphonic acid. | 1892. | Société pour l'Industrie Chimique à Bâle. | **Appearance of dyestuff** : grayish black powder.—**Behaviour with reagents** : the same as direct gray R.—**Dyes** : unmordanted cotton steel gray to bluish black shades. |
| Ethylation of the product obtained by combination of 1 mol. of diazotised ethoxybenzidine with 1 mol. of phenol and 1 mol. of salicylic acid. | | 1887. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $14464^{87}$.<br>Am. Pat. 380067.<br>Ger. Pat. $46134^{87}$.<br>Fr. Pats. 186566 and 186567.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff** : brownish yellow powder.—**In water** : sparingly soluble.—**In alcohol** : more easily soluble.—**On addition of hydrochloric acid to the aqueous solution** : greenish precipitate.—**On addition of caustic soda to the aqueous solution** : reddish yellow precipitate.—**In conc. sulphuric acid** : violet solution ; greenish brown precipitate on dilution with water.—**Dyes** : unmordanted cotton yellow. |
| 1 mol. ethoxybenzidine. | 1 mol. β-naphthylamine-β-sulphonic acid + 1 mol. β-naphthylamine-δ-sulphonic acid. | 1887. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $14464^{87}$.<br>Am. Pat. 380067.<br>Ger. Pat. $46134^{87}$.<br>Fr. Pats. 186566 and 186567.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff** : greenish crystalline powder.—**In water** : red solution.—**In alcohol** : sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution** : violet precipitate.—**On addition of caustic soda** : no change.—**In conc. sulphuric acid** : blue solution ; black precipitate on dilution with water.—**Dyes** : unmordanted cotton red from an alkaline bath. |
| 1 mol. ethoxybenzidine. | 2 mols. α-naphtholmonosulphonic acid NW. | 1887. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $14464^{87}$.<br>Am. Pat. 380067.<br>Ger. Pat. $46134^{87}$.<br>Fr. Pats. 186566 and 186567. | **Appearance of dyestuff** : black powder with greenish lustre.—**In water** : easily soluble hot, with reddish blue colour.—**In alcohol** : sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution** : no change.—**On addition of caustic soda** : solution becomes reddish violet.—**In conc. sulphuric acid** : dark blue solution ; violet precipitate on dilution with water.—**Dyes** : unmordanted cotton reddish blue. |
| 1 mol. ethoxybenzidine. | 1 mol. β-naphthol-δ-disulphonic acid + 1 mol. α-naphtholmonosulphonic acid NW. | 1887. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $14464^{87}$.<br>Am. Pat. 380067.<br>Ger. Pat. $46134^{87}$.<br>Fr. Pats. 186566 and 186567. | **Appearance of dyestuff** : dark bronzy powder.—**In water** : blue solution.—**In alcohol** : insoluble.—**On addition of hydrochloric acid to the aqueous solution** : blue precipitate.—**On addition of caustic soda** : solution becomes reddish blue.—**In conc. sulphuric acid** : blue solution ; blue precipitate on dilution with water.—**Dyes** : unmordanted cotton blue. |
| 1 mol. ethoxybenzidine. | 1 mol. β-naphthol-δ-disulphonic acid + 1 mol. amidonaphtholmonosulphonic acid G (or γ) in alkaline solution. | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. $16699^{89}$.<br>Ger. Pat. 57857. | **Appearance of dyestuff** : black powder.—**In water** : blackish blue solution.—**In alcohol** : insoluble.—**On addition of hydrochloric acid to the aqueous solution** : blue precipitate.—**On addition of caustic soda to the aqueous solution** : no change.—**In conc. sulphuric acid** : blackish blue solution ; blue precipitate on dilution with water.—**Dyes** : unmordanted cotton a black blue. |
| 1 mol. ethoxybenzidine. | 2 mols. amidonaphtholsulphonic acid G (or γ) in alkaline solution. | 1889. | L. Gans.<br>L. Cassella & Co.<br>Eng. Pat. $16699^{89}$.<br>Ger. Pat. $55648^{89}$.<br>T. Baldensperger.<br>J. Soc. Chem. Ind. 1891, 762.<br>A. Kertész.<br>Chem. Zeit. 15, 701. | **Appearance of dyestuff** : black powder.—**In water** : blackish blue solution.—**In alcohol** : sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution** : blue precipitate.—**On addition of caustic soda to the aqueous solution** : no change.—**In conc. sulphuric acid** : blackish blue solution ; reddish blue precipitate on dilution with water.—**Dyes** : unmordanted cotton blue black.—By diazotisation on the fibre and combination with naphthols, etc., extremely fast deep " ingrain " blacks are obtained. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 305 | **Oxamine Black BR.** [*Remy.*] | Sodium salt of dimethoxy-diphenyl-disazo-phenylene-diamine-oxamic-α-naphthol-sulphonic acid. | $C_{32}H_{24}N_6SO_9Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}[1]\,NH_2\\ [3]\,NH\cdot CO\cdot CO_2Na\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N_2-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,OH\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 306 | **Diazurine B.** [*By.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-α-naphthyl-amine-5-sulphonic acid. | $C_{34}H_{26}N_6S_2O_8Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[4]-N_2-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [5]\,SO_3Na\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N_2-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [5]\,SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 307 | **Benzopurpurine 10 B.** [*By.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-naphthionic acid. | $C_{34}H_{26}N_6O_8S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[4]\,SO_3Na\\ [1]\,NH_2\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |
| 308 | **Heliotrope B.** [*By.*] [*A.*] [*L.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-ethyl-β-naphthylamine-β-sulphonic acid. | $C_{38}H_{32}N_6O_8S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[2]\,NHC_2H_5\\ [7]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[1]\,C_{10}H_5\left\{\begin{array}{l}[7]\,SO_3Na\\ [2]\,NHC_2H_5\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |
| 309 | **Azo Violet.** [*By.*] | Sodium salt of dimethoxy-diphenyl-disazo-naphthionic-α-naphthol-*p*-sulphonic acid. | $C_{34}H_{25}N_5O_9S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,NH_2\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[4]\,SO_3Na\\ [1]\,OH\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |
| 310 | **Dianisidine Blue.** [*By.*] [*M.*]<br>**Azophor Blue.** | Copper derivative of dimethoxy-diphenyl-disazo-bi-β-naphthol. | |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N_2-[1]\,C_{10}H_6\,[2]\,O\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N_2-[1]\,C_{10}H_6\,[2]\,O\\ [3]\,OCH_3\end{array}\right.\end{array}\!\!>Cu$ |
| 311 | **Benzoazurine G.*** [*By.*] [*A.*] [*L.*]<br>**Bengal Blue G.** | Sodium salt of dimethoxy-diphenyl-disazo-bi-α-naphthol-*p*-sulphonic acid. | $C_{34}H_{24}N_4O_{10}S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,OH\\ [4]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[4]\,SO_3Na\\ [1]\,OH\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |
| 312 | **Benzoazurine 3 G.** [*By.*] [*Lev.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-α-naphthol-*p*-sulphonic acid. | $C_{34}H_{24}N_4O_{10}S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[1]\,OH\\ [5]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N=N-[2]\,C_{10}H_5\left\{\begin{array}{l}[5]\,SO_3Na\\ [1]\,OH\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |
| 313 | **Chlorazol Blue R & 3 G.** [*R. H.*] | Dimethoxy-diphenyl-disazo-bi-chloro-α-naphthol-sulphonic acid. | $C_{34}H_{22}N_4Cl_2O_{10}S_2Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}[3]\,OCH_3\\ [4]-N_2-C_{10}H_4Cl\left\{\begin{array}{l}[1]\,OH\\ [4\text{ or }5]\,SO_3Na\end{array}\right.\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}[4]-N_2-C_{10}H_4Cl\left\{\begin{array}{l}[1]\,OH\\ [4\text{ or }5]\,SO_3Na\end{array}\right.\\ [3]\,OCH_3\end{array}\right.\end{array}$ |

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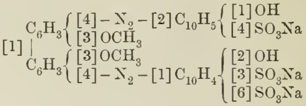
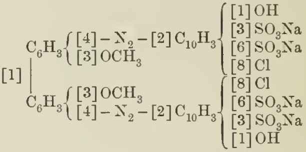
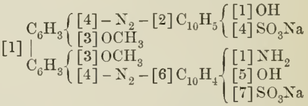
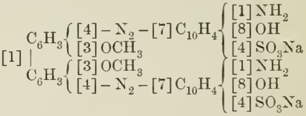
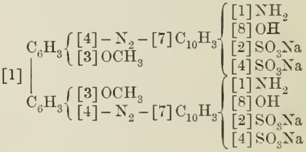
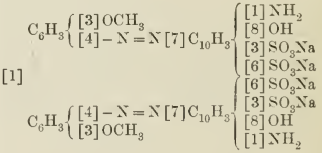
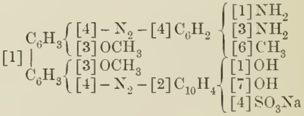
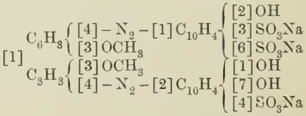
* **Benzoazurine R is a mixture of**

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Dianisidine. | *m*-Phenylene-diamine-oxamic acid + α-naphthol-sulphonic acid (1 : 4). | 1894. | Markfeldt.<br>Eng. Pat. 22114.<br>Fr. Pat. 252140. | **Appearance of dyestuff**: dark bronzy powder.— **In water**: easily soluble.—**On addition of hydrochloric acid to the aqueous solution**: black blue precipitate.—**On addition of caustic soda**: solution magenta red.—**In conc. sulphuric acid**: greenish blue solution; blue black precipitate on dilution.—**Dyes**: unmordanted cotton black. Gives deep blue blacks by diazotisation and development on the fibre. |
| Dianisidine. | 2 mols. of α-naphthyl-amine-sulphonic acid L. | | | **Appearance of dyestuff**: dark blue powder.—**In water**: brownish red solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: soluble red precipitate.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution.—**Dyes**: dull light-sensitive shades which after diazotisation and development yield fast colours. |
| Dianisidine. | 2 mols. naphthionic acid. | 1885. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $14424^{85}$ (amended).<br>Ger. Pat. $38802^{85}$.<br>Am. Pat. 481954.<br>Fr. Pat. 173042. | **Appearance of dyestuff**: brownish red powder.—**In water**: carmine red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**On addition of caustic soda to the aqueous solution**: red flocculent precipitate.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution with water.—**Dyes**: unmordanted cotton carmine red from an alkaline bath. |
| Dianisidine. | 2 mols. ethyl-β-naphthyl-amine-δ-sulphonic acid. | 1887. | E. Hassenkamp and C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $17083^{86}$.<br>Ger. Pat. $43204^{87}$, addn. to $41761^{86}$. | **Appearance of dyestuff**: brown powder.—**In water**: magenta red solution. **On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: colour becomes reddish violet.—**On addition of caustic soda to the aqueous solution**: scarcely any change.—**In conc. sulphuric acid**: blue solution; bluish violet precipitate on dilution with water.—**Dyes**: unmordanted cotton reddish violet from an alkaline bath. |
| Dianisidine. | 1 mol. naphthionic acid + 1 mol. α-naphthol-monosulphonic acid NW. | 1886. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pats. $14424^{85}$ & $7283^{86}$.<br>Ger. Pat. $40247^{86}$, addn. to 38802.<br>Am. Pat. 447302. | **Appearance of dyestuff**: blackish blue powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**Dilute acetic acid**: blue violet colour.—**On addition of caustic soda to the aqueous solution**: magenta red colour.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution with water.—**Dyes**: unmordanted cotton bluish violet from a soap bath. |
| Combination of the tetrazo compound of dianisidine in presence of copper salts with β-naphthol on the fibre. | | 1893. | Storck.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $21087^{93}$.<br>Ger. Pat. 80409.<br>Fr. Pat. 233876.<br>See Färberzeitung, 1893-94, 271, 371, 381, and 384. | Is formed upon the cotton fibre as a reddish blue fast to washing and fairly fast to chlorine and light. In order to produce the colour the cotton is first padded in an alkaline solution of β-naphthol, dried, and then immersed or printed with a solution of tetradiphenyl acetate containing a copper salt. The tetradiphenyl solution is either produced as required by diazotisation of Dianisidine, or ready-prepared tetrazo compounds of the latter are employed, such as Azophor Blue [*M.*]. |
| Dianisidine. | 2 mols. α-naphthol-sulphonic acid NW. | 1885. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $14424^{85}$ (amended).<br>Am. Pat. 357273.<br>Ger. Pat. $38802^{85}$. | **Appearance of dyestuff**: bluish black powder.—**In water**: blue violet solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**Dilute acetic acid**: no change.—**On addition of caustic soda to the aqueous solution**: magenta red coloration.—**In conc. sulphuric acid**: blue solution; bluish violet precipitate on dilution with water.—**Dyes**: cotton blue from an alkaline bath; the dyed material becomes red on heating, blue again on cooling. |
| Dianisidine. | 2 mols. α-naphthol-monosulphonic acid L. | 1885. | C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $14424^{85}$.<br>Am. Pat. 357273.<br>Ger. Pat. $38802^{85}$. | **Appearance of dyestuff**: gray black powder.—**In water**: bluish violet solution.—**In alcohol**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish violet precipitate.—**On addition of caustic soda to the aqueous solution**: colour becomes violet red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton blue from an alkaline bath. |
| Dianisidine. | Chloro-α-naphthol-4 or 5-sulphonic acid. | 1898. | Turner and Dean.<br>Read Holliday & Sons.<br>Eng. Pat. $12085^{98}$. | **Appearance of dyestuff**: blue black powder.—**In water**: violet solution.—**On addition of hydrochloric acid**: little change.—**On addition of caustic soda**: crimson solution.—**In conc. sulphuric acid**: greenish blue (R) or green (3 G) solution.—**Dyes**: unmordanted cotton from a salt bath blue. Very fast to light when coppered. |

Benzoazurine G and Azo Blue.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 314 | **Congo Blue 2 B.** [*A.*] [*By.*] | Sodium salt of dimethoxy-diphenyl-disazo-α-naphthol-*p*-sulphonic-β-naphthol-disulphonic acid. | $C_{34}H_{23}N_4S_3O_{13}Na_3$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\{[4]}SO_3Na\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[1]}C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\{[3]}SO_3Na\\{[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 315 | **Diamine Brilliant Blue.** [*C.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-1 : 8-chloro-naphthol-disulphonic acid. | $C_{34}H_{20}N_4S_4O_{16}Cl_2Na_4$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[2]}C_{10}H_3\left\{\begin{array}{l}{[1]}OH\\{[3]}SO_3Na\\{[6]}SO_3Na\\{[8]}Cl\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[2]}C_{10}H_3\left\{\begin{array}{l}{[8]}Cl\\{[6]}SO_3Na\\{[3]}SO_3Na\\{[1]}OH\end{array}\right.\end{array}\right.\end{array}$ |
| 316 | **Oxamine Blue B.** [*B.*] | Sodium salt of dimethoxy-diphenyl-disazo-α-naphthol-sulphonic-amido-naphthol-sulphonic acid. | $C_{34}H_{25}N_5S_2O_{10}Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[2]}C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\{[4]}SO_3Na\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[6]}C_{10}H_4\left\{\begin{array}{l}{[1]}NH_2\\{[5]}OH\\{[7]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 317 | **Chicago Blue B.** [*A.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-amido-naphthol-sulphonic acid. | $C_{34}H_{26}N_6S_2O_{10}Na_2$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[7]}C_{10}H_4\left\{\begin{array}{l}{[1]}NH_2\\{[8]}OH\\{[4]}SO_3Na\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[7]}C_{10}H_4\left\{\begin{array}{l}{[1]}NH_2\\{[8]}OH\\{[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 318 | **Chicago Blue 6 B.*** [*A.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-amido-naphthol-disulphonic acid. | $C_{34}H_{24}N_6S_4O_{16}Na_4$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[7]}C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\{[8]}OH\\{[2]}SO_3Na\\{[4]}SO_3Na\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[7]}C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\{[8]}OH\\{[2]}SO_3Na\\{[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 319 | **Diamine Sky Blue.** [*C.*]<br>**Benzo Sky Blue** [*By.*]<br>**Congo Sky Blue.** [*A.*] [*Lev.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-amido-naphthol-disulphonic acid. | $C_{34}H_{24}N_6O_{16}S_4Na_4$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N=N{[7]}C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\{[8]}OH\\{[3]}SO_3Na\\{[6]}SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N{[7]}C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\{[3]}SO_3Na\\{[8]}OH\\{[1]}NH_2\end{array}\right.\\{[3]}OCH_3\end{array}\right.\end{array}$ |
| 320 | **Direct Violet BB.** [*Bl.*] | Sodium salt of dimethoxy-diphenyl-disazo-*m*-tolylene-diamine-dioxy-naphthalene-sulphonic acid. | $C_{31}H_{27}N_6O_7SNa$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[4]}C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\{[3]}NH_2\\{[6]}CH_3\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[2]}C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\{[7]}OH\\{[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 321 | **Indazurine B.** [*Bl.*] | Sodium salt of dimethoxy-diphenyl-disazo-β-naphthol-disulphonic-dioxy-naphthalene-sulphonic acid. | $C_{34}H_{23}N_4S_3O_{14}Na_3$ |  $[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[4]}-N_2-{[1]}C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\{[3]}SO_3Na\\{[6]}SO_3Na\end{array}\right.\\{[3]}OCH_3\end{array}\right.\\ C_3H_3\left\{\begin{array}{l}{[3]}OCH_3\\{[4]}-N_2-{[2]}C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\{[7]}OH\\{[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |

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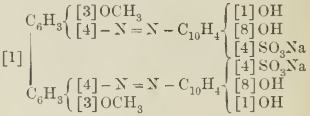
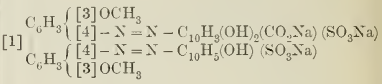
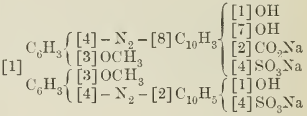
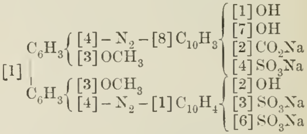
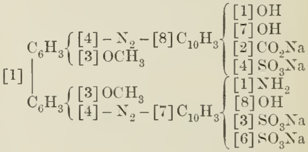
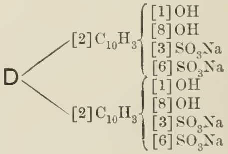
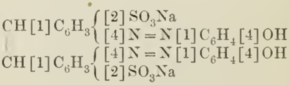
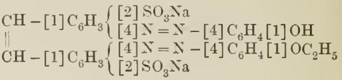
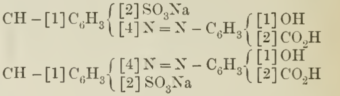
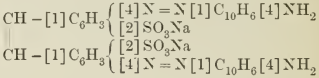
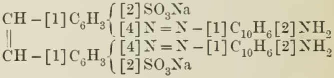
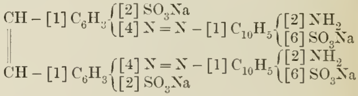
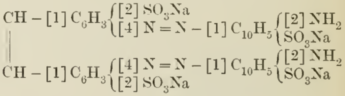
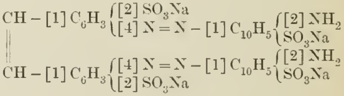
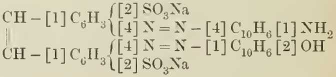
* Chicago Blue 4 B & RW are mixed azo dyestuffs from dianisidine.

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Dianisidine. | β-Naphthol-disulphonic acid R + α-naphthol-sulphonic acid NW. | 1890. | G. Schultz.<br>Berlin Aniline Co.<br>Am. Pat. $467162^{92}$.<br>Ger. Pat. 40247.<br>Compare J. Soc. Chem. Ind. 1897, 674. | **Appearance of dyestuff:** brown metallic glistening powder.—**In water:** blue solution.—**On addition of hydrochloric acid:** dark blue precipitate.—**On addition of caustic soda:** solution magenta red.—**In conc. sulphuric acid:** blue solution; blue precipitate on dilution.—**Dyes:** unmordanted cotton direct blue. |
| Dianisidine. | 2 mols. of 1 : 8-chloronaphthol-3 : 6-disulphonic acid. | 1893. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $1920^{94}$.<br>Am. Pats. 532125 & 535037.<br>Ger. Pats. 79055 & 82285.<br>Fr. Pat. 235271. | **Appearance of dyestuff:** gray blue powder.—**In water:** bluish violet solution.—**On addition of hydrochloric acid:** soluble violet precipitate.—**On addition of caustic soda:** solution cherry red.—**In conc. sulphuric acid:** greenish blue solution; violet on dilution.—**Dyes:** unmordanted cotton a fairly fast blue. |
| Dianisidine. | 1 : 5-Amidonaphthol-7-sulphonic acid + α-naphthol-sulphonic acid NW. | 1893. | Bernthsen & Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $2370^{93}$.<br>Am. Pat. 558344.<br>Ger. Pat. $82572^{93}$.<br>Fr. Pat. 229263. | **Appearance of dyestuff:** gray powder.—**In water:** easily soluble with dark blue colour.—**On addition of caustic soda:** solution reddish violet.—**In conc. sulphuric acid:** bluish green solution; violet on dilution.—**Dyes:** unmordanted cotton indigo blue of good fastness to washing and light. |
| Dianisidine. | 2 mols. of 1 : 8-amidonaphthol-4-sulphonic acid. | 1893. | Möller.<br>Berlin Aniline Co. | **Appearance of dyestuff:** blue powder.—**In water or alcohol:** blue solution.—**On addition of hydrochloric acid to the aqueous solution:** bluish violet precipitate.—**On addition of caustic soda:** blue solution.—**In conc. sulphuric acid:** bluish green solution; on dilution blue solution and then bluish violet flocks.—**Dyes:** unmordanted cotton direct blue. |
| Dianisidine. | 2 mols. of 1 : 8-amidonaphthol-2 : 4-disulphonic acid. | 1894. | Möller.<br>Berlin Aniline Co. | **Appearance of dyestuff:** blue powder.—**In water:** pure blue solution.—**On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** bluish violet solution.—**In conc. sulphuric acid:** blue green solution, becoming pure blue on dilution.—**Dyes:** unmordanted cotton and wool direct blue. |
| Dianisidine. | 2 mols. amidonaphthol-disulphonic acid H. (in alkaline solution). | 1890.<br>1890. | Bammann & Ulrich.<br>M. Hoffmann.<br>L. Cassella & Co.<br>Eng. Pat. $1742^{91}$.<br>Am. Pat. 464135.<br>Ger. Pat. 74593.<br>Fr. Pat. 201770. | **Appearance of dyestuff:** bluish gray powder.—**In water:** pure blue solution.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda to the aqueous solution:** colour becomes redder and duller.—**In conc. sulphuric acid:** bluish green solution; pure blue on dilution with water.—**Dyes:** unmordanted cotton a pure blue from an alkaline bath; after coppering very fast to light. |
| Dianisidine. | 1 : 7-Dioxynaphthalene-sulphonic acid + *m*-tolylene-diamine. | 1894. | Müller.<br>Am. Pat. $524069^{94}$. | **Appearance of dyestuff:** greenish black powder.—**In water:** violet solution.—**In alcohol:** deep red solution.—**On addition of hydrochloric acid to the aqueous solution:** bluer.—**On addition of caustic soda:** solution red.—**In conc. sulphuric acid:** blue solution; blue precipitate on dilution.—**Dyes:** unmordanted cotton bluish violet. |
| Dianisidine. | 1 : 7-Dioxynaphthalene-sulphonic acid + β-naphthol-disulphonic acid R. | 1894. | Müller.<br>Am. Pat. $524069^{94}$. | **Appearance of dyestuff:** black blue powder.—**In water:** blue solution.—**On addition of hydrochloric acid to the aqueous solution:** bluer.—**On addition of caustic soda:** solution red.—**In conc. sulphuric acid:** blue solution; reddish blue precipitate on dilution.—**Dyes:** unmordanted cotton reddish blue. |

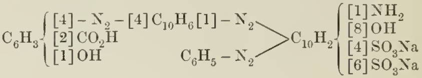
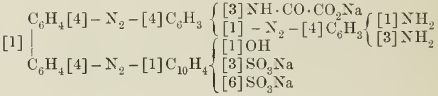
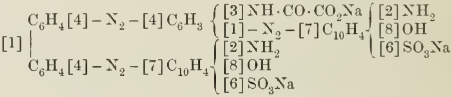
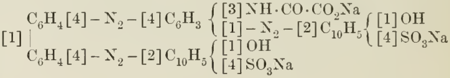
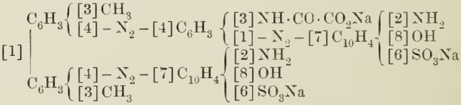
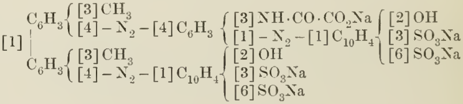
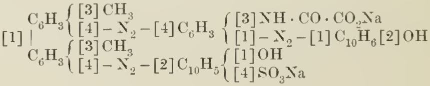
1 : 8 : 4 : 6-amidonaphthol-disulphonic acid, and another component.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 322 | **Brilliant Azurine 5 G.** [*By.*] | Sodium salt of dimethoxy-diphenyl-disazo-bi-dioxy-naphthalene-sulphonic acid. | $\mathrm{C_{34}H_{24}N_4O_{12}S_2Na_2}$ |  $[1]\left\vert\begin{array}{l}\mathrm{C_6H_3}\left\{\begin{array}{l}{[3]}\,\mathrm{OCH_3}\\ {[4]}-\mathrm{N=N-C_{10}H_4}\end{array}\right.\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[8]}\,\mathrm{OH}\\ {[4]}\,\mathrm{SO_3Na}\end{array}\right.\\ \mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}-\mathrm{N=N-C_{10}H_4}\\ {[3]}\,\mathrm{OCH_3}\end{array}\right.\left\{\begin{array}{l}{[4]}\,\mathrm{SO_3Na}\\ {[8]}\,\mathrm{OH}\\ {[1]}\,\mathrm{OH}\end{array}\right.\end{array}\right.$ |
| 323 | **Direct Blue B.** [*I.*] | Sodium salt of dimethoxy-diphenyl-disazo-dioxy-naphthoic-sulphonic-α-naphthol-p-sulphonic acid. | $\mathrm{C_{35}H_{23}N_4O_{13}S_2Na_3}$ |  $[1]\begin{array}{l}\mathrm{C_6H_3}\left\{\begin{array}{l}{[3]}\,\mathrm{OCH_3}\\ {[4]}-\mathrm{N=N-C_{10}H_3(OH)_2(CO_2Na)\,(SO_3Na)}\end{array}\right.\\ \mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}-\mathrm{N=N-C_{10}H_5(OH)\,(SO_3Na)}\\ {[3]}\,\mathrm{OCH_3}\end{array}\right.\end{array}$ |
| 324 | **Indazurine GM.** [*Bl.*] | Sodium salt of dimethoxy-diphenyl-disazo-dioxy-naphthoic-sulphonic-α-naphthol-p-sulphonic acid. | $\mathrm{C_{35}H_{23}N_4S_2O_{13}Na_3}$ |  $[1]\begin{array}{l}\mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}-\mathrm{N_2}-{[8]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[7]}\,\mathrm{OH}\\ {[2]}\,\mathrm{CO_2Na}\\ {[4]}\,\mathrm{SO_3Na}\end{array}\right.\\ {[3]}\,\mathrm{OCH_3}\end{array}\right.\\ \mathrm{C_6H_3}\left\{\begin{array}{l}{[3]}\,\mathrm{OCH_3}\\ {[4]}-\mathrm{N_2}-{[2]}\,\mathrm{C_{10}H_5}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[4]}\,\mathrm{SO_3Na}\end{array}\right.\end{array}\right.\end{array}$ |
| 325 | **Indazurine BB.** [*Bl.*] | Sodium salt of dimethoxy-diphenyl-disazo-dioxy-naphthoic-sulphonic-β-naphthol-disulphonic acid. | $\mathrm{C_{35}H_{22}N_4S_3O_{16}Na_4}$ |  $[1]\left\vert\begin{array}{l}\mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}-\mathrm{N_2}-{[8]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[7]}\,\mathrm{OH}\\ {[2]}\,\mathrm{CO_2Na}\\ {[4]}\,\mathrm{SO_3Na}\end{array}\right.\\ {[3]}\,\mathrm{OCH_3}\end{array}\right.\\ \mathrm{C_6H_3}\left\{\begin{array}{l}{[3]}\,\mathrm{OCH_3}\\ {[4]}-\mathrm{N_2}-{[1]}\,\mathrm{C_{10}H_4}\left\{\begin{array}{l}{[2]}\,\mathrm{OH}\\ {[3]}\,\mathrm{SO_3Na}\\ {[6]}\,\mathrm{SO_3Na}\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 326 | **Indazurine 5 GM.** [*Bl.*] | Sodium salt of dimethoxy-diphenyl-disazo-dioxy-naphthoic-sulphonic-amidonaphthol-disulphonic acid. | $\mathrm{C_{35}H_{23}N_5S_3O_{16}Na_4}$ |  $[1]\left\vert\begin{array}{l}\mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}-\mathrm{N_2}-{[8]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[7]}\,\mathrm{OH}\\ {[2]}\,\mathrm{CO_2Na}\\ {[4]}\,\mathrm{SO_3Na}\end{array}\right.\\ {[3]}\,\mathrm{OCH_3}\end{array}\right.\\ \mathrm{C_6H_3}\left\{\begin{array}{l}{[3]}\,\mathrm{OCH_3}\\ {[4]}-\mathrm{N_2}-{[7]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{NH_2}\\ {[8]}\,\mathrm{OH}\\ {[3]}\,\mathrm{SO_3Na}\\ {[6]}\,\mathrm{SO_3Na}\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 327 | **Dianil Blue B.** [*M.*] | | |  $\mathrm{D}\left\langle\begin{array}{l}{[2]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[8]}\,\mathrm{OH}\\ {[3]}\,\mathrm{SO_3Na}\\ {[6]}\,\mathrm{SO_3Na}\end{array}\right.\\ {[2]}\,\mathrm{C_{10}H_3}\left\{\begin{array}{l}{[1]}\,\mathrm{OH}\\ {[8]}\,\mathrm{OH}\\ {[3]}\,\mathrm{SO_3Na}\\ {[6]}\,\mathrm{SO_3Na}\end{array}\right.\end{array}\right.$<br>[D = residue of a paradiamine.] |
| 328 | **Brilliant Yellow.** [*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-phenol. | $\mathrm{C_{26}H_{18}N_4O_8S_2Na_2}$ |  $\begin{array}{l}\mathrm{CH}\,{[1]}\,\mathrm{C_6H_3}\left\{\begin{array}{l}{[2]}\,\mathrm{SO_3Na}\\ {[4]}\,\mathrm{N=N}\,{[1]}\,\mathrm{C_6H_4}\,{[4]}\,\mathrm{OH}\end{array}\right.\\ \mathrm{CH}\,{[1]}\,\mathrm{C_6H_3}\left\{\begin{array}{l}{[4]}\,\mathrm{N=N}\,{[1]}\,\mathrm{C_6H_4}\,{[4]}\,\mathrm{OH}\\ {[2]}\,\mathrm{SO_3Na}\end{array}\right.\end{array}$ |

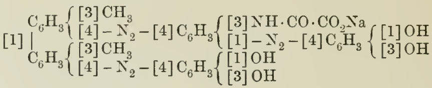
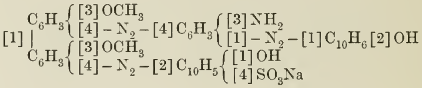
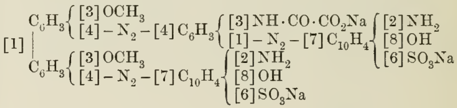
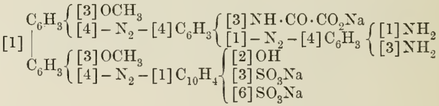
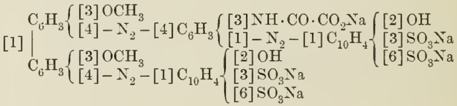
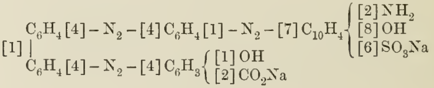
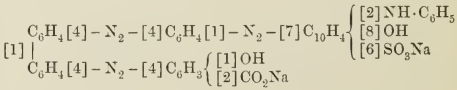
| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Dianisidine. | 2 mols. dioxynaphthalene-mono-sulphonic acid (1 : 8 : 4). | 1889. | M. Ulrich and C. Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $14424^{85}$ (amended).<br>Ger. Pat. $57166^{89}$. | **Appearance of dyestuff** : grayish black powder.— **In water** : bluish violet solution.—**In alcohol** : slightly soluble.—**On addition of hydrochloric acid to the aqueous solution** : blue precipitate.—**On addition of caustic soda** : solution becomes red.—**In conc. sulphuric acid** : greenish blue solution ; dark reddish blue precipitate on dilution with water.—**Dyes** : unmordanted cotton blue. |
| Dianisidine. | 1 mol. dioxy-naphthoic-sulphonic acid + 1 mol. α-naphthol-*p*-sulphonic acid. | 1892. | Société pour l'Industrie Chimique à Bâle.<br>Am. Pat. $493563^{93}$.<br>Fr. Pat. $220468^{92}$.<br>Ger. Pat. 67000. | **Appearance of dyestuff** : grayish black powder.—**In water** : easily soluble.—**In alcohol** : sparingly soluble with a reddish blue colour.—**On addition of hydrochloric acid to the aqueous solution** : bluish black precipitate.—**On addition of caustic soda to the aqueous solution** : reddish violet.—**In conc. sulphuric acid** : greenish blue solution ; violet precipitate on dilution with water.—**Dyes** : unmordanted cotton steel blue to black blue shades. |
| Dianisidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + α-naphthol-sulphonic acid NW. | 1894. | Müller.<br>Am. Pat. 524070. | **Appearance of dyestuff** : greenish black powder.—**In water** : reddish blue solution.—**On addition of hydrochloric acid** : no change.—**On addition of caustic soda** : solution reddish violet.—**In conc. sulphuric acid** : greenish blue solution ; violet precipitate on dilution.—**Dyes** : unmordanted cotton blue. |
| Dianisidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + β-naphthol-disulphonic acid R. | 1894. | Müller.<br>Am. Pat. 524070. | **Appearance of dyestuff** : black blue powder.—**In water** : blue solution.—**On addition of hydrochloric acid** : solution slightly bluer.—**On addition of caustic soda** : solution redder.—**In conc. sulphuric acid** : greenish blue solution ; blue precipitate on dilution.—**Dyes** : unmordanted cotton blue. |
| Dianisidine. | 1 : 7-Dioxy-2-naphthoic-4-sulphonic acid + 1 : 8-amido-naphthol-3 : 6-disulphonic acid. | 1894. | Müller.<br>Am. Pat. 524070. | **Appearance of dyestuff** : greenish black powder.—**In water** : pure blue solution.—**On addition of hydrochloric acid** : no change.—**On addition of caustic soda** : solution redder.—**In conc. sulphuric acid** : bluish green solution ; on dilution bluish violet.—**Dyes** : unmordanted cotton greenish blue. |
| Combination of tetrazotised paradiamine with 2 mols. of 1 : 8-dioxynaphthalene-3 : 6-disulphonic acid. | | 1890. | Steinicke. | **Appearance of dyestuff** : blue powder.—**In water** : blue solution.—**On addition of hydrochloric acid or caustic soda** : no change.—**In conc. sulphuric acid** : deep blue solution, becoming bluish violet on dilution.—**Dyes** : unmordanted cotton from a salt bath blue shades of moderate fastness to light and good fastness to acids. The fastness to washing is improved by chroming. |
| Diamido-stilbene-disulphonic acid. | 2 mols. of phenol. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$.<br>Am. Pat. 350229.<br>Ger. Pat. $38735^{86}$. | **Appearance of dyestuff** : light brown powder.—**In water** : reddish yellow solution.—**On addition of hydrochloric acid to the aqueous solution** : violet precipitate.—**On addition of caustic soda to the aqueous solution** : yellowish red colour.—**In conc. sulphuric acid** : reddish violet solution ; violet precipitate on dilution with water.—**Dyes** : unmordanted cotton yellow from an acid bath. Chiefly used for paper-staining. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 329 | **Chrysophenine.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-phenetol-phenol. | $C_{28}H_{22}N_4O_8S_2Na_2$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[4]\,C_6H_4\,[1]\,OH}\end{cases}\\ \Vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[4]\,C_6H_4\,[1]\,OC_2H_5}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 330 | **Hessian Yellow.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-salicylic acid. | $C_{28}H_{16}N_4O_{12}S_2Na_4$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-C_6H_3}\begin{cases}\mathrm{[1]\,OH}\\ \mathrm{[2]\,CO_2H}\end{cases}\end{cases}\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-C_6H_3}\begin{cases}\mathrm{[1]\,OH}\\ \mathrm{[2]\,CO_2H}\end{cases}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 331 | **Hessian Bordeaux.**<br>[*L.*] | Sodium salt of disulpho-stilbene-disazo-bi-α-naphthyl-amine. | $C_{34}H_{24}N_6S_2O_6Na_2$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N\,[1]\,C_{10}H_6\,[4]\,NH_2}\\ \mathrm{[2]\,SO_3Na}\end{cases}\\ \vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N\,[1]\,C_{10}H_6\,[4]\,NH_2}\end{cases}\end{array}$ |
| 332 | **Hessian Purple N.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-β-naphthyl-amine. | $C_{34}H_{24}N_6O_6S_2Na_2$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[1]\,C_{10}H_6\,[2]\,NH_2}\end{cases}\\ \Vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[1]\,C_{10}H_6\,[2]\,NH_2}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 333 | **Brilliant Hessian Purple.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-β-naphthyl-amine-β-sulphonic acid. | $C_{34}H_{22}N_6O_{12}S_4Na_4$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{[6]\,SO_3Na}\end{cases}\end{cases}\\ \Vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{[6]\,SO_3Na}\end{cases}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 334 | **Hessian Purple B.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-β-naphthyl-amine-sulphonic acid. | $C_{34}H_{22}N_6O_{12}S_4Na_4$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{SO_3Na}\end{cases}\end{cases}\\ \vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{SO_3Na}\end{cases}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 335 | **Hessian Purple D.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-bi-β-naphthyl-amine-sulphonic acid. | $C_{34}H_{22}N_6O_{12}S_4Na_4$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{SO_3Na}\end{cases}\end{cases}\\ \Vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[1]\,C_{10}H_5}\begin{cases}\mathrm{[2]\,NH_2}\\ \mathrm{SO_3Na}\end{cases}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |
| 336 | **Hessian Violet.**<br>[*L.*] [*A.*] [*By.*] | Sodium salt of disulpho-stilbene-disazo-α-naphthyl-amine-β-naphthol. | $C_{34}H_{23}N_5O_7S_2Na_2$ |  $\begin{array}{l}\mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[2]\,SO_3Na}\\ \mathrm{[4]\,N=N-[4]\,C_{10}H_6\,[1]\,NH_2}\end{cases}\\ \vert\\ \mathrm{CH-[1]\,C_6H_3}\begin{cases}\mathrm{[4]\,N=N-[1]\,C_{10}H_6\,[2]\,OH}\\ \mathrm{[2]\,SO_3Na}\end{cases}\end{array}$ |

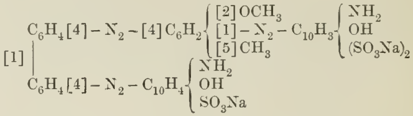
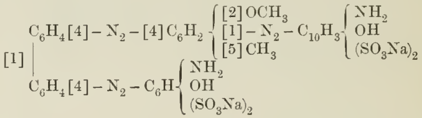
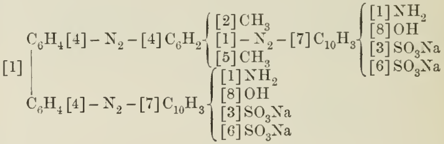
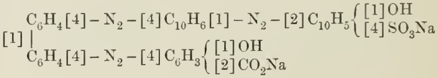
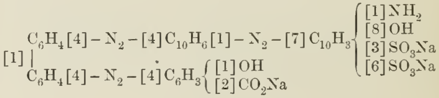
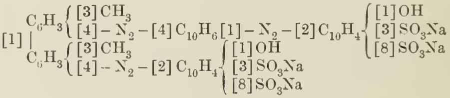
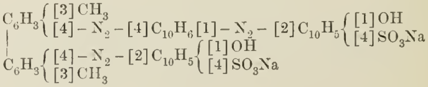
| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Tetrazo Compound from | Combined with | | | |
| Ethylation of "Brilliant Yellow" (preceding). | | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4243^{86}$.<br>Am. Pat. $3794^{87}$.<br>Ger. Pat. 42466.<br>See Ber. 27, 3357. | **Appearance of dyestuff**: orange yellow powder.—**In water**: sparingly soluble cold, easily hot, with an orange yellow colour.—**On addition of hydrochloric acid to the hot aqueous solution**: brown precipitate.—**Dilute acetic acid**: scarcely any change.—**On addition of caustic soda to the hot aqueous solution**: yellow coloration and orange flocks.—**In conc. sulphuric acid**: reddish violet solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton or wool yellow from a neutral or acid bath, silk from an acetic acid bath. Very fast to light, washing, acids, and chlorine. |
| Diamido-stilbene-disulphonic acid. | 2 mols. of salicylic acid. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Am. Pat. 350229.<br>Ger. Pat. 38735. | **Appearance of dyestuff**: ochre yellow powder.—**In water**: brownish yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: blackish precipitate.—**Dilute acetic acid**: scarcely any change.—**On addition of caustic soda to the aqueous solution**: cherry red coloration.—**In conc. sulphuric acid**: reddish violet solution; blackish precipitate on dilution with water.—**Dyes**: unmordanted cotton yellow from a neutral or acid bath, very fast to light but sensitive to alkalies, soap, and copper salts. |
| Diamido-stilbene-disulphonic acid. | 2 mols. of α-naphthylamine. | 1886. | Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$.<br>Am. Pat. 350230.<br>Ger. Pat. 38735. | **Appearance of dyestuff**: greenish glistening powder.—**In water**: deep red solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: red precipitate.—**In conc. sulphuric acid**: bluish violet solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton bordeaux red, diazotisable on the fibre. |
| Diamido-stilbene-disulphonic acid. | 2 mols. of β-naphthylamine. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Am. Pat. 350230.<br>Ger. Pat. $38735^{86}$. | **Appearance of dyestuff**: brownish red powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish black precipitate.—**Dilute acetic acid**: violet black precipitate.—**On addition of caustic soda to the aqueous solution**: red coloration and red precipitate.—**In conc. sulphuric acid**: blue solution; bluish black precipitate on dilution with water.—**Dyes**: unmordanted cotton bluish red from a soap bath; not fast to light or acids. |
| 1 mol. of diamido-stilbene-disulphonic acid. | 2 mols. of β-naphthylamine-mono-sulphonic acid β. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Am. Pat. 350230.<br>Ger. Pat. $38735^{86}$. | **Appearance of dyestuff**: dark red powder.—**In water**: purple red solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: bluish black precipitate.—**On addition of caustic soda to the aqueous solution**: carmine red precipitate.—**In conc. sulphuric acid**: blue solution; bluish black precipitate on dilution with water.—**Dyes**: unmordanted cotton bluish red. |
| 1 mol. of diamido-stilbene-disulphonic acid. | 2 mols. of β-naphthylamine sulphonic acid β (or a mixture of β and δ). | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Am. Pat. 250230.<br>Ger. Pats. $38735^{86}$ & $40575^{86}$. | **Appearance of dyestuff**: brown powder.—**In water**: cherry red solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish black precipitate.—**Dilute acetic acid**: solution becomes darker.—**On addition of caustic soda to the aqueous solution**: reddish violet precipitate, soluble in water.—**In conc. sulphuric acid**: violet solution; brown precipitate on dilution with water.—**Dyes**: unmordanted cotton bluish red from a soap bath. |
| 1 mol. of diamido-stilbene disulphonic acid. | 2 mols. of β-naphthylamine monosulphonic acid γ. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Am. Pat. 350230.<br>Ger. Pat. $38735^{86}$. | **Appearance of dyestuff**: black powder.—**In water**: orange red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**Dilute acetic acid**: no change.—**On addition of caustic soda to the aqueous solution**: bluer.—**In conc. sulphuric acid**: violet solution; brown on dilution with water.—**Dyes**: unmordanted cotton bluish red from a soap bath. |
| 1 mol. of diamido-stilbene disulphonic acid. | 1 mol. of α-naphthylamine and 1 mol. of β-naphthol. | 1886. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$ (amended).<br>Ger. Pats. $38735^{86}$ & $40575^{86}$. | **Appearance of dyestuff**: black powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**Dilute acetic acid**: solution becomes bluish violet.—**On addition of caustic soda**: solution becomes bluish violet—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution with water.—**Dyes**: unmordanted cotton violet from a soap bath; not fast to light, and rather sensitive to acids. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 337 | **Chrome Patent Green A & N.** [*K.*] | Sodium salt of benzene-azo-amido-naphthol-disulphonic-acid-azo-α-naphthalene-azo-salicylic acid. |  $C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[4]C_{10}H_6[1]-N_2 \\ {[2]}CO_2H \\ {[1]}OH \qquad C_6H_5-N_2\end{array}\right\rangle C_{10}H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[8]}OH\\ {[4]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.$ |
| 338 | **Oxamine Violet GRF.** [*R.*] | Sodium salt of diphenyl-disazo-*m*-phenylene-oxamic-acid-azo-phenylene-diamine-β-naphthol-disulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\\ C_6H_4[4]-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 339 | **Oxamine Black MB.** [*R.*] | Sodium salt of diphenyl-disazo-*m*-phenylene-oxamic-acid-azo-bi-amido-naphthol-sulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4[4]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 340 | **Oxamine Violet RR.** [*R.*] | Sodium salt of diphenyl-disazo-phenylene-oxamic-acid-azo-bi-α-naphthol-*p*-sulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_4[4]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.$ |
| 341 | **Oxamine Black MT.** [*R.*] | Sodium salt of ditolyl-disazo-phenylene-oxamic-acid-azo-bi-amido-naphthol-sulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ {[3]}CH_3\end{array}\right.\end{array}\right.$ |
| 342 | **Oxamine Violet MT.** [*R.*] | Sodium salt of ditolyl-disazo-phenylene-oxamic-acid-azo-bi-β-naphthol-disulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |
| 343 | **Oxamine Violet BBR.** [*R.*] | Sodium salt of ditolyl-disazo-phenylene-oxamic-azo-β-naphthol-α-naphthol-sulphonic acid. |  $[1]\left\lvert\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[1]C_{10}H_6[2]OH\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.$ |

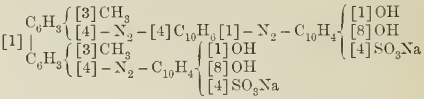
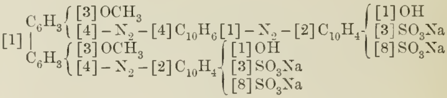
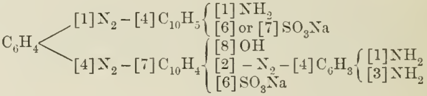
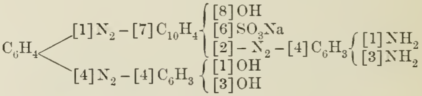
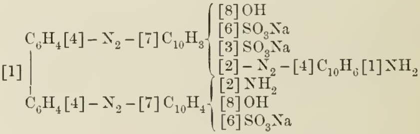
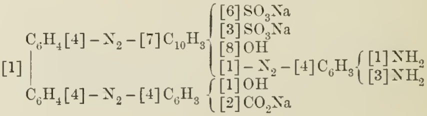
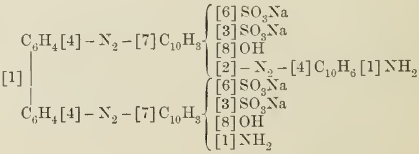
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Diazotised salicylic-azo-α-naphthylamine and diazobenzene coupled with 1 : 8-amidonaphthol-disulphonic acid K. | 1898. | Elbel.<br>Kalle & Co.<br>Eng. Pat. 23893$^{98}$.<br>Fr. Pat. 282619$^{98}$. | **Appearance of dyestuff**; chocolate brown powder.—**In cold water**: greenish blue solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: blue violet precipitate.—**In conc. sulphuric acid**: green solution; on dilution greenish blue solution and dark precipitate.—**Dyes**: wool by the one-bath chrome method a fairly dark bluish green. |
| Benzidine (tetraz.)<br>↙ ↘<br>β-Naphthol-disulphonic acid R. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>*m*-phenylenediamine. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. 86791. | **Appearance of dyestuff**: bronzy powder.—**In water**: easily soluble.—**On addition of hydrochloric acid**: reddish violet precipitate.—**On addition of caustic soda**: solution becomes cherry red.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton from a salt bath reddish violet. |
| Benzidine (tetraz.)<br>↙ ↘<br>Amidonaphthol-sulphonic acid γ. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>amidonaphthol-sulphonic acid γ. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. 86791. | **Appearance of dyestuff**: bronzy powder.—**In water**: easily soluble.—**On addition of hydrochloric acid**: black blue precipitate.—**On addition of caustic soda**: violet black precipitate.—**In conc. sulphuric acid**: pure blue solution; reddish violet precipitate on dilution.—**Dyes**: unmordanted cotton black, which by diazotisation on the fibre and development with *m*-tolylene diamine yields a very fine deep black. |
| Benzidine (tetraz.)<br>↙ ↘<br>α-Naphthol-sulphonic acid NW. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>α-naphthol-sulphonic acid NW. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. 86791$^{94}$. | **Appearance of dyestuff**: dark bronzy powder.—**In water**: bluish red solution.—**On addition of hydrochloric acid**: bluish red precipitate.—**On addition of caustic soda**: violet red solution.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton violet from a salt bath. |
| Tolidine (tetraz.)<br>↙ ↘<br>Amidonaphthol-sulphonic acid γ. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>amidonaphthol-sulphonic acid γ. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. 86791$^{94}$. | **Appearance of dyestuff**: bronzy powder.—**In water**: easily soluble. **On addition of hydrochloric acid**: black blue precipitate.—**On addition of caustic soda**: blue black precipitate.—**In conc. sulphuric acid**: pure blue solution; violet black precipitate on dilution.—**Dyes**: unmordanted cotton black. By diazotisation and development gives deep blacks. |
| Tolidine (tetraz.)<br>↙ ↘<br>β-Naphthol-disulphonic acid R. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>β-naphthol-disulphonic acid R. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. 86791$^{94}$. | **Appearance of dyestuff**: dark violet powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid**: reddish violet solution or precipitate.—**On addition of caustic soda**: bluish red precipitate.—**In conc. sulphuric acid**: blue solution, changing to reddish violet on dilution, and finally giving a violet precipitate.—**Dyes**: unmordanted cotton violet from a salt bath. |
| Tolidine (tetraz.)<br>↙ ↘<br>α-Naphthol-sulphonic acid NW. — Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>β-naphthol. | 1894. | Markfeldt.<br>Eng. Pat. 22114$^{94}$.<br>Ger. Pat. 86791.<br>Fr. Pat. 252140. | **Appearance of dyestuff**: dark bronzy powder.—**In water**: easily soluble.—**On addition of hydrochloric acid**: bluish red precipitate.—**On addition of caustic soda**: violet red solution.—**In conc. sulphuric acid**: blue solution; violet precipitate on dilution.—**Dyes**: unmordanted cotton violet from a salt bath. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 344 | **Oxamine Red MT.** [*R.*] | Sodium salt of ditolyl-disazo-phenylene-oxamic-acid-azo-bi-resorcin. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[3]}OH\end{array}\right.\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[3]}OH\end{array}\right.\end{array}\right.\end{array}$ |
| 345 | **Oxamine Blue BB.** [*R.*] | Sodium salt of dimethoxy-diphenyl-disazo-amidobenzene-azo-β-naphthol-α-naphthol-*p*-sulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH_2\\ {[1]}-N_2-[1]C_{10}H_6[2]OH\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 346 | **Oxamine Black MD.** [*R.*] | Sodium salt of dimethoxy-diphenyl-disazo-phenylene-oxamic-acid-azo-bi-amidonaphthol-sulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 347 | **Oxamine Blue BT.** [*R.*] | Sodium salt of dimethoxy-diphenyl-disazo-phenylene-oxamic-acid-azo-*m*-phenylene-diamine-β-naphthol-disulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 348 | **Oxamine Blue MD.** [*R.*] | Sodium salt of dimethoxy-diphenyl-disazo-phenylene-oxamic-acid-azo-bi-β-naphthol-disulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[3]}NH\cdot CO\cdot CO_2Na\\ {[1]}-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[1]C_{10}H_4\left\{\begin{array}{l}{[2]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 349 | **Crumpsall Direct Fast Brown B.** [*Lev.*] | Sodium salt of diphenyl-disazo-benzene-azo-amidonaphthol-sulphonic-salicylic acid. |  $[1]\begin{array}{l}C_6H_4[4]-N_2-[4]C_6H_4[1]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |
| 350 | **Crumpsall Direct Fast Brown O.** [*Lev.*] | Sodium salt of diphenyl-disazo-benzene-azo-phenyl-amidonaphthol-sulphonic-salicylic acid. |  $[1]\begin{array}{l}C_6H_4[4]-N_2-[4]C_6H_4[1]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH\cdot C_6H_5\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |

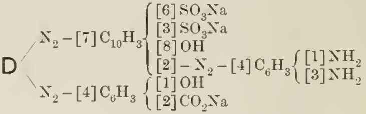
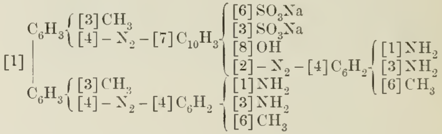
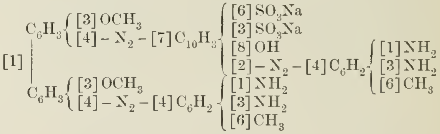
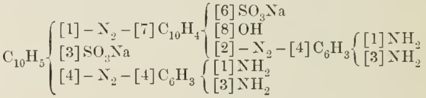
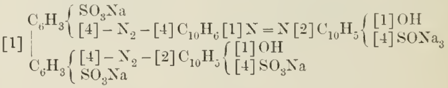
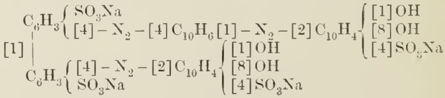
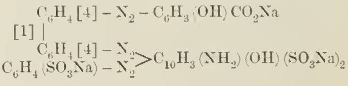
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Tolidine (tetraz.)<br>Resorcin. Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>resorcin. | 1894. | Markfeldt.<br>Eng. Pat. $22114^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. $86791^{94}$. | **Appearance of dyestuff**: dark powder.—**In water**: soluble hot with brownish red colour.—**In alcohol**: nearly insoluble.—**On addition of hydrochloric acid to the aqueous solution**: reddish brown precipitate.—**On addition of caustic soda**: rather redder.—**In conc. sulphuric acid**: blue solution; reddish brown precipitate on dilution.—**Dyes**: unmordanted cotton from an alkaline salt bath a fine brownish red. |
| Dianisidine (tetraz.)<br>α-Naphthol-sulphonic acid NW. Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>β-naphthol.<br>Finally saponified. | 1894. | Markfeldt.<br>Eng. Pat. $22114^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. $86792^{94}$. | **Appearance of dyestuff**: bronzy powder.—**In water**: easily soluble.—**In alcohol**: blue solution; red on warming.—**On addition of hydrochloric acid**: bluish violet precipitate.—**On addition of caustic soda**: magenta red solution.—**In conc. sulphuric acid**: greenish blue solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton from alkaline salt bath blue. Diazotised and developed on the fibre gives bluish black shades. |
| Dianisidine (tetraz.)<br>Amido-naphthol-sulphonic acid γ. Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>amido-naphthol-sulphonic acid γ. | 1894. | Markfeldt.<br>Eng. Pat. $22114^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. $86791^{94}$. | **Appearance of dyestuff**: dark bronzy powder.—**In water**: blue black solution.—**On addition of hydrochloric acid**: blackish blue precipitate.—**On addition of caustic soda**: bluish black precipitate.—**In conc. sulphuric acid**: bluish green solution; blackish blue precipitate on dilution.—**Dyes**: unmordanted cotton direct, and can be diazotised and developed on the fibre to a deep black. |
| Dianisidine (tetraz.)<br>β-Naphthol-disulphonic acid R. Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>*m*-phenylene-diamine. | 1894. | Markfeldt.<br>Eng. Pat. $22114^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. $86791^{94}$. | **Appearance of dyestuff**: bronzy powder.—**In water**: easily soluble.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: solution becomes magenta red.—**In conc. sulphuric acid**: greenish blue solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton from a salt bath dark reddish blue. |
| Dianisidine (tetraz.)<br>β-Naphthol-disulphonic acid R. Phenylene-*m*-diamine-oxamic acid (diaz.)<br>↓<br>β-naphthol-disulphonic acid R. | 1894. | Markfeldt.<br>Eng. Pat. $22114^{94}$.<br>Fr. Pat. 252140.<br>Ger. Pat. $86791^{94}$. | **Appearance of dyestuff**: black powder.—**In water**: easily soluble.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: solution becomes reddish violet.—**In conc. sulphuric acid**: greenish blue solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton blue from an alkaline bath. |
| Benzidine (tetraz.)<br>Salicylic acid. Aniline (diaz.)<br>↓<br>amido-naphthol-sulphonic acid γ. | 1895. | Mensching.<br>Levinstein Limd.<br>Eng. Pat. $23523^{95}$.<br>Am. Pat. 622961. | **Appearance of dyestuff**: blackish brown powder.—**In water**: soluble, with brown colour.—**In alcohol**: fairly soluble.—**On addition of hydrochloric acid to the aqueous solution**: redder.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: violet solution; brown on dilution.—**Dyes**: unmordanted cotton dark brown shades. |
| Benzidine (tetraz.)<br>Salicylic acid. Aniline (diaz.)<br>↓<br>phenyl-amido-naphthol-sulphonic acid γ. | 1895. | Mensching.<br>Levinstein Limd.<br>Eng. Pats. $20548^{95}$ & $23523^{95}$.<br>Am. Pat 622961. | **Appearance of dyestuff**: blackish brown powder.—**In water**: soluble, with brown colour.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: violet solution; brown on dilution.—**Dyes**: unmordanted cotton olive brown shades very fast to light. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 351 | **Direct Indigo Blue BK.** [*I.*] | Sodium salt of diphenyl-disazo-cresol-ether-azo-amidonaphthol-disulphonic-amido-naphthol-sulphonic acid. |  $\begin{array}{l} C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}{[2]}OCH_3\\ {[1]}-N_2-C_{10}H_3\left\{\begin{array}{l}NH_2\\ OH\\ (SO_3Na)_2\end{array}\right.\\ {[5]}CH_3\end{array}\right.\\ {[1]}\vert\\ C_6H_4[4]-N_2-C_{10}H_4\left\{\begin{array}{l}NH_2\\ OH\\ SO_3Na\end{array}\right.\end{array}$ |
| 352 | **Direct Indigo Blue A.** [*I.*] | Sodium salt of diphenyl-disazo-cresol-ether-azo-amidonaphthol-disulphonic-amidophenol-disulphonic acid. |  $\begin{array}{l} C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}{[2]}OCH_3\\ {[1]}-N_2-C_{10}H_3\left\{\begin{array}{l}NH_2\\ OH\\ (SO_3Na)_2\end{array}\right.\\ {[5]}CH_3\end{array}\right.\\ {[1]}\vert\\ C_6H_4[4]-N_2-C_6H\left\{\begin{array}{l}NH_2\\ OH\\ (SO_3Na)_2\end{array}\right.\end{array}$ |
| 353 | **Melogene Blue BH.** [*K. S.*]<br>**Diamine Beta Black.** [*C.*] | Sodium salt of diphenyl-disazo-*p*-xylene-azo-bi-amido-naphthol-disulphonic acid. |  $\begin{array}{l} C_6H_4[4]-N_2-[4]C_6H_2\left\{\begin{array}{l}{[2]}CH_3\\ {[1]}-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[5]}CH_3\end{array}\right.\\ {[1]}\vert\\ C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\end{array}$ |
| 354 | **Benzo Gray.** [*By.*] | Sodium salt of diphenyl-disazo-α-naphthalene-azo-α-naphthol-sulphonic-salicylic acid. |  $\begin{array}{l} C_6H_4[4]-N_2-[4]C_{10}H_6[1]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\\ {[1]}\vert\\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |
| 355 | **Benzo Olive.** [*By.*] | Sodium salt of diphenyl-disazo-α-naphthalene-azo-amidonaphthol-disulphonic-salicylic acid. |  $\begin{array}{l} C_6H_4[4]-N_2-[4]C_{10}H_6[1]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[8]}OH\\ {[3]}SO_3Na\\ {[6]}SO_3Na\end{array}\right.\\ {[1]}\vert\\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$ |
| 356 | **Congo Fast Blue R.** [*A.*] | Sodium salt of ditolyl-disazo-α-naphthalene-azo-bi-α-naphthol-disulphonic acid. |  $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_{10}H_6[1]-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[3]}SO_3Na\\ {[8]}SO_3Na\end{array}\right.\end{array}\right.\\ {[1]}\vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[3]}SO_3Na\\ {[8]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$ |
| 357 | **Benzo Black Blue R.** [*By.*] | Sodium salt of ditolyl-disazo-α-naphthalene-azo-bi-α-naphthol-sulphonic acid. |  $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_{10}H_6[1]-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\\ {[3]}CH_3\end{array}\right.\end{array}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Benzidine (tetraz.)<br>↙ ↘<br>Amido-naphthol-sulphonic acid. Amidocresol-ether (diaz.)<br>↓<br>amido-naphthol-disulphonic acid. | 1893. | Société pour l'Industrie Chimique à Bâle.<br>Fr. Pat. $233901^{93}$.<br>Ger. Pat. $83244^{93}$. | **Solution in water**: blue.—**Dyes**: cotton direct from an alkaline bath, half wool from a weakly acid bath, indigo blue of good fastness to light, acids, and alkalies. Can be diazotised on the fibre and developed to a black with tolylene diamine. |
| Benzidine (tetraz.)<br>↙ ↘<br>Amidophenol-disulphonic acid. Amidocresol-ether (diaz.)<br>↓<br>amido-naphthol-disulphonic acid. | 1893. | Société pour l'Industrie Chimique à Bâle.<br>Fr. Pat. $233901^{93}$.<br>Ger. Pat. $83244^{93}$. | **Appearance of dyestuff**: gray powder.—**In water**: blue solution.—**On addition of hydrochloric acid or caustic soda**: soluble blue precipitate.—**In conc. sulphuric acid**: blue solution; on dilution blue solution and precipitate.—**Dyes**: cotton from a slightly alkaline bath, half wool from a slightly acid bath, indigo blue shades of good fastness to light, acids, and alkalies. |
| Benzidine (tetraz.)<br>↙ ↘<br>Amido-naphthol-disulphonic acid H. *p*-Xylidine<br>↓<br>amido-naphthol-disulphonic acid H. | 1896. | Böniger.<br>Eng. Pat. $28810^{96}$.<br>Am. Pat. 591616.<br>Fr. Pat. 262109. | **Appearance of dyestuff**: blue black powder.—**In water**: easily soluble, with violet blue colour.—**On addition of hydrochloric acid**: violet precipitate.—**On addition of caustic soda**: solution violet.—**In conc. sulphuric acid**: blue solution; bluish violet precipitate on dilution.—**Dyes**: unmordanted cotton direct black blue, which by diazotisation on the fibre and development with β-naphthol gives a fine black fast to washing and fairly fast to light. |
| Benzidine (tetraz.)<br>↙ ↘<br>Salicylic acid. α-Naphthylamine (diaz.)<br>↓<br>α-naphthol-sulphonic acid NW. | 1890. | Lauch.<br>Fr. Bayer & Co.<br>Eng. Pat. $13235^{90}$.<br>Ger. Pat. $57331^{90}$.<br>Fr. Pat. 187365. | **Appearance of dyestuff**: grayish black powder.—**In water**: bordeaux brown solution.—**On addition of hydrochloric acid to the aqueous solution**: black precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: blue solution; black precipitate on dilution with water.—**Dyes**: unmordanted cotton gray. |
| Benzidine (tetraz.)<br>↙ ↘<br>Salicylic acid. α-Naphthylamine (diaz.)<br>↓<br>amido-naphthol-disulphonic acid H. | 1891. | Lauch, Ulrich, & Duisberg.<br>Fr. Bayer & Co. | **Appearance of dyestuff**: black powder.—**In water**: dark moss-green solution.—**On addition of hydrochloric acid**: blackish gray precipitate.—**On addition of caustic soda**: solution dark brown.—**In conc. sulphuric acid**: violet solution; greenish black precipitate on dilution.—**Dyes**: unmordanted cotton from a neutral salt bath greenish olive; tolerably fast to light, soap, and acid, but browned by alkalies. |
| Tolidine (tetraz.)<br>↙ ↘<br>α-Naphthol-ε-disulphonic acid. α-Naphthylamine (diaz.)<br>↓<br>α-naphthol-ε-disulphonic acid. | 1890. | G. Schultz.<br>Berlin Aniline Co.<br>Ger. Pat. $60921^{91}$.<br>See Jour. Soc. Chem. Ind. 1897, 673. | **Appearance of dyestuff**: blue powder.—**In water**: blue solution.—**In alcohol**: reddish violet solution.—**On addition of hydrochloric acid or caustic soda to the aqueous solution**: blue precipitate.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton direct blue, fairly fast to light and milling. |
| Tolidine (tetraz.)<br>↙ ↘<br>α-Naphthol-sulphonic acid NW. α-Naphthylamine (diaz.)<br>↓<br>α-naphthol-sulphonic acid NW. | 1887. | R. Lauch.<br>Fr. Bayer & Co.<br>Eng. Pat. $16484^{87}$.<br>Am. Pat. $440639^{90}$.<br>Fr. Pat. 187365. | **Appearance of dyestuff**: grayish black powder.—**In water**: bluish violet solution.—**In alcohol**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: violet precipitate.—**In conc. sulphuric acid**: blue solution; bluish violet precipitate on dilution with water.—**Dyes**: unmordanted cotton dark bluish violet from a soap bath; tolerably fast to light, washing, acid, and alkali. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 358 | **Benzo Indigo Blue.** [*By.*] | Sodium salt of ditolyl-disazo-*a*-naphthalene-azo-bi-dioxynaphthalene-sulphonic acid. |  $$[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_{10}H_6[1]-N_2-C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$$ |
| 359 | **Congo Fast Blue B.** [*A.*] | Sodium salt of dimethoxy-diphenyl-disazo-*a*-naphthalene-azo-bi-*a*-naphthol-disulphonic acid. |  $$[1]\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_{10}H_6[1]-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[3]}SO_3Na\\ {[8]}SO_3Na\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[3]}SO_3Na\\ {[8]}SO_3Na\end{array}\right.\end{array}\right.\end{array}$$ |
| 360 | **Columbia Black FB & FF extra.** [*A.*] | Sodium salt of benzene-disazo-*a*-naphthylamine-sulphonic-acid-naphthol-sulphonic-acid-azo-*m*-phenylene-diamine. |  $$C_6H_4\left\langle\begin{array}{l}{[1]}N_2-[4]C_{10}H_5\left\{\begin{array}{l}{[1]}NH_2\\ {[6]}\text{ or }[7]SO_3Na\end{array}\right.\\ {[4]}N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[8]}OH\\ {[2]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\\ {[6]}SO_3Na\end{array}\right.\end{array}\right.$$ |
| 361 | **Isodiphenyl Black.** [*G.*] | Sodium salt of benzene-disazo-naphthol-sulphonic-acid-azo-*m*-phenylene-diamine-resorcin. |  $$C_6H_4\left\langle\begin{array}{l}{[1]}N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[8]}OH\\ {[6]}SO_3Na\\ {[2]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\\ {[4]}N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[3]}OH\end{array}\right.\end{array}\right.$$ |
| 362 | **Direct Black V.** [*K. S.*] | Sodium salt of diphenyl-disazo-naphthol-disulphonic-azo-*a*-naphthylamine-amidonaphthol-sulphonic acid. |  $$[1]\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[8]}OH\\ {[6]}SO_3Na\\ {[3]}SO_3Na\\ {[2]}-N_2-[4]C_{10}H_6[1]NH_2\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[2]}NH_2\\ {[8]}OH\\ {[6]}SO_3Na\end{array}\right.\end{array}$$ |
| 363 | **Diamine Bronze G.** [*C.*] | Sodium salt of diphenyl-disazo-naphthol-disulphonic-azo-*m*-phenylene-diamine-salicylic acid. |  $$[1]\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[1]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}$$ |
| 364 | **Direct Indone Blue R.** [*K. S.*] | Sodium salt of diphenyl-disazo-naphthol-disulphonic-*a*-naphthylamine-amidonaphthol-disulphonic acid. |  $$[1]\begin{array}{l} C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[2]}-N_2-[4]C_{10}H_6[1]NH_2\end{array}\right.\\ \vert\\ C_6H_4[4]-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[1]}NH_2\end{array}\right.\end{array}$$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Tolidine (tetraz.)<br>↙ ↘<br>Dioxynaphthalenesulphonic acid S. \| α-Naphthylamine (diaz.)<br>↓<br>dioxynaphthalenesulphonic acid S. | 1891. | Lauch, Ulrich, & Duisberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $3297^{90}$.<br>Am. Pat. $501118^{93}$.<br>Ger. Pat. $57912^{90}$. | **Appearance of dyestuff:** gray powder.—**In water:** violet solution.—**On addition of hydrochloric acid:** bluish violet precipitate.—**On addition of caustic soda:** solution reddish violet.—**In conc. sulphuric acid:** greenish blue solution; violet blue precipitate on dilution.—**Dyes:** unmordanted cotton indigo blue, tolerably fast to light and soap, but reddened by alkalies. |
| Dianisidine (tetraz.)<br>↙ ↘<br>α-Naphthol-ε-disulphonic acid. \| α-Naphthylamine (diaz.)<br>↓<br>α-naphthol-ε-disulphonic acid. | 1890. | G. Schultz.<br>Berlin Aniline Co.<br>Ger. Pat. 57444.<br>See J. Soc. Chem. Ind. 1897, 674. | **Appearance of dyestuff:** violet powder.—**In water:** blue solution.—**In alcohol:** violet blue solution.—**On addition of hydrochloric acid or caustic soda:** blue flocculent precipitate.—**In conc. sulphuric acid:** cornflower blue solution; blue precipitate on dilution.—**Dyes:** unmordanted cotton direct blue. |
| *p*-Phen. diamine (tetraz.)<br>↙ ↘<br>α-Naphthylamine-sulph. acid Cleve. \| Amidonaphthol-sulph. acid γ (diaz.)<br>↓<br>*m*-diamine. | 1896. | Clausius.<br>Berlin Aniline Co.<br>Compare<br>Meister, Lucius, & Brüning.<br>Am. Pat. 679221.<br>Ger. Pats. 131986 & 131987.<br>Chem. Zeit. 1902, 561. | **Dyes:** unmordanted cotton direct black. |
| *p*-Phen. diamine (tetraz.)<br>↙ ↘<br>Resorcin. \| Amidonaphthol-sulph. acid γ (diaz.)<br>↓<br>*m*-phen. diamine. | 1897. | Ris and Simon.<br>J. R. Geigy & Co.<br>Eng. Pat. $20278^{97}$.<br>Am. Pat. 615497.<br>Fr. Pat. 270151. | **Appearance of dyestuff:** grayish black powder.—**In water:** sparingly soluble cold, soluble hot with a violet black colour.—**On addition of hydrochloric acid or caustic soda:** black precipitate.—**In conc. sulphuric acid:** blackish blue solution; black precipitate on dilution.—**Dyes:** unmordanted cotton black which is fixed fast to washing by treatment with formaldehyde. |
| Benzidine (tetraz.)<br>↙ ↘<br>Amidonaphthol-sulph. acid γ. \| Amidonaphthol-disulph. acid 2 R. (diaz.)<br>↓<br>α-naphthylamine. | 1896. | Böniger.<br>Fr. Bayer & Co.<br>Eng. Pat. $15294^{96}$.<br>Am. Pat. 601033.<br>Ger. Pat. 109161.<br>Fr. Pat. 256950. | **Appearance of dyestuff:** gray powder.—**In water:** violet black solution.—**On addition of hydrochloric acid:** blue black precipitate.—**On addition of caustic soda:** solution becomes reddish violet.—**In conc. sulphuric acid:** blue solution; blue black precipitate on dilution.—**Dyes:** unmordanted cotton a violet black of good fastness to washing. Diazotised on the fibre and developed with β-naphthol it gives a dark blue, with phenylene diamine a black, which are very fast to washing. |
| Benzidine (tetraz.)<br>↙ ↘<br>Salicylic acid. \| Amidonaphthol-disulph. acid H. (diaz.)<br>↓<br>*m*-phen. diamine. | 1891. | M. Hoffmann & C. Krohn.<br>L. Cassella & Co.<br>Eng. Pat. $6972^{91}$.<br>Ger. Pat. $75762^{91}$. | **Appearance of dyestuff:** blackish powder.—**In water:** insoluble cold, chocolate brown solution hot.—**In alcohol:** insoluble.—**On addition of hydrochloric acid to aqueous solution:** purple brown precipitate.—**On addition of caustic soda:** solution becomes yellower.—**In conc. sulphuric acid:** bluish violet solution; black precipitate on dilution.—**Dyes:** unmordanted cotton yellowish brown of metallic appearance, which by treatment with copper salts is converted into a deep brown fast to light and washing. |
| Benzidine (tetraz.)<br>↙ ↘<br>Amidonaphthol-disulph. acid H. \| Amidonaphthol-disulph. acid 2 R. (diaz.)<br>↓<br>α-naphthylamine. | 1896. | Böniger.<br>Eng. Pat. $15294^{96}$.<br>Am. Pat. 601033.<br>Fr. Pat. 256950.<br>Ger. Pat. 109161. | **Appearance of dyestuff:** bluish black powder.—**In water:** easily soluble with blue black colour.—**On addition of hydrochloric acid:** dark blue precipitate.—**On addition of caustic soda:** violet solution.—**In conc. sulphuric acid:** blue solution; dark blue precipitate on dilution.—**Dyes:** unmordanted cotton gray blue to indigo blue of good fastness to light and washing. By diazotisation and development with β-naphthol or phenylene diamine it is converted into fast dark blue or black. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 365 | **Trisulphone Brown B, G, & 2 G.** [*K. S.*] | |  $D\left\langle\begin{array}{l}N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[2]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\\ N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}OH\\ {[2]}CO_2Na\end{array}\right.\end{array}\right.$ <br>(D = residue of benzidine, tolidine, or dianisidine.) |
| 366 | **Columbia Black R.** [*A.*] | Sodium salt of ditolyl-disazo-naphthol-disulphonic acid-azo-bi-*m*-tolylene-diamine. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[2]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\end{array}\right.\end{array}$ |
| 367 | **Columbia Black B.*** [*A.*] | Sodium salt of dimethoxy-diphenyl-disazo-naphthol-disulphonic-acid-azo-bi-*m*-tolylene-diamine. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[7]C_{10}H_3\left\{\begin{array}{l}{[6]}SO_3Na\\ {[3]}SO_3Na\\ {[8]}OH\\ {[2]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[3]}OCH_3\\ {[4]}-N_2-[4]C_6H_2\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\\ {[6]}CH_3\end{array}\right.\end{array}\right.\end{array}$ |
| 368 | **Coumassie Union Blacks.** [*Lev.*] | Sodium salt of sulpho-naphthalene-disazo-naphthol-sulphonic-acid-azo-bi-*m*-phenylene-diamine (or *m*-tolylene diamine or resorcin). | For instance—  $C_{10}H_5\left\{\begin{array}{l}{[1]}-N_2-[7]C_{10}H_4\left\{\begin{array}{l}{[6]}SO_3Na\\ {[8]}OH\\ {[2]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.\\ {[3]}SO_3Na\\ {[4]}-N_2-[4]C_6H_3\left\{\begin{array}{l}{[1]}NH_2\\ {[3]}NH_2\end{array}\right.\end{array}\right.$ |
| 369 | **Benzo Black Blue G.** [*By.*] | Sodium salt of disulpho-diphenyl-disazo-α-naphthalene-azo-bi-α-naphthol-*p*-sulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}SO_3Na\\ {[4]}-N_2-[4]C_{10}H_6[1]N=N[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SONa_3\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[2]C_{10}H_5\left\{\begin{array}{l}{[1]}OH\\ {[4]}SO_3Na\end{array}\right.\\ SO_3Na\end{array}\right.\end{array}$ |
| 370 | **Benzo Black Blue 5 G.** [*By.*] | Sodium salt of disulpho-diphenyl-disazo-α-naphthalene-azo-bi-dioxynaphthalene-sulphonic acid. |  $[1]\begin{array}{l}C_6H_3\left\{\begin{array}{l}SO_3Na\\ {[4]}-N_2-[4]C_{10}H_6[1]-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[4]}SO_3Na\end{array}\right.\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N_2-[2]C_{10}H_4\left\{\begin{array}{l}{[1]}OH\\ {[8]}OH\\ {[4]}SO_3Na\end{array}\right.\\ SO_3Na\end{array}\right.\end{array}$ |
| 371 | **Columbia Green.** [*A.*]<br>**Direct Green CO.** [*L.*] | Sodium salt of diphenyl-disazo-salicylic-acid-amido-naphthol-sulphonic-acid-azo-benzene-sulphonic acid. |  $\begin{array}{l}C_6H_4[4]-N_2-C_6H_3(OH)CO_2Na\\ {[1]}\,\vert\\ C_6H_4[4]-N_2\\ C_6H_4(SO_3Na)-N_2\end{array}>C_{10}H_3(NH_2)(OH)(SO_3Na)_2$ |

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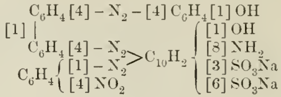
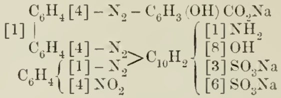
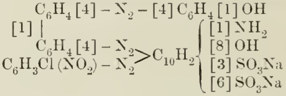
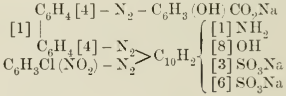
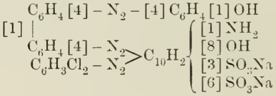
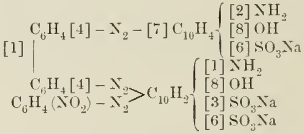
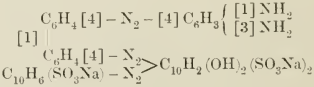
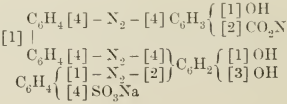
* Columbia Blacks 2 BX & 2 BW [A.]

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Paradiamine (tetraz.)<br>↙ ↘<br>Salicylic acid. Amido-naphthol-disulph. acid 2 R (diaz.)<br>↓<br>*m*-Diamine. | 1897. | Böniger.<br>Eng. Pat. 5746$^{98}$.<br>Am. Pat. 608024.<br>Fr. Pat. 275733. | **Appearance of dyestuff**: brown powder.—**In water**: easily soluble to coffee brown solution.—**On addition of hydrochloric acid**: blackish brown precipitate.—**On addition of caustic soda**: reddish brown solution.—**In conc. sulphuric acid**: bluish violet; dark brown precipitate on dilution.—**Dyes**: unmordanted cotton yellowish to dark brown shades, which by subsequent treatment with bichromate and copper sulphate are rendered very fast to washing and light. |
| Tolidine (tetraz.)<br>↙ ↘<br>*m*-Tolylene diamine Amidonaphthol-disulph. acid R (diaz.)<br>↓<br>*m*-Tolylene diamine. | 1893. | Kirchhoff. | **Appearance of dyestuff**: black powder.—**In water**: brown black solution.—**In alcohol**: brown black solution.—**On addition of hydrochloric acid to the aqueous solution**: black flocculent precipitate.—**On addition of caustic soda**: brown solution.—**In conc. sulphuric acid**: pure blue solution; on dilution violet black flocculent precipitate.—**Dyes**: unmordanted cotton direct black. |
| Dianisidine (tetraz.)<br>↙ ↘<br>*m*-Tolylene diamine. Amidonaphthol-disulph. acid R (diaz.)<br>↓<br>*m*-Tolylene diamine. | 1893. | Kirchhoff. | **Appearance of dyestuff**: black powder.—**In water or alcohol**: violet black solution.—**On addition of hydrochloric acid to the aqueous solution**: dark flocculent precipitate.—**On addition of caustic soda**: solution reddish violet.—**In conc. sulphuric acid**: blue black solution; on dilution becoming bluish violet and then giving a violet black flocculent precipitate.—**Dyes**: unmordanted cotton black. |
| Naphth. diamine sulph. acid (tetraz.)<br>↙ ↘<br>*m*-Diamine or resorcin. Amidonaphthol-sulph. acid γ (diaz.)<br>↓<br>*m*-Diamine or resorcin. | 1896. | R. Herz.<br>Levinstein Limd.<br>Eng. Pat. 17065$^{96}$.<br>Am. Pat. 619194.<br>Ger. Pat. 115990. | **Appearance of dyestuff**: black powder.—**In water**: violet solution.—**On addition of hydrochloric acid or caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: blue solution, becoming blackish blue on dilution with water.—**Dyes**: mixed and union goods black. |
| Benzidine disulph. acid (tetraz).<br>↙ ↘<br>α Naphthol-sulph. acid NW. α-Naphthylamine (diaz.)<br>↓<br>α-Naphthol-sulph. acid NW. | 1887. | R. Lauch & M. Kahn.<br>Fr. Bayer & Co.<br>Ger. Pat. 44779$^{87}$.<br>Griess & Duisberg.<br>Ber. 22, 2463. | **Appearance of dyestuff**: black powder.—**In water**: blue black solution.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: black blue precipitate.—**On addition of caustic soda**: solution becomes blue.—**In conc. sulphuric acid**: blackish green solution; blackish blue precipitate on dilution with water.—**Dyes**: unmordanted cotton black blue shades from an alkaline bath. |
| Benzidine disulph. acid (tetraz.)<br>↙ ↘<br>Dioxynaphth. sulph. acid S. α-Naphthylamine (diaz.)<br>↓<br>Dioxynaphth. sulph. acid S. | 1892. | Kahn, Lauch, & Ulrich. | **Appearance of dyestuff**: gray powder.—**In water**: easily soluble with blackish blue colour.—**On addition of hydrochloric acid**: dark greenish blue precipitate and greenish solution.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: black green solution; dark greenish blue precipitate on dilution.—**Dyes**: unmordanted cotton greenish black, tolerably fast to light, washing, and acids, but affected by alkalies. |
| Benzidine (tetraz.) ↗ Salicylic acid.<br>Benzidine (tetraz.) ↘ Amidonaphthol-sulph. acid.<br>Sulphanilic acid (diaz.) ↗ Amidonaphthol-sulph. acid. | 1893. | Möller & Kirchhoff. | **Appearance of dyestuff**: black powder.—**In water**: green solution.—**On addition of hydrochloric acid**: green flocculent precipitate.—**On addition of caustic soda**: greenish black solution.—**In conc. sulphuric acid**: blue violet solution; on dilution green flocks.—**Dyes**: cotton direct green. |

are trisazo dyestuffs of the same group.

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 372 | **Diamine Green B.**<br>[*C.*] | Sodium salt of diphenyl-disazo-phenol-disulpho-amidonaphthol-azo-nitrobenzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_4\,[1]\,OH \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_4\left\{\begin{array}{l}{[1]}-N_2\\ {[4]}\,NO_2\end{array}\right. \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[8]}\,NH_2\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 373 | **Diamine Green G.**<br>[*C.*] | Sodium salt of diphenyl-disazo-salicylic acid-di-sulpho-amido-naphthol-azo-nitro-benzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-C_6H_3\,(OH)\,CO_2Na \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_4\left\{\begin{array}{l}{[1]}-N_2\\ {[4]}\,NO_2\end{array}\right. \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 374 | **Diphenyl Green G.**<br>[*G.*] | Sodium salt of diphenyl-disazo-phenol-disulpho-amidonaphthol-azo-chloronitrobenzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_4\,[1]\,OH \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_3Cl\,(NO_2)-N_2 \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 375 | **Diphenyl Green 3 G.**<br>[*G.*] | Sodium salt of diphenyl-disazo-salicylic-disulpho-amidonaphthol-azo-chloronitrobenzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-C_6H_3\,(OH)\,CO_2Na \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_3Cl\,(NO_2)-N_2 \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 376 | **Chloramine Green B.**<br>[*K. S.*] | Sodium salt of diphenyl-disazo-phenol (or salicylic)-disulpho-amido-naphthol-azo-dichloro-benzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_4\,[1]\,OH \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_3Cl_2-N_2 \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 377 | **Diamine Black HW.**<br>[*C.*] | Sodium salt of diphenyl-disazo-sulpho-amido-naphthol-disulpho-amidonaphthol-azo-nitrobenzene. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[7]\,C_{10}H_4\left\{\begin{array}{l}{[2]}\,NH_2\\ {[8]}\,OH\\ {[6]}\,SO_3Na\end{array}\right. \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_6H_4\,(NO_2)-N_2 \end{array}\right> C_{10}H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[8]}\,OH\\ {[3]}\,SO_3Na\\ {[6]}\,SO_3Na\end{array}\right. \end{array}$ |
| 378 | **Dianil Black R.**<br>[*M.*] | Sodium salt of diphenyl-disazo-*m*-phenylene-diamine-disulpho-dioxy-naphthalene-azo-naphthalene-sulphonic acid. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2 \\ C_{10}H_6\,(SO_3Na)-N_2 \end{array}\right> C_{10}H_2\,(OH)_2\,(SO_3Na)_2 \end{array}$ |
| 379 | **Congo Brown G.**<br>[*A.*] | Sodium salt of sulpho-benzene-azo-resorcinol-azo-diphenyl-azo-salicylic acid. |  $\begin{array}{l} C_6H_4\,[4]-N_2-[4]\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ {[1]}\,\vert \\ \left.\begin{array}{r} C_6H_4\,[4]-N_2-[4] \\ C_6H_4\left\{\begin{array}{l}{[1]}-N_2-[2]\\ {[4]}\,SO_3Na\end{array}\right. \end{array}\right\} C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right. \end{array}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Benzidine (tetraz.)<br>*p*-Nitraniline (diaz.)<br>→ Phenol.<br>→ Amidonaphthol-disulph. acid H. | 1891. | M. Hoffmann & C. Daimler.<br>L. Cassella & Co.<br>Eng. Pat. $15725^{91}$. | **Appearance of dyestuff**: dark powder.—**In water**: dull green solution.—**In alcohol**: bluish green solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish black precipitate.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: violet solution; black precipitate on dilution.—**After reduction with zinc dust**: becomes bright blue on paper.—**Dyes**: unmordanted cotton green shades. |
| Benzidine (tetraz.)<br>*p*-Nitraniline (diaz.)<br>→ Salicylic acid.<br>→ Amidonaphthol-disulph. acid H. | 1891. | M. Hoffmann & C. Daimler.<br>L. Cassella & Co.<br>Eng. Pat. $15725^{91}$.<br>Am. Pat. 514599.<br>Ger. Pat. $66351^{91}$.<br>Fr. Pat. 201770. | **Appearance of dyestuff**: black powder.—**In water**: dark green solution.—**On addition of hydrochloric acid**: bluish black precipitate.—**On addition of caustic soda**: solution becomes yellower.—**In conc. sulphuric acid**: violet solution; black precipitate on dilution.—**Dyes**: unmordanted cotton from neutral salt bath green, tolerably fast to light, washing, and alkalies, but dulled somewhat by acids and sensitive to copper. Very fast on wool and silk. |
| Benzidine (tetraz.)<br>*o*-Chlor-*p*-nitraniline (diaz.)<br>→ Phenol.<br>→ Amidonaphthol-disulph. acid H. | 1898. | Simon.<br>J. R. Geigy & Co.<br>Am. Pat. $628233^{99}$. | **Appearance of dyestuff**: black powder.—**In water**: dark green solution.—**In alcohol**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: black precipitate.—**On addition of caustic soda**: dull green solution.—**In conc. sulphuric acid**: violet solution; black precipitate on dilution.—**Dyes**: unmordanted cotton green. |
| Benzidine (tetraz.)<br>*o*-Chlor-*p*-nitraniline (diaz.)<br>→ Salicylic acid.<br>→ Amidonaphthol-disulph. acid H. | 1898. | Simon.<br>J. R. Geigy & Co.<br>Am. Pat. $628233^{99}$. | **Appearance of dyestuff**: dark powder.—**In water**: green solution.—**In alcohol**: sparingly soluble with green colour.—**On addition of hydrochloric acid to the aqueous solution**: green precipitate.—**On addition of caustic soda**: dull green solution.—**In conc. sulphuric acid**: reddish violet solution; green precipitate on dilution.—**Dyes**: unmordanted cotton green. |
| Benzidine (tetraz.)<br>Dichloraniline (diaz.)<br>→ Phenol (or salicylic acid.<br>→ Amidonaphthol-disulph. acid H. | 1898. | Böniger & Lapott.<br>Sandoz & Co., Basle.<br>Eng. Pat. $8503^{99}$.<br>Am. Pat. 627679.<br>Fr. Pat. 287971. | **Appearance of dyestuff**: dark bronzy powder.—**In water**: easily soluble to green solution.—**In alcohol**: easily soluble to green solution.—**On addition of hydrochloric acid to the aqueous solution**: violet black precipitate.—**On addition of caustic soda**: black green solution.—**In conc. sulphuric acid**: violet solution; violet black precipitate on dilution.—**Dyes**: unmordanted cotton bright green, the brightest and fastest to alkalies of the direct cotton greens. Dyes level shades on union goods and half-silk. |
| Benzidine (tetraz.)<br>*p*-Nitraniline (diaz.)<br>→ Amidonaphthol-sulph. acid γ.<br>→ Amidonaphthol-disulph. acid H. | 1891. | L. Cassella & Co.<br>Ger. Pats. $66351^{91}$ & 70399. | **Appearance of dyestuff**: blackish gray powder.—**In water**: blackish blue solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: blue solution; blue precipitate on dilution.—**Dyes**: unmordanted cotton greenish black shades which are fast to hot pressing. |
| Benzidine (tetraz.)<br>Naphthionic acid (diaz.)<br>→ *m*-Phenylene diamine.<br>→ Dioxynaphthalene-disulph. acid. | 1894. | Schmidt & Ernst. | **Appearance of dyestuff**: small bronzy crystals.—**In water**: sparingly soluble with reddish violet colour.—**On addition of hydrochloric acid**: precipitate.—**On addition of caustic soda**: blue solution.—**In conc. sulphuric acid**: dark blue solution; on dilution, reddish violet solution and precipitate.—**Dyes**: unmordanted cotton direct black. |
| Benzidine (tetraz.)<br>Sulphanilic acid (diaz.)<br>→ Salicylic acid.<br>→ Resorcin. | 1888. | Strassburger.<br>Berlin Aniline Co.<br>Eng. Pat. $10653^{88}$.<br>Am. Pat. 399581.<br>Ger. Pats. $46328^{88}$ & $46501^{88}$.<br>Fr. Pat. 192331. | **Appearance of dyestuff**: brown powder.—**In water**: red solution.—**In alcohol**: brown solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: red colour.—**In conc. sulphuric acid**: reddish violet solution; dark reddish brown precipitate on dilution with water.—**Dyes**: unmordanted cotton brown, of moderate fastness which is increased by subsequent coppering. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 380 | **Congo Brown R.** [*A.*] | Sodium salt of sulpho-naphthalene-azo-resorcin-azo-diphenyl-azo-salicylic acid. | $\begin{array}{l} \quad C_6H_4\,{[4]}-N_2-{[4]}\,C_6H_3\left\{\begin{array}{l}{[1]}\,OH\\ {[2]}\,CO_2Na\end{array}\right. \\ {[1]}\,\vert \\ \quad \left.\begin{array}{r} C_6H_4\,{[4]}-N_2-{[4]} \\ C_{10}H_6\left\{\begin{array}{l}{[1]}-N_2-{[2]}\\ {[5]}\,SO_3Na\end{array}\right.\end{array}\right\} C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right. \end{array}$ |
| 381 | **Azo Corinth.** [*O.*] | Sodium salt of sulpho-naphthalene-azo-resorcin-azo-ditolyl-azo-amido-phenol-sulphonic acid. | $\begin{array}{l} C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N_2-C_6H_2\,(NH_2)\,(OH)\,(SO_3Na)\end{array}\right. \\ \vert \\ C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N_2\end{array}\right. \\ C_{10}H_6(SO_3Na)-N_2 \end{array} > C_6H_2\,(OH)_2$ |
| 382 | **Alizarine Yellow FS.** [*D. H.*] | Diphenyl-tolyl-car-binol-trisazo-tri-salicylic acid. | $HO\cdot C \left\langle \begin{array}{l} C_6H_4-N_2-C_6H_3\,(OH)\,CO_2H \\ C_7H_6-N_2-C_6H_3\,(OH)\,CO_2H \\ C_6H_4-N_2-C_6H_3\,(OH)\,CO_2H \end{array}\right.$ |

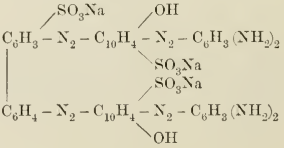
## V. TETRAKISAZO

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 383 | **Direct Brown J.** [*I.*] | Sodium salt of carboxy-benzene-azo-phenylene-brown. | $\begin{array}{r} \left.\begin{array}{r} C_6H_4\,(CO_2Na)-N=N-{[2]} \\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-{[4]}\end{array}\right. \end{array}\right\} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \\ \left.\begin{array}{r} {[3]}-N=N-{[4]} \\ C_6H_4\,(CO_2Na)-N=N-{[2]} \end{array}\right\} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \end{array}$ |
| 384 | **Benzo Brown G.** [*By.*] | Sodium salt of sulpho-benzene-azo-phenylene-brown. | $\begin{array}{l} C_6H_4\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}-N=N-{[2]}\end{array}\right. \\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-{[4]}\\ {[3]}-N=N-{[4]}\end{array}\right. \\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-{[2]}\\ {[4]}SO_3Na\end{array}\right. \end{array} \begin{array}{l} \} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \\ \} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \end{array}$ |
| 385 | **Benzo Brown B.** [*By.*] | Sodium salt of sulpho-naphthalene-azo-phenylene-brown. | $\begin{array}{l} C_{10}H_6\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}-N=N-{[2]}\end{array}\right. \\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-{[4]}\\ {[3]}-N=N-{[4]}\end{array}\right. \\ C_{10}H_6\left\{\begin{array}{l}{[1]}-N=N-{[2]}\\ {[4]}\,SO_3Na\end{array}\right. \end{array} \begin{array}{l} \} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \\ \} C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \end{array}$ |
| 386 | **Toluylene Brown R.** [*O.*] [*By.*] | Sodium salt of sulpho-toluene-disazo-bi-*m*-phenylene-diamine-azo-naphtha-lene-sulphonic acid. | $\begin{array}{r} C_{10}H_6\,(SO_3Na)-N_2 \\ C_6H_2\,(CH_3)\,(SO_3Na)\left\{\begin{array}{l}{[1]}-N_2\\ {[3]}-N_2\end{array}\right. \\ C_{10}H_6\,(SO_3Na)-N_2 \end{array} \begin{array}{l} > C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \\ > C_6H_2\left\{\begin{array}{l}{[1]}\,NH_2\\ {[3]}\,NH_2\end{array}\right. \end{array}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Benzidine (tetraz.) → Salicylic acid.<br>Benzidine (tetraz.) → Resorcin.<br>α-Naphthamine sulph. acid L (diaz.) → Resorcin. | 1888. | Strassburger.<br>Berlin Aniline Co.<br>Eng. Pat. $10653^{88}$.<br>Am. Pat. 399581.<br>Ger. Pats. 46328 & 46501. | **Appearance of dyestuff**: dark brownish red powder.—**In water**: red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: red colour.—**In conc. sulphuric acid**: violet solution; on dilution with water a dark reddish brown precipitate.—**Dyes**: unmordanted cotton brown of moderate fastness which is increased by subsequent coppering. |
| Tolidine (tetraz.) → Amidophenol-sulph. acid.<br>Tolidine (tetraz.) → Resorcin.<br>Naphthionic acid (diaz.) → Resorcin. | 1892. | Rudolph & Voges.<br>K. Oehler.<br>Eng. Pat. $13402^{93}$.<br>Am. Pat. 516381.<br>Ger. Pat. 71182. | **Appearance of dyestuff**: blackish brown powder.—**In water**: reddish brown solution.—**On addition of hydrochloric acid**: reddish brown precipitate.—**On addition of caustic soda**: bluish red solution.—**In conc. sulphuric acid**: bluish violet solution; reddish brown precipitate on dilution.—**Dyes**: unmordanted cotton currant brown from a soap bath. |
| Magenta (diaz.) → Salicylic acid.<br>Magenta (diaz.) → Salicylic acid.<br>Magenta (diaz.) → Salicylic acid. | 1890. | Julius.<br>Bad. Anil. & Soda Fabrik.<br>Ger. Pat. 58893. | **Appearance of dyestuff**: yellowish brown paste.—**In water**: insoluble.—**In alcohol**: very slightly soluble.—**On addition of caustic soda**: orange yellow solution.—**In conc. sulphuric acid**: green solution; brown precipitate on dilution.—**Dyes**: chromed wool a tolerably fast yellow. |

## COLOURING MATTERS.

| Method of Preparation. | | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|---|
| Diazo Compound from | Combined with | | | |
| *m*-Amidobenzoic acid (2 mols.) | Bismarck Brown (1 mol.) | 1891. | R. Gnehm & J. Schmid.<br>Société pour l'Industrie Chimique à Bâle.<br>Am. Pat. 491422.<br>Fr. Pat. 219925.<br>Ger. Pat. 76127. | **Appearance of dyestuff**: brown powder.—**In water**: yellowish brown solution.—**On addition of hydrochloric acid**: dark brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: brown solution; brown precipitate on dilution.—**Dyes**: unmordanted cotton brown. |
| Sulphanilic acid (2 mols.) | Bismarck Brown (1 mol.) | 1887. | M. Herzberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $16493^{87}$.<br>Ger. Pat. $46804^{87}$. | **Appearance of dyestuff**: brownish black powder.—**In water**: reddish brown solution.—**In alcohol**: partially soluble. **On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: brown flocculent precipitate (if the solution is strong).—**In conc. sulphuric acid**: violet brown solution; on dilution with water, pure violet; on further dilution, a brown precipitate.—**Dyes**: unmordanted cotton yellowish brown from a neutral salt bath. |
| Naphthionic acid (2 mols.) | Bismarck Brown (1 mol.) | 1887. | M. Herzberg.<br>Fr. Bayer & Co.<br>Eng. Pat. $16493^{87}$.<br>Ger. Pat. $46804^{87}$. | **Appearance of dyestuff**: brownish black powder.—**In water**: reddish brown solution.—**In alcohol**: partially soluble.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**In conc. sulphuric acid**: dull violet solution; brown precipitate on dilution with water.—**Dyes**: unmordanted cotton brown from a neutral salt bath. |
| Naphthionic acid (diaz.) →<br>Tolylene diam. sulph. acid (tetraz.) →<br>Naphthionic acid (diaz.) → | *m*-Phen. diamine.<br>*m*-Phen. diamine. | 1889. | Rudolph.<br>K. Oehler & Co.<br>Eng. Pat. $11000^{89}$.<br>Am. Pat. $465116^{91}$.<br>Ger. Pat. $58657^{89}$. | **Appearance of dyestuff**: black brown powder.—**In water**: brown solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: dull reddish violet solution.—**Dyes**: unmordanted cotton from a soap bath brown shades, tolerably fast to washing, alkalies, and acids, but not to light. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 387 | **Hessian Brown B B.** [*L.*] | Sodium salt of diphenyl-disazo-bi-resorcinol-azo-benzene-sulphonic acid. | $\begin{array}{l}\left.\begin{array}{l}C_6H_4\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}-N=N-[4]\end{array}\right.\\ \quad C_6H_4\,[4]-N=N-[2]\end{array}\right\}C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right.\\ {[1]}\ \vert\\ \left.\begin{array}{l}\quad C_6H_4\,[4]-N=N-[2]\\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-[4]\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right\}C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right.\end{array}$ |
| 388 | **Hessian Brown M M.** [*L.*] | Sodium salt of ditolyl-disazo-bi-resorcinol-azo-benzene-sulphonic acid. | $\begin{array}{l}\left.\begin{array}{l}C_6H_4\left\{\begin{array}{l}{[4]}\,SO_3Na\\ {[1]}-N=N-[4]\end{array}\right.\\ C_6H_3\left\{\begin{array}{l}{[4]}-N=N-[2]\\ {[3]}\,CH_3\end{array}\right.\end{array}\right\}C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right.\\ {[1]}\ \vert\\ \left.\begin{array}{l}C_6H_3\left\{\begin{array}{l}{[3]}\,CH_3\\ {[4]}-N=N-[2]\end{array}\right.\\ C_6H_4\left\{\begin{array}{l}{[1]}-N=N-[4]\\ {[4]}\,SO_3Na\end{array}\right.\end{array}\right\}C_6H_2\left\{\begin{array}{l}{[1]}\,OH\\ {[3]}\,OH\end{array}\right.\end{array}$ |
| 389 | **Direct Heliotrope B.** [*R.*] | Sodium salt of sulpho-α-naphthol-azo-diphenyl-azo-toluene-disazo-bi-α-naphthol-*p*-sulphonic acid. | $\begin{array}{l}C_6H_4\,[4]-N_2-[4]\,C_6H_2\left\{\begin{array}{l}{[6]}\,CH_3\\ {[3]}-N_2-C_{10}H_5\,(OH)\,SO_3Na\\ {[1]}-N_2-C_{10}H_5\,(OH)\,SO_3Na\end{array}\right.\\ {[1]}\ \vert\\ C_6H_4\,[4]-N_2-C_{10}H_5\,(OH)\,SO_3Na\end{array}$ |
| 390 | **Mekong Yellow G.** [*D. H.*] | Sodium salt of bi-diphenyl-tetrakisazo-dioxydiphenyl-methane-bi-salicylic acid. | $\begin{array}{l}C_6H_4-N_2-C_6H_3\,(OH)\,CO_2Na\\ \vert\\ \left.\begin{array}{l}C_6H_4-N_2-C_6H_3\,(OH)\\ C_6H_4-N_2-C_6H_3\,(OH)\end{array}\right>CH_2\\ \vert\\ C_6H_4-N_2-C_6H_3\,(OH)\,CO_2Na\end{array}$ |
| 391 | **Mekong Yellow R.** [*D. H.*] | Sodium salt of bi-ditolyl-tetrakisazo-dioxydiphenyl-methane-bi-salicylic acid. | $\begin{array}{l}C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\,CO_2Na\\ \vert\\ \left.\begin{array}{l}C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\\ C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\end{array}\right>CH_2\\ \vert\\ C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\,CO_2Na\end{array}$ |
| 392 | **Azo Orange R.** [*D. H.*] | Sodium salt of bi-ditolyl-tetrakisazo-dioxydiphenyl-methane-bi-naphthionic acid. | $\begin{array}{l}C_6H_3\,(CH_3)-N_2-C_{10}H_5\,(NH_2)\,SO_3Na\\ \vert\\ \left.\begin{array}{l}C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\\ C_6H_3\,(CH_3)-N_2-C_6H_3\,(OH)\end{array}\right>CH_2\\ \vert\\ C_6H_3\,(CH_3)-N_2-C_{10}H_5\,(NH_2)\,SO_3Na\end{array}$ |
| 393 | **Cuba Black.**<br>**Dianil Black.**<br>[*Petersen.*] | Sodium salt of sulpho-diphenyl-disazo-bi-sulpho-naphthol-disazo-bi-*m*-phenylene diamine. |  $\begin{array}{l}\overset{\diagup SO_3Na}{C_6H_3}-N_2-\underset{\diagdown SO_3Na}{\overset{\diagup OH}{C_{10}H_4}}-N_2-C_6H_3\,(NH_2)_2\\ \vert\\ C_6H_4-N_2-\underset{\diagdown OH}{\overset{\diagup SO_3Na}{C_{10}H_4}}-N_2-C_6H_3\,(NH_2)_2\end{array}$ |

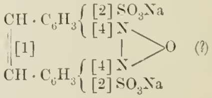
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Sulphanilic acid (diaz.) → Resorcin.<br>Benzidine (tetraz.) → Resorcin. → Resorcin.<br>Sulphanilic acid (diaz.) → Resorcin. | 1889. | BENDER.<br>A. LEONHARDT & Co. | **Appearance of dyestuff:** blackish brown powder.—**In water:** brown solution.—**On addition of hydrochloric acid:** brown precipitate.—**On addition of caustic soda:** deep red solution.—**In conc. sulphuric acid:** violet black solution; brown precipitate on dilution.—**Dyes:** unmordanted cotton brown. |
| Sulphanilic acid (diaz.) → Resorcin.<br>Tolidine (tetraz.) → Resorcin. → Resorcin.<br>Sulphanilic acid (diaz.) → Resorcin. | 1889. | BENDER.<br>A. LEONHARDT & Co. | **Appearance of dyestuff:** brown powder.—**In water:** brown solution.—**On addition of hydrochloric acid:** brown precipitate.—**On addition of caustic soda:** reddish brown solution.—**In conc. sulphuric acid:** violet black solution; brown precipitate on dilution.—**Dyes:** unmordanted cotton brown of good fastness to acid and alkali, tolerable fastness to washing, and medium fastness to light, which is improved by coppering. |
| Benzidine (tetraz.)<br>→ α-Naphthol sulph. acid NW.<br>→ Tol.-*m*-diam. oxamic acid (diaz.) ↓ α-Naphthol-sulph. acid NW.<br>Product saponified, again diazotised and combined with a third mol. of α-naphthol sulph. acid NW. | 1895. | MARKFELDT.<br>Ger. Pat. 99126. | **Appearance of dyestuff:** bronzy powder.—**In water:** easily soluble.—**On addition of hydrochloric acid:** reddish violet precipitate.—**On addition of caustic soda:** solution rather bluer.—**In conc. sulphuric acid:** blue solution; reddish violet precipitate on dilution.—**Dyes:** unmordanted cotton a violet of pure shade. |
| Benzidine (tetraz.) → Salicylic acid.<br>Benzidine (tetraz.) → Dioxydiphenyl-methane. ← Benzidine (tetraz.)<br>Benzidine (tetraz.) → Salicylic acid. | 1893. | BRACK.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $8511^{93}$.<br>Am. Pat. $519523^{94}$.<br>Ger. Pat. 80816.<br>Fr. Pat. $228593^{93}$. | **Appearance of dyestuff:** yellowish brown powder.—**In water:** yellowish brown solution.—**On addition of hydrochloric acid:** brown precipitate.—**On addition of caustic soda:** reddish brown solution.—**In conc. sulphuric acid:** violet solution; brown precipitate on dilution.—**Dyes:** unmordanted cotton greenish yellow from a soap bath. |
| Tolidine (tetraz.) → Salicylic acid.<br>Tolidine (tetraz.) → Dioxydiphenyl-methane. ← Tolidine (tetraz.)<br>Tolidine (tetraz.) → Salicylic acid. | 1893. | BRACK.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $8511^{93}$.<br>Am. Pat. $519523^{94}$. | **Appearance of dyestuff:** dark brown powder.—**In water:** soluble, yellowish brown solution.—**On addition of hydrochloric acid:** dark brown precipitate.—**On addition of caustic soda:** solution redder.—**In conc. sulphuric acid:** blue violet solution; blackish brown precipitate on dilution.—**Dyes:** unmordanted cotton yellow. |
| Tolidine (tetraz.) → Naphthionic acid.<br>Tolidine (tetraz.) → Dioxydiphenyl-methane. ← Tolidine (tetraz.)<br>Tolidine (tetraz.) → Naphthionic acid. | 1893. | BRACK.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $8511^{93}$.<br>Am. Pat. $516468^{94}$.<br>Ger. Pat. 79082. | **Appearance of dyestuff:** brick red powder.—**In water:** brownish yellow solution.—**On addition of hydrochloric acid:** dark gray precipitate.—**On addition of caustic soda:** solution redder.—**In conc. sulphuric acid:** blue solution; dark gray precipitate on dilution.—**Dyes:** unmordanted cotton orange. |
| Benzidine sulph. acid (tetraz.)<br>Amidonaphthol sulph. acid γ (diaz.) ↓ *m*-Phenylene diamine.<br>Amidonaphthol sulph. acid γ (diaz.) ↓ *m*-Phenylene diamine. | 1896. | FERD. PETERSEN & Co.<br>Eng. Pat. $13743^{96}$.<br>Am. Pat. $578580^{97}$.<br>Fr. Pat. $257245^{96}$. | **Appearance of dyestuff:** black powder.—**In water:** soluble.—**On addition of hydrochloric acid or caustic soda:** insoluble precipitate.—**In conc. sulphuric acid:** dark blue solution; black precipitate on dilution.—**Dyes:** unmordanted cotton from an alkaline bath black. |

## VI. NITROSO

*(Quinone*

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 394 | **Dinitrosoresorcin.**<br>**Fast Green O.** [*M.*]<br>**Dark Green.** [*B.*]<br>**Chlorin.** [*D.H.*]<br>**Russian Green.** [*L.*]<br>**Fast Myrtle Green.**<br>**Alsace Green.** | Dinitroso-resorcinol. (Dioximidoquinone.) | $C_6H_4N_2O_4$ | $C_6H_2\left\{\begin{array}{l}[1]\,O\\ [2]\,NOH\\ [3]\,O\\ [4]\,NOH\end{array}\right.$ |
| 395 | **Gambine R.** [*H.*] | *β*-Nitroso-*α*-naphthol. (Naphthoquinone-oxim.) | $C_{10}H_7NO_2$ | $C_6H_4\left\{\begin{array}{l}[1]\,CO-C=NOH\\ \qquad\qquad\;\;\vert\\ [2]\,CH=CH\end{array}\right.$ |
| 396 | **Gambine Y.** [*H.*]<br>**Alsace Green J.** | *α*-Nitroso-*β*-naphthol (*β*-Naphtho-quinone-*α*-oxim.) | $C_{10}H_7NO_2$ | $C_6H_4\left\{\begin{array}{l}[1]\,C(NOH)\cdot CO\\ \qquad\qquad\qquad\;\vert\\ [2]\,CH=\!=\!=CH\end{array}\right.$ |
| 397 | **Dioxine.** [*L.*]<br>**Gambine B.** [*H.*] | Nitroso-dioxy-naphthalene. (Oxy-*β*-naphthoquinone-oxime.) | $C_{10}H_7NO_3$ | $C_{10}H_5\left\{\begin{array}{l}[1]=N\cdot OH\\ [2]=O\\ [7]-OH\end{array}\right.$ |
| 398 | **Naphthol Green B.** [*C.*] | Ferrous sodium salt of nitroso-*β*-naphthol-*β*-mono-sulphonic acid. | $C_{20}H_{10}N_2O_{10}S_2FeNa_2$ | $C_{10}H_5\left\{\begin{array}{l}[1]=NO-Fe-ON=[1]\\ [2]=O\qquad\qquad\quad O=[2]\\ [6]\,SO_3Na\qquad NaO_3S\,[6]\end{array}\right\}C_{10}H_5$ |

## VII. STILBENE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 399 | **Sun Yellow.** [*G.*]<br>**Jaune Soleil.**<br>**Curcumine S.** [*L.*]<br>**Maize.** | Sodium salt of the so-called azoxy-stilbene-disulphonic acid. | $C_{14}H_8N_2O_7S_2Na_2$<br>(?) |  $\begin{array}{l}CH\cdot C_6H_3\left\{\begin{array}{l}[2]\,SO_3Na\\ [4]\,N\end{array}\right.\\ \Vert\,[1]\qquad\qquad\quad\vert\;\;>O\quad(?)\\ CH\cdot C_6H_3\left\{\begin{array}{l}[4]\,N\\ [2]\,SO_3Na\end{array}\right.\end{array}$ |

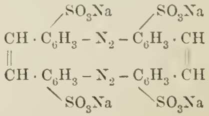
## COLOURING MATTERS.

*Oximes.*)

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of nitrous acid upon resorcinol. | 1875. | Fitz.<br>Ber. (1875) **8**, 631.<br>Goldschmidt & Strauss.<br>Ber. (1887) **20**, 1607.<br>Kostanecki.<br>Ber. (1887) **20**, 3137.<br>J. Soc. Chem. Ind. 1890, 1126. | **Appearance of dyestuff**: dark green paste or grayish brown powder.—**In water**: sparingly soluble cold, more easily hot.—**In dilute caustic soda**: soluble.—**On heating the powder**: it deflagrates.—**Dyes**: iron-mordanted cotton green, tolerably fast to light and soap; iron-mordanted wool dark green, very fast to soap. Padded on cotton and steamed it gives a fast brown which acts as a mordant for basic colours. |
| Action of nitrous acid upon α-naphthol. | 1875. | Fuchs.<br>Ber. (1875) **8**, 625, 1026.<br>Worms.<br>Ber. (1882) **15**, 1816.<br>Goldschmidt.<br>Ber. (1884) **17**, 215, 801.<br>Goldschmidt & Schmidt.<br>Ber. (1884) **17**, 2065.<br>M. Ilinski.<br>Ber. (1884) **17**, 2589.<br>R. Henriques & M. Ilinski.<br>Ber. (1885) **18**, 706.<br>Kostanecki.<br>Ber. (1887) **20**, 3147.<br>J. Soc. Chem. Ind. 1890, 1126. | **Appearance of dyestuff**: greenish yellow paste.—**In water**: slightly soluble with a yellow colour.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: clear yellow solution.—**In conc. sulphuric acid**: reddish brown solution; on dilution with water, yellow solution and brown flocculent precipitate.—**Dyes**: iron-mordanted fabrics green; on chrome mordants cutch brown. The shades are very fast to light and washing. |
| Action of nitrous acid upon β-naphthol. | 1875. | Fuchs.<br>Ber. (1875) **8**, 1026.<br>Stenhouse & Groves.<br>Ann. (1877) **189**, 145.<br>H. Köhler.<br>Ger. Pat. $25469^{83}$ (lapsed).<br>Ber. (1883) **16**, 3080.<br>R. Henriques & M. Ilinski.<br>Ber. (1885) **18**, 704.<br>Kostanecki.<br>Ber. (1887) **20**, 3147.<br>J. Soc. Chem. Ind. 1890, 1126. | **Appearance of dyestuff**: olive green paste.—**In water**: slightly soluble with a yellow colour.—**In alcohol**: reddish yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: greenish yellow fluorescence.—**In conc. sulphuric acid**: dark brown solution; flocculent precipitate on dilution with water.—**Dyes**: iron-mordanted fabrics green. |
| Action of nitrous acid upon (2 : 7)-dioxynaphthalene. | 1889. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pats. $17223^{89}$ & $14230^{89}$.<br>Ger. Pat. $55204^{89}$. | **Appearance of dyestuff**: red paste.—**In water**: insoluble.—**In alcohol**: yellowish red solution.—**In conc. sulphuric acid**: green solution; red precipitate on dilution with water.—**Dyes**: bright green shades on iron mordants, brown on chrome mordants; very fast to light. |
| Action of nitrous acid upon β-naphthol-mono-sulphonic acid S and conversion into the ferrous sodium salt. | 1883. | Otto Hoffmann.<br>Ber. (1885) **18**, 46.<br>Frankfurter Anilinfarben Fabrik Gans & Co.<br>Eng. Pat. $2269^{84}$.<br>Am. Pat. 316036.<br>Ger. Pat. $28065^{84}$,<br>& addn. $28901^{84}$.<br>J. Soc. Chem. Ind. (1885) **4**, 204; (1890) **9**, 1126. | **Appearance of dyestuff**: dark green powder.—**In water**: yellowish green solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: colour becomes bluish green.—**In conc. sulphuric acid**: yellowish brown solution; yellow solution on dilution with water, which gives a precipitate of Prussian blue on adding potassium ferro- and ferri-cyanide.—**On ignition**: leaves a residue of iron sulphide.—**Dyes**: wool green from an acid bath containing an iron salt, very fast to light, good fastness to alkali and acid. |

## COLOURING MATTERS.

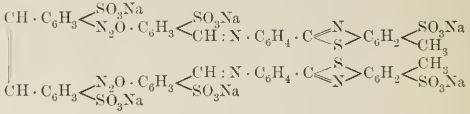
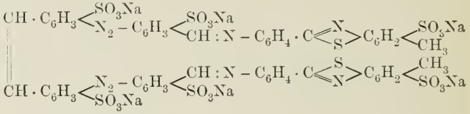
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating *p*-nitrotoluene-sulphonic acid with aqueous caustic soda. | 1883. | Joh. Walter.<br>J. R. Geigy & Co.<br>Bull. de Mulhouse 1887, 99.<br>G. Schultz and F. Bender.<br>Ber. **19**, 3234.<br>A. Leonhardt & Co.<br>Eng. Pat. $4387^{86}$.<br>Am. Pat. 360553.<br>Ger. Pat. 38735. | **Appearance of dyestuff**: brown powder.—**In water**: soluble with brownish yellow colour.—**In conc. sulphuric acid**: violet; yellow on dilution with a little water.—**Dyes**: wool and silk reddish yellow from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 400 | **Direct Yellow G.**<br>[*K.*]<br>**Direct Yellow R.** | Sodium salt of the so-called dinitroso-stilbene-disulphonic acid. | | The constitution of this and the preceding compound, which are probably substantially identical, is still uncertain. It is likely that they contain a double stilbene group. The reaction also gives rise to a certain proportion of by-products sensitive to alkalies and containing aldehyde groups, which compounds are present in smaller amount the more concentrated the caustic soda employed and the lower is the temperature of the reaction. |
| 401 | **Mikado Yellow.**<br>[*L.*]<br>**Mikado Gold Yellow 2 G, 4 G, 6 G, 8 G.** [*L.*]<br>**Direct Yellow 2 G, 4 G.** [*K.*] | | | |
| 402 | **Stilbene Yellow G, 4 G, 6 G, 8 G.**<br>[*Cl. Co.*] | | | |
| 403 | **Diphenyl-citronine G.** [*G.*] | | | |
| 404 | **Diphenyl Fast Yellow.**<br>[*G.*] | | | |
| 405 | **Mikado Brown B, 3 GO, M.**<br>[*L.*] | | | |
| 406 | **Mikado Orange G to 4 R.**<br>[*L.*]<br>**Direct Orange 2 R.**<br>[*K.*]<br>**Direct Orange G.**<br>[*G.*] | | | The reddest shade mark probably has the formula—<br> |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of conc. caustic soda solution upon *p*-nitrotoluene-sulphonic acid at 60° – 85°. | 1892. | O. Fischer & Hepp.<br>Ber. **26**, 2233; **28**, 2281.<br>Kalle & Co.<br>Eng. Pat. $23672^{92}$.<br>Ger. Pat. 79241.<br>Fr. Pat. 226635. | **Appearance of dyestuff**: reddish brown powder.—**In water**: soluble with a reddish yellow colour.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow coloration, with excess brown precipitate.—**On addition of caustic soda to the aqueous solution**: yellow precipitate.—**In conc. sulphuric acid**: cherry red solution, becoming yellow on dilution.—**Dyes**: cotton direct from a salt bath in yellow shades of good fastness to washing, acids, light, and chlorine. Silk is dyed from a slightly acid bath. |
| Treatment of the condensation-products of *p*-nitrotoluene-sulphonic acid and caustic soda (preceding products) with oxidising agents such as nitric acid. | 1886. | Bender.<br>Leonhardt & Co.<br>Ger. Pat. 42466.<br>O. Fischer & Hepp.<br>Ber. **26**, 2234. Compare Ber. **30**, 2618, 3097; **31**, 354, 1078.<br>Kalle & Co.<br>Eng. Pat. $23672^{92}$.<br>Fr. Pat. 226635. | **Appearance of dyestuff**: yellow or brownish powder.—**In water**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow solution or precipitate.—**On addition of caustic soda to the aqueous solution**: yellow solution or precipitate.—**In conc. sulphuric acid**: orange to red solution; yellow on dilution.—**Dyes**: cotton direct from a salt bath yellow shades of good fastness to washing, acids, alkalies, light, and chlorine. |
| Alkaline condensation-products of dinitrodibenzyl-disulphonic acid and dinitrostilbene-disulphonic acid. | 1897. | A. G. Green & A. R. Wahl.<br>Ber. **30**, 3097; **31**, 1078.<br>The Clayton Aniline Co.<br>Eng. Pats. $5351^{97}$; $21553^{97}$; $21399^{97}$; $3393^{98}$.<br>Ger. Pats. 113514; 113513.<br>Fr. Pats. 272384; 273018; 273037. | **Appearance of dyestuff**: orange yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: yellow solution or precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: orange to yellowish red solution; yellow on dilution.—**Dyes**: cotton from a salt or sodium sulphate bath direct in greenish yellow shades, fast to alkalies, acids, washing, light, and chlorine. |
| (*a*) Condensation of dinitro-dibenzyl-disulphonic acid with aniline in presence of caustic soda.<br>(*b*) Condensation of dinitro-stilbene-disulphonic acid with aniline in presence of caustic soda. | 1897.<br>1897. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $18990^{97}$.<br>Am. Pat. 613911.<br>Ger. Pat. 101760.<br>Fr. Pat. 269466.<br>A. G. Green & A. R. Wahl.<br>Eng. Pats. $21399^{97}$ & $21553^{97}$.<br>Fr. Pat. 273018.<br>Ger. Pat. 113514. | **Appearance of dyestuff**: yellow powder.—**In water**: pure yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution**: orange yellow precipitate.—**In conc. sulphuric acid**: orange solution; brownish yellow precipitate on dilution.—**Dyes**: cotton direct in greenish yellow shades, fast to washing and alkalies. |
| (*a*) Condensation of dinitro-dibenzyl-disulphonic acid with primuline or dehydrothio-toluidine-sulphonic acid in presence of caustic soda.<br>(*b*) Condensation of dinitro-stilbene-disulphonic acid with primuline or dehydro-thiotoluidine-sulphonic acid in presence of caustic soda. | 1897.<br>1897. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $18990^{97}$.<br>Ger. Pat. 100613.<br>Fr. Pat. 269466.<br>A. G. Green & A. R. Wahl.<br>Eng. Pats. $21399^{97}$ & $21553^{97}$.<br>Fr. Pat. 273018.<br>Ger. Pat. 113514. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: brownish orange yellow precipitate.—**On addition of caustic soda to the aqueous solution**: orange yellow precipitate.—**In conc. sulphuric acid**: red solution; brownish yellow precipitate on dilution.—**Dyes**: cotton direct yellow, fast to washing and alkalies. |
| Action of alkalies upon *p*-nitro-toluene-sulphonic acid in presence of oxidisable substances. | 1888. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $2664^{88}$.<br>Am. Pats. 395115 & 396527.<br>Ger. Pats. $46252^{88}$ & $48528^{88}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: soluble with a brown colour.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: brown precipitate.—**On addition of caustic soda to the aqueous solution**: no precipitate.—**In conc. sulphuric acid**: violet black colour; on dilution with water, brown precipitate.—**Dyes**: unmordanted cotton brown. |
| (1) Action of alkalies upon *p*-nitrotoluene-sulphonic acid in presence of oxidisable substances.<br>(2) Action of alkaline reducing agents upon Direct Yellow. | 1888.<br>1892. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $2664^{88}$.<br>Am. Pats. 395115 & 396527.<br>Ger. Pats. 46252 & 48528.<br>J. Soc. Dyers and Colorists, 1889, 106.<br>J. Soc. Chem. Ind. 1890, 53.<br>Hepp.<br>Ber. **26**. 2233; **28**, 2281. | **Appearance of dyestuff**: orange powders.—**In water**; soluble with an orange yellow colour.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: dark brown precipitate.—**On addition of caustic soda to the aqueous solution**: orange precipitate.—**In conc. sulphuric acid**: violet to blue colour; on dilution with water, brown precipitate.—**Dyes**: unmordanted cotton shades varying from yellow orange to reddish orange, of good fastness to washing, light, and chlorine. |

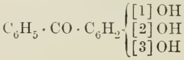
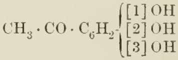
| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 407 | **Polychromine B.** [*G.*]<br>**Fast Cotton Brown R.** [*G.*]<br>**Direct Brown R.** [*G.*] | | $C_{26}H_{20}N_6O_6S_2Na_2$ (?) | |
| 408 | **Diphenyl Orange RR.** [*G.*] | | | |
| 409 | **Chicago Orange RR.** [*G.*] | | | |
| 410 | **Arnica Yellow.** [*G.*] | | | |
| 411 | **Diphenyl Chrysoïne G.** [*G.*] | | | |
| 412 | **Diphenyl Chrysoïne RR.** [*G.*] | | | |
| 413 | **Diphenyl Fast Brown G.** [*G.*] | | | |
| 414 | **Diphenyl Catechine G.** [*G.*] | | | |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Boiling equal mols. of *p*-nitro-toluene-sulphonic acid and *p*-phenylene-diamine with aqueous caustic soda. | 1890. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $15671^{90}$.<br>Am. Pat. $455952^{91}$.<br>Ger. Pat. $59290^{90}$.<br>Fr. Pat. $208626^{90}$. | **Appearance of dyestuff**: reddish brown powder.—**In water**: orange brown solution.—**On addition of hydrochloric acid to the aqueous solution**: blue black precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: reddish violet solution; bluish black precipitate on dilution with water.—**Dyes**: unmordanted cotton orange brown from a neutral or alkaline bath. Yields various shades of "ingrain" brown by diazotisation upon the fibre and "development" with phenylene diamine, etc. |
| Condensation of *p*-nitrotoluene-sulphonic acid (2 mols.) with *p*-phenylene-diamine (1 mol.) in presence of strong aqueous caustic soda. | 1899. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $6651^{99}$.<br>Am. Pat. 636065.<br>Fr. Pat. 286620.<br>Ger. Pat. app. G. 13069.<br>Compare Eng. Pats. $21553^{97}$ & $21399^{97}$. | **Appearance of dyestuff**: light brown powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid**: bluish black precipitate.—**On addition of caustic soda**: orange precipitate.—**In conc. sulphuric acid**: red solution; bluish black precipitate on dilution.—**Dyes**: unmordanted cotton reddish orange. Converted into a bordeaux on the fibre by diazotisation and development with betanaphthol. |
| Condensation of *p*-nitrotoluene-sulphonic acid with benzidine in presence of caustic soda. | 1892. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $788^{93}$.<br>Fr. Pat. $227271^{93}$.<br>Ger. Pat. $75326^{93}$.<br>Compare Ber. 1894, ref. 824. | **Appearance of dyestuff**: brown powder.—**In water**: orange yellow solution.—**On addition of hydrochloric or acetic acid**: brown flocculent precipitate.—**On addition of caustic soda**: orange brown precipitate.—**In conc. sulphuric acid**: violet solution; brown precipitate on dilution.—**Dyes**: unmordanted cotton from a salt bath orange. |
| Condensation of *p*-nitrotoluene-sulphonic acid with *p*-amido-phenol in presence of boiling aqueous caustic soda. | 1892. | C. Ris.<br>J. R. Geigy & Co.<br>Fr. Pat. $222554^{92}$. | **Appearance of dyestuff**: brown powder.—**In water**: brownish yellow solution.—**On addition of hydrochloric acid**: brownish black precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: violet solution; on dilution dark brown precipitate.—**Dyes**: unmordanted cotton golden yellow from a salt bath; moderately fast to light and soap. |
| Ethylation of the product of the condensation of *p*-nitro-toluene-sulphonic acid (2 mols.) with *p*-amidophenol (1 mol.) in presence of aqueous caustic soda. | 1899. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $6651^{99}$.<br>Am. Pat. 636065.<br>Fr. Pat. 286620.<br>Ger. Pat. app. G. 13069. | **Appearance of dyestuff**: yellowish brown powder.—**In water**: golden yellow solution.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: blackish brown precipitate.—**On addition of caustic soda**: orange precipitate.—**In conc. sulphuric acid**: violet red solution; blackish brown precipitate on dilution.—**Dyes**: unmordanted cotton golden yellow. |
| Diazotisation of the alkaline condensation-product of di-nitrodibenzyl-disulphonic acid and aniline, combination of the diazo compound with phenol, and ethylation. | 1899. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $6651^{99}$.<br>Am. Pat. 644462.<br>Ger. Pat. 117729.<br>Fr. Pat. 286620. | **Appearance of dyestuff**: reddish brown powder.—**In water**: reddish orange solution.—**On addition of hydrochloric acid**: blackish brown precipitate.—**On addition of caustic soda**: reddish brown precipitate.—**In conc. sulphuric acid**: pure blue solution; brownish black precipitate on dilution.—**Dyes**: unmordanted cotton reddish orange. |
| Diazotisation of the alkaline condensation-product of di-nitrodibenzyl-disulphonic acid and aniline, and combination of the diazo compound with phenyl-amidonaphthol-sul-phonic acid γ. | 1899. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $6651^{99}$.<br>Am. Pat. 644462.<br>Ger. Pat. 117729.<br>Fr. Pat. 286620.<br>Compare A. G. Green & A. R. Wahl.<br>Eng. Pats. $21399^{97}$ & $21553^{97}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: dark yellowish brown solution.—**On addition of hydrochloric acid**: blackish brown precipitate.—**On addition of caustic soda**: dark brown precipitate.—**In conc. sulphuric acid**: dark blue solution; blackish brown precipitate on dilution.—**Dyes**: unmordanted cotton yellowish dark brown. |
| Diazotisation of the alkaline condensation-product of di-nitrodibenzyl-disulphonic acid and aniline, and combination of the diazo compound with dimethyl-amidonaphthol-sulphonic acid γ. | 1899. | C. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $6651^{99}$.<br>Am. Pat. 644462.<br>Ger. Pat. 117729.<br>Fr. Pat. 286620.<br>Compare A. G. Green & A. R. Wahl.<br>Eng. Pats. $21399^{97}$ & $21553^{97}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: yellowish brown solution.—**On addition of hydrochloric acid**: dark brown precipitate.—**On addition of caustic soda**: brown precipitate.—**In conc. sulphuric acid**: blackish violet blue solution; blackish brown precipitate on dilution.—**Dyes**: unmordanted cotton cutch brown. |

| No. | Commercial Name. | Scientific Name. | Constitutional Formula. |
|---|---|---|---|
| 415 | **Curcuphenine** [*Cl. Co.*] | Sodium sulphonate of the dehydrothiotoluidide of azoxystilbene aldehyde. | Probably :<br><br>$CH \cdot C_6H_3 <^{SO_3Na}_{N_2O} \cdot C_6H_3 <^{SO_3Na}_{CH:N} \cdot C_6H_4 \cdot C \lessgtr^{N}_{S} > C_6H_2 <^{SO_3Na}_{CH_3}$<br>$\Vert$<br>$CH \cdot C_6H_3 <^{N_2O}_{SO_3Na} \cdot C_6H_3 <^{CH:N}_{SO_3Na} \cdot C_6H_4 \cdot C \lessgtr^{S}_{N} > C_6H_2 <^{CH_3}_{SO_3Na}$ |
| 416 | **Chlorophenine Orange RR & RO.*** [*Cl. Co.*] | Sodium sulphonate of the dehydrothiotoluidide of azostilbene aldehyde. | Probably :<br><br>$CH \cdot C_6H_3 <^{SO_3Na}_{N_2} - C_6H_3 <^{SO_3Na}_{CH:N} - C_6H_4 \cdot C \lessgtr^{N}_{S} > C_6H_2 <^{SO_3Na}_{CH_3}$<br>$\Vert$<br>$CH \cdot C_6H_3 <^{N_2}_{SO_3Na} - C_6H_3 <^{CH:N}_{SO_3Na} - C_6H_4 \cdot C \lessgtr^{S}_{N} > C_6H_2 <^{CH_3}_{SO_3Na}$ |

## VIII. OXYKETONE, OXYQUINONE, AND

*(Not including*

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 417 | **Alizarine Yellow A.** [*B.*] | Trioxybenzophenone. | $C_{13}H_{10}O_4$ | <br>$C_6H_5 \cdot CO \cdot C_6H_2 \begin{cases} [1]\ OH \\ [2]\ OH \\ [3]\ OH \end{cases}$ |
| 418 | **Alizarine Yellow C.** [*B.*] | Gallacetophenone. (trioxyacetophenone.) | $C_8H_8O_4$ | <br>$CH_3 \cdot CO \cdot C_6H_2 \begin{cases} [1]\ OH \\ [2]\ OH \\ [3]\ OH \end{cases}$ |
| 419 | **Galloflavine.** [*B.*] |  | $C_{13}H_6O_9$ (?) |  |

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* Chlorophenine Orange R and GO are inter-

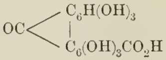
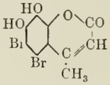
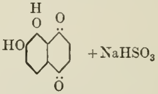
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of *p*-nitrotoluene-sulphonic acid with dehydrothiotoluidine-sulphonic acid in presence of very weak aqueous caustic soda. | 1896. | A. G. Green & A. R. Wahl.<br>The Clayton Aniline Co.<br>Eng. Pat. $12922^{96}$.<br>Fr. Pat. $264755^{97}$.<br>Ger. Pat. $99575^{97}$. | **Appearance of dyestuff**: bright orange yellow powder.—**In water**: yellow solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: no precipitate.—**In conc. sulphuric acid**: red solution; brownish yellow precipitate on dilution.—**Hydrochloric acid and sodium nitrite**: the compound is hydrolysed, dehydrothiotoluidine-sulphonic acid being split off and precipitated as its diazo compound, whilst a yellow stilbene dyestuff remains in solution. This latter is much more soluble than the original colour, and gives with hydrazines and tertiary amines the characteristic reactions of an aldehyde.—**Dyes**: unmordanted cotton direct yellow shades completely fast to alkalies and washing. |
| Reduction of Curcuphenine with glucose and caustic soda. | 1896. | A. G. Green & A. R. Wahl.<br>Eng. Pat. $12922^{96}$.<br>Fr. Pat. $264755^{97}$.<br>Ger. Pat. $100421^{97}$. | **Appearance of dyestuff**: orange red powder.—**In water**: bright orange solution.—**On addition of hydrochloric acid**: dark precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: blue solution.—**Hydrochloric acid and sodium nitrite**: hydrolysed like Curcuphenine. Diazo-dehydrothiotoluidine-sulphonic acid precipitates whilst an orange stilbene dyestuff possessing aldehyde properties remains in solution.—**Dyes**: unmordanted cotton a bright orange fast to alkalies and washing. |

## OXYLACTONE COLOURING MATTERS.

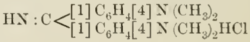
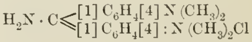
*Anthracene Derivatives.)*

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of benzoic acid or benzotrichloride with pyrogallol. | 1889. | R. Bohn.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $8373^{89}$; $9428^{89}$; $10095^{90}$.<br>Am. Pat. $198281^{89}$.<br>Ger. Pats. $49149^{89}$; $50450^{89}$; $50451^{89}$; $54661^{90}$.<br>Fr. Pat. $198281^{89}$.<br>A. Eichengrun.<br>Ann. **269**, 295.<br>J. Soc. Chem. Ind. 1893, 35. | **Appearance of dyestuff**: grayish yellow paste.—**In boiling water**: soluble.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: deep yellow solution which quickly changes from formation of a green oxidation product.—**In conc. sulphuric acid**: yellow solution; white precipitate on dilution with water.—**Dyes**: cotton mordanted with alumina and lime a fast golden yellow. Used for printing. |
| Condensation of acetic acid with pyrogallol in presence of zinc chloride. | 1881. | Nencki & Siebert.<br>Jour. Pr. Chem. **23**, 147 & 538.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $8373^{89}$ and $9429^{89}$.<br>Am. Pats. $415088^{89}$; $443402^{90}$; $452210^{91}$.<br>Ger. Pats. $49149^{89}$ & $50238^{89}$. | **Appearance of dyestuff**: yellowish or white flakes or yellowish white paste.—**In hot water**: easily soluble.—**In alcohol**: easily soluble.—**In aqueous caustic soda**: soluble with a brown colour, which gets darker on exposure to air.—**In conc. sulphuric acid**: light yellow solution.—**Dyes**: cotton mordanted with alumina yellow, with chromium brown, and with iron black. |
| Moderate oxidation of gallic acid in aqueous or alcoholic alkaline solution by means of air. | 1886. | R. Bohn.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $6413^{86}$.<br>Am. Pat. 348613.<br>Ger. Pat. $37934^{86}$.<br>Fr. Pat. $175835^{86}$.<br>R. Bohn and C. Gräbe.<br>Ber. (1887) **20**, 2327.<br>Ding. Pol. J. **263**, 205.<br>J. Soc. Chem. Ind. 1887, 285, 437, 722. | **Appearance of dyestuff**: greenish yellow paste.—**In water**: insoluble.—**In boiling alcohol**: slightly soluble with light yellow colour and slight greenish fluorescence.—**On addition of hydrochloric acid to the paste diluted with water**: hardly any change, colour rather brighter.—**On addition of caustic soda**: yellowish brown solution.—**In conc. sulphuric acid**: reddish yellow solution, grayish white precipitate on dilution with water.—**Dyes**: chrome mordanted wool yellow fast to light and soap. Gives a greenish yellow colour when printed on cotton with a chromium mordant. |

mediate reduction products of Curcuphenine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 420 | **Alizarine Yellow in paste.** [*M.*] | Ellagic acid. | $C_{14}H_8O_9$ |  $OC\left\langle\begin{array}{l}C_6H(OH)_3\\ \vert\\ C_6(OH)_3CO_2H\end{array}\right.$ |
| 421 | **Resoflavine.** [*B.*] | | | |
| 422 | **Anthracene Yellow.** [*By.*] | Dibromodioxy-β-methyl-coumarine. | $C_{10}H_6Br_2O_4$ |  |
| 423 | **Alizarine Black S.** [*B.*]<br>**Naphthazarine S.**<br>**Alizarine Blue Black SW.** [*B.*] | Sodium bisulphite compound of naphthazarin (dioxynaphthoquinone). | $C_{10}H_7SO_7Na$ |  |
| 424 | **Alizarine Dark Green.** [*B.*] | | | |

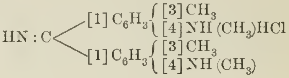
## IX. DIPHENYLMETHANE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 425 | **Auramine.**<br>**Auramine O.**<br>[*B.*] [*M.*] [*G.*] [*I.*]<br>**Pyoktannin Aureum**<br>(medicinal). | Hydrochloride of imido-tetramethyl-diamido-diphenyl-methane. | $C_{17}H_{22}N_3Cl + H_2O$ |  $HN:C\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4[4]\,N\,(CH_3)_2HCl\end{array}\right.$<br>*Or*<br> $H_2N\cdot C\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4[4]:N\,(CH_3)_2Cl\end{array}\right.$ |

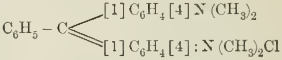
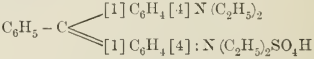
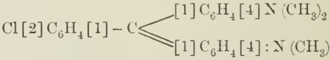
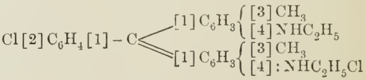
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Extraction of divi-divi or myrobolans with water and decomposition of the ellagotannic acid obtained, with acids or alkali. | 1887. | Meister, Lucius, & Brüning.<br>Barth & Goldschmiedt.<br>Ber. **11**, 846 ; **12**, 1239. | **Appearance of dyestuff**: brownish white paste.—**In water**: insoluble.—**In alcohol**: very sparingly soluble.—**In aqueous caustic soda**: brownish yellow solution.—**In conc. sulphuric acid**: reddish brown solution ; on dilution the acid is precipitated.—**Dyes**: chromed wool a weak and dull but very fast sulphur yellow. |
| Oxidation of *m*-dioxybenzoic acid in sulphuric acid solution by means of ammonium persulphate. | 1895. | O. Bally.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $17660^{95}$.<br>Am. Pat. 618000.<br>Ger. Pat. $85390^{95}$.<br>Fr. Pat. 250422. | **Appearance of dyestuff**: yellow or greenish yellow paste.—**In water**: nearly insoluble.—**In alcohol**: yellow solution.—**In aqueous caustic soda**: yellowish red solution.—**In sodium carbonate**: solution first yellow, then becoming green.—**In conc. sulphuric acid**: yellow solution ; yellow precipitate on dilution.—**Dyes**: wool mordanted with chrome or alumina a very beautiful and fast yellow. |
| Treatment of dioxy-β-methyl-coumarine with bromine. | 1889. | R. E. Schmidt.<br>Fr. Bayer & Co.<br>Eng. Pat. $8411^{90}$.<br>Ger. Pat. $52927^{89}$. | **Appearance of dyestuff**: nearly white paste.—**In water**: sparingly soluble.—**In aqueous caustic soda**: brownish yellow solution from which acids reprecipitate it as a white flocculent precipitate.—**In conc. sulphuric acid**: pale brownish solution.—**Dyes**: chrome mordanted wool greenish yellow. |
| Action of zinc and conc. sulphuric acid or of sulphuric anhydride and flowers of sulphur upon dinitronaphthalene and treatment of the dioxynaphthoquinone formed with sodium hydric sulphite. | 1861.<br>1887. | Z. Roussin.<br>Jour. Pr. Chem. **84**, 181.<br>C. Liebermann.<br>Ber. (1870) **3**, 905 ; **28**, 1456.<br>Ann. (1872) **162**, 328.<br>R. Bohn (bisulphite-comp.)<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $7833^{87}$.<br>Am. Pats. $368054^{87}$ & $379150^{88}$.<br>Ger. Pat. $41518^{87}$.<br>Fr. Pat. $182962^{87}$.<br>See also Ber. **27**, 3462 ; **28**, 1456, 2234 ; and Ann. **286**, 27. | **Appearance of dyestuff**: black paste.—**In water**: insoluble cold, with a reddish brown colour on boiling.—**In alcohol**: yellowish brown solution with green fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: brownish red colour.—**On addition of caustic soda**: beautiful blue solution.—**In conc. sulphuric acid**: dull yellowish green solution, on heating becoming carmine red with evolution of sulphurous acid.—**On dilution with water**: brownish solution and black precipitate.—**Dyes**: chrome mordanted wool black ; gives a black when printed on cotton with a chromium mordant. Very fast. |
| Treatment of naphthazarine melt with phenols. | 1897. | O. Bally.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $10597^{98}$.<br>Am. Pats. 619114 & 619115.<br>Ger. Pat. $103150^{97}$.<br>Fr. Pat. 277996. | **Appearance of dyestuff**: grayish brown powder.—**In water**: fairly soluble with violet colour.—**In alcohol**: violet blue solution.—**In aqueous caustic soda**: greenish blue solution.—**In conc. sulphuric acid**: violet solution ; becomes redder on dilution, and gives a dark precipitate.—**Dyes**: chromed wool gray green to greenish black shades. |

## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Heating tetramethyldiamidobenzophenone with ammonium chloride and zinc chloride at 150°-160°.<br>(*b*) Heating tetramethyldiamidodiphenylmethane with sulphur in a stream of ammonia gas. | 1883. | H. Caro & A. Kern.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $5512^{84}$ ; $12022^{86}$ ; $12549^{89}$ ; $16666^{90}$.<br>Am. Pat. $301802^{84}$.<br>Ger. Pats. $29060^{84}$ ; $31936^{84}$ ; $38433^{86}$ ; $53614^{89}$ ; $58277^{90}$.<br>Fr. Pats. $160990^{84}$ ; $164099^{84}$ ; $200613^{89}$.<br>C. Graebe.<br>Mon. Scien. 1887, 600.<br>Ber. **20**, 3260.<br>W. Fehrmann.<br>Ber. **20**, 2844.<br>Ding. Pol. J. **253**, 86.<br>J. Soc. Chem. Ind. (1884) **3**, 475 ; (1888) **7**, 30, 117.<br>Walter.<br>Bull. Mulh. 1895, 82.<br>A. Stock.<br>Ber. **33**, 318. | **Appearance of dyestuff**: sulphur yellow powder.— **In water**: light yellow solution.—**In alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: solution becomes clear ; on boiling the colour is decomposed with formation of tetramethyldiamidobenzophenone and ammonium chloride.—**On addition of caustic soda to the aqueous solution**: white precipitate ; this precipitate is taken up by ether and the ethereal solution is turned yellow by a drop of acetic acid.—**In conc. sulphuric acid**: colourless solution ; yellow on dilution.—**Dyes**: silk and tannin mordanted cotton a greenish yellow. Is much used for staining paper. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 426 | **Auramine G.**<br>[*B.*] [*G.*] [*I.*] | Hydrochloride of imido-dimethyl-diamidoditolyl-methane. | $C_{17}H_{22}N_3Cl$ |  $HN:C\left\langle\begin{array}{l}[1]\,C_6H_3\begin{cases}[3]\,CH_3\\ [4]\,NH\,(CH_3)HCl\end{cases}\\ [1]\,C_6H_3\begin{cases}[3]\,CH_3\\ [4]\,NH\,(CH_3)\end{cases}\end{array}\right.$ |

## X. TRIPHENYLMETHANE AND DIPHENYL-

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 427 | **Malachite Green.***<br>[*M.*] [*K.*] [*A.*] [*T. M.*]<br>**Malachite Green B.** [*B.*]<br>**New Victoria Green.** [*B.*]<br>**New Green.** [*By.*]<br>**Fast Green.** [*C.*]<br>**Vert Diamant.** [*Mo.*]<br>**Bitter-almond-oil Green.**<br>**Benzal Green.**<br>**Diamond Green B.** [*B.*] | Zinc-double-chloride, oxalate, ferric-double-chloride of tetra-methyldi-*p*-amido-triphenyl-carbinol. | *Zinc-double-choride:*<br>$(C_{23}H_{25}N_2Cl)_3 + 2ZnCl_2 + 2H_2O$<br>*Oxalate:*<br>$(C_{23}H_{24}N_2)_2(C_2H_2O_4)_3$ | *Hydrochloride:*<br> $C_6H_5-C\left\langle\begin{array}{l}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]:N\,(CH_3)_2Cl\end{array}\right.$ |
| 428 | **Brilliant Green.**<br>[*B.*] [*By.*] [*C.*] [*M.*]<br>**Malachite Green G.** [*B.*]<br>**New Victoria Green.**<br>**Ethyl Green.** [*A.*]<br>**Emerald Green.** [*By.*]<br>**Fast Green J.** [*Mo.*] | Sulphate or zinc-double-chloride (rarely oxalate) of tetraethyl-diamido-triphenyl-carbinol. | *Sulphate:*<br>$C_{27}H_{34}N_2O_4S$ | *Sulphate:*<br> $C_6H_5-C\left\langle\begin{array}{l}[1]\,C_6H_4\,[4]\,N\,(C_2H_5)_2\\ [1]\,C_6H_4\,[4]:N\,(C_2H_5)_2SO_4H\end{array}\right.$ |
| 429 | **Setoglaucine.**<br>[*G.*]<br>**New Fast Green 3 B.** [*I.*] | Hydrochloride of tetramethyl-diamido-*o*-chloro-triphenyl-carbinol. | $C_{23}H_{24}N_2Cl_2$ |  $Cl\,[2]\,C_6H_4\,[1]-C\left\langle\begin{array}{l}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]:N\,(CH_3)_2Cl\end{array}\right.$ |
| 430 | **Setocyanine.**<br>[*G.*]<br>**Brilliant Glacier Blue.** [*I.*] | Hydrochloride of diethyl-diamido-*o*-chloro-phenyl-ditolyl-carbinol. | $C_{25}H_{28}N_2Cl$ |  $Cl\,[2]\,C_6H_4\,[1]-C\left\langle\begin{array}{l}[1]\,C_6H_3\begin{cases}[3]\,CH_3\\ [4]\,NHC_2H_5\end{cases}\\ [1]\,C_6H_3\begin{cases}[3]\,CH_3\\ [4]:NHC_2H_5Cl\end{cases}\end{array}\right.$ |

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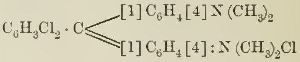
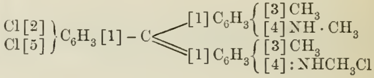
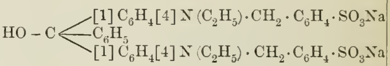
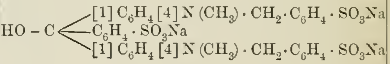
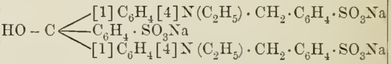
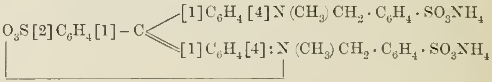
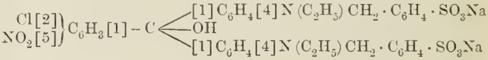
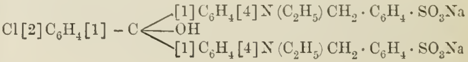
* The picrate, which is insoluble in water but soluble in alcohol, comes into commerce

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating dimethyl-diamido-di-*o*-tolyl-methane (obtained from monomethyl-*o*-toluidine and formaldehyde) with sulphur in a stream of ammonia gas. | 1892. | Société pour l'Industrie Chimique à Bâle.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 10465$^{92}$.<br>Am. Pat. 488430$^{92}$.<br>Ger. Pat. 67478$^{92}$.<br>Fr. Pat. 222275$^{92}$. | **Appearance of dyestuff**: yellow powder.—**In water**: bright yellow solution; colour decomposed on boiling.—**On addition of hydrochloric acid**: no change of colour; on boiling decomposition into the ketone and ammonium chloride.—**On addition of caustic soda**: white precipitate of the base soluble in ether.—**In conc. sulphuric acid**: colourless solution; on dilution light yellow.—**Dyes**: tannin mordanted cotton a greener yellow than Auramine O. |

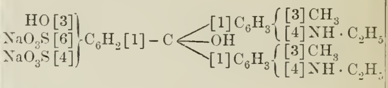
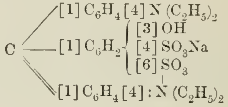
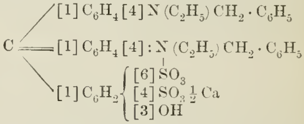
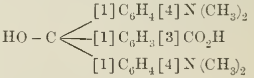
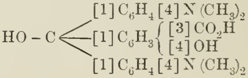
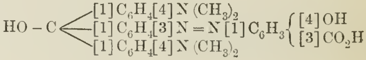
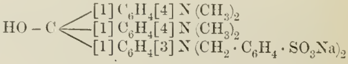
## NAPHTHYLMETHANE COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of benzaldehyde upon dimethylaniline in presence of sulphuric acid or other condensing agent and oxidation of the tetramethyldiamidotriphenylmethane produced. | 1877.<br>1878. | O. Fischer (from benzaldehyde).<br>Ber. **10**, 1625; **11**, 950, 1081; **12**, 791, 2348; **14**, 2520.<br>Ann. (1881) **206**, 129.<br>Eng. Pat. 4762$^{79}$.<br>O. Doebner (from benzotrichloride)<br>Ber. (1878) **11**, 1236.<br>Ann. (1883) **217**, 250.<br>Actiengesellschaft für Anilinfabrikation.<br>Eng. Pat. 828$^{78}$.<br>Ger. Pat. 4322$^{78}$.<br>Fr. Bayer & Co.<br>Eng. Pat. (prov. only) 1976$^{78}$.<br>Ber. **12**, 796.<br>O. Mühlhäuser.<br>Ding. Pol. J. **263**, 249, 295.<br>J. Soc. Chem. Ind. 1887, 433. | **Appearance of dyestuff**: the oxalate forms green metallic glistening plates, the zinc-double-chloride brass yellow prismatic crystals.—**In water**: bluish green solution.—**In alcohol or amyl alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes reddish yellow.—**On addition of caustic soda**: pale green precipitate; the ethereal solution of the precipitate becomes green on addition of acetic acid.—**In conc. sulphuric acid**: yellow solution; green on dilution with water.—**Dyes**: silk, wool, jute, and leather a bluish green directly, cotton after having been mordanted with tannin and tartar emetic. |
| Action of benzaldehyde upon diethylaniline and oxidation of the tetraethyldiamidotriphenylmethane produced. | 1879.<br>1880. | Bindschedler & Busch.<br>O. Doebner.<br>Ber. **13**, 2229.<br>O. Fischer.<br>Ber. **14**, 2520.<br>Bad. Anil. & Soda Fabrik.<br>O. Mühlhäuser.<br>Ding. Pol. J. **263**, 249, 295.<br>J. Soc. Chem. Ind. 1887, 433. | **Appearance of dyestuff**: the sulphate forms golden glistening crystals.—**In water or alcohol**: green solution.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes reddish yellow.—**On addition of caustic soda to the aqueous solution**: decolorised with formation of a pale green precipitate.—**In conc. sulphuric acid**: yellow solution; on dilution with water it becomes reddish yellow, yellowish green, and finally green.—**Dyes**: silk, wool, jute, leather, and cotton mordanted with tannin and tartar emetic, a yellower shade of green than Malachite Green. |
| Action of *o*-chlorobenzaldehyde upon dimethylaniline and oxidation of the tetramethyl-diamido-chloro-triphenyl-methane produced. | 1896. | Sandmeyer & Schmid.<br>J. R. Geigy & Co.<br>Ger. Pat. 94126$^{96}$. | **Appearance of dyestuff**: copper red powder.—**In water**: moderately soluble cold, easily hot.—**In alcohol**: easily soluble with bluish green colour.—**On addition of hydrochloric acid**: reddish yellow solution.—**On addition of caustic soda**: blue black precipitate, quickly changing to reddish brown.—**In conc. sulphuric acid**: reddish yellow solution; green on dilution.—**Dyes**: silk and tannined cotton bluish green. |
| Action of *o*-chlorobenzaldehyde upon monoethyl-*o*-toluidine and oxidation of the leuco base obtained. | 1896. | Sandmeyer & Schmid.<br>J. R. Geigy & Co.<br>Ger. Pat. 94126$^{96}$. | **Appearance of dyestuff**: grayish green powder.—**In water**: scarcely soluble cold, easily hot to a greenish blue solution.—**In alcohol**: easily soluble.—**On addition of hydrochloric acid**: yellow solution.—**On addition of caustic soda**: brownish yellow precipitate.—**In conc. sulphuric acid**: reddish yellow solution; green on dilution.—**Dyes**: silk and tannined cotton greenish blue. |

as **Malachite Green spirit-soluble** [*A.*], and is used for colouring spirit varnishes.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 431 | **Victoria Green 3 B.** [*B.*]<br>**New Fast Green 3 B.** [*I.*] | Hydrochloride or zinc-double-chloride of tetramethyldiamidodichlorotriphenylcarbinol. | *Hydrochloride:*<br>$C_{23}H_{23}N_2Cl_3$ | *Hydrochloride:*<br> $\mathrm{C_6H_3Cl_2 \cdot C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N\,(CH_3)_2} \\ \mathrm{[1]\,C_6H_4\,[4]:N\,(CH_3)_2Cl}\end{array}\right.$ |
| 432 | **Glacier Blue.** [*I.*] | Zinc-double-chloride of dimethyldiamido-di-*o*-tolyl-dichlorophenyl-carbinol. | *Hydrochloride:*<br>$C_{23}H_{23}N_2Cl_3$ |  $\left.\begin{array}{l}\mathrm{Cl\,[2]}\\ \mathrm{Cl\,[5]}\end{array}\right\}\mathrm{C_6H_3\,[1]-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_3}\left\{\begin{array}{l}\mathrm{[3]\,CH_3}\\ \mathrm{[4]\,NH\cdot CH_3}\end{array}\right.\\ \mathrm{[1]\,C_6H_3}\left\{\begin{array}{l}\mathrm{[3]\,CH_3}\\ \mathrm{[4]:NHCH_3Cl}\end{array}\right.\end{array}\right.$ |
| 433 | **Guinea Green B.** [*A.*] | Sodium salt of diethyldibenzyldiamido-triphenylcarbinol-disulphonic acid. | $C_{37}H_{36}N_2O_7S_2Na_2$ |  $\mathrm{HO-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4[4]\,N\,(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\\ \mathrm{C_6H_5}\\ \mathrm{[1]\,C_6H_4[4]\,N\,(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\end{array}\right.$ |
| 434 | **Light Green S F bluish.** [*B.*]<br>**Acid Green.** [*By.*] [*M.*] [*D. H.*] [*N. I.*] | Sodium salt of dimethyldibenzyldiamido-triphenylcarbinol-trisulphonic acid. | $C_{35}H_{31}N_2O_{10}S_3Na_3$ |  $\mathrm{HO-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N\,(CH_3)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\\ \mathrm{C_6H_4\cdot SO_3Na}\\ \mathrm{[1]\,C_6H_4\,[4]\,N\,(CH_3)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\end{array}\right.$ |
| 435 | **Light Green S F yellowish.** [*B.*]<br>**Acid Green.** [*By.*] [*M.*] [*T. M.*] [*O.*]<br>**Acid Green extra conc.** [*C.*] | Sodium salt of diethyldibenzyldiamido-triphenylcarbinol-trisulphonic acid. | $C_{37}H_{35}N_2O_{10}S_3Na_3$ |  $\mathrm{HO-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\\ \mathrm{C_6H_4\cdot SO_3Na}\\ \mathrm{[1]\,C_6H_4\,[4]\,N\,(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3Na}\end{array}\right.$ |
| 436 | **Erioglaucine A.** [*G.*] | Acid ammonium salt of the trisulphonic acid of diethyldibenzyl-diamido-triphenyl-carbinol.<br>$C_{35}H_{38}N_4S_3O_9$ | |  $\mathrm{O_3S\,[2]\,C_6H_4\,[1]-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N\,(CH_3)\,CH_2\cdot C_6H_4\cdot SO_3NH_4}\\ \mathrm{[1]\,C_6H_4\,[4]:N\,(CH_3)\,CH_2\cdot C_6H_4\cdot SO_3NH_4}\end{array}\right.$ |
| 437 | **Night Blue B.** [*T. M.*] | Sodium salt of *o*-chloro-*m*-nitro-diethyldibenzyl-diamido-triphenyl-carbinol-disulphonic acid.<br>$C_{37}H_{34}N_3ClS_2O_9Na_2$ | |  $\left.\begin{array}{l}\mathrm{Cl\,[2]}\\ \mathrm{NO_2\,[5]}\end{array}\right\}\mathrm{C_6H_3\,[1]-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na}\\ \mathrm{OH}\\ \mathrm{[1]\,C_6H_4\,[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na}\end{array}\right.$ |
| 438 | **Night Green 2 B.** [*T. M.*] | Sodium salt of chloro-diethyldibenzyl-diamido-triphenyl-carbinol-disulphonic acid.<br>$C_{37}H_{35}N_2S_2O_7ClNa_2$ | |  $\mathrm{Cl\,[2]\,C_6H_4\,[1]-C}\left\langle\begin{array}{l}\mathrm{[1]\,C_6H_4\,[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na}\\ \mathrm{OH}\\ \mathrm{[1]\,C_6H_4\,[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na}\end{array}\right.$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of dichlorobenzaldehyde upon dimethylaniline and oxidation of the tetramethyldiamidodichlorotriphenylmethane produced. | 1878.<br>1883. | ACTIENGESELLSCHAFT FÜR ANILINFABRIKATION. (from chlorinated benzotrichloride).<br>Ger. Pat. $4988^{78}$.<br>BINDSCHEDLER & BUSCH (from dichlorobenzaldehyde).<br>O. FISCHER.<br>Ger. Pat. $25827^{83}$. | **Appearance of dyestuff:** green metallic glistening crystalline powder.—**In water:** sparingly soluble cold, more easily hot with a greenish blue colour; the hot solution gelatinises on cooling.—**In alcohol:** easily soluble with greenish blue colour.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes yellowish green, then yellow.—**On addition of caustic soda to the aqueous solution:** reddish yellow with slight precipitate.—**In conc. sulphuric acid:** yellow; on dilution with water reddish yellow, on further dilution yellowish green.—**Dyes;** bluer shades than malachite green upon silk and wool, and upon cotton mordanted with tannin and tartar emetic. |
| Action of dichlorobenzaldehyde upon monomethyl-*o*-toluidine and oxidation of the leuco base obtained. | 1892. | SCHMID & BACHELUT.<br>SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BÂLE.<br>Eng. Pat. $22741^{93}$.<br>Am. Pat. 525627.<br>Ger. Pat. $71370^{92}$.<br>Fr. Pat. 234576.<br>GNEHM & BÄNZIGER.<br>Ber. **29**, 875. | **Appearance of dyestuff:** reddish coppery powder.—**In hot water:** greenish blue solution.—**In alcohol:** blue solution.—**On addition of hydrochloric acid:** dark green precipitate, yellow with large excess.—**On addition of caustic soda:** yellowish orange precipitate.—**In conc. sulphuric acid:** yellow solution; green precipitate on dilution.—**Dyes:** silk, wool, and tannined cotton a greenish blue, fast to washing. |
| Condensation of benzaldehyde with benzylethylaniline-sulphonic acid and oxidation of the diethyldibenzyldiamidotriphenylmethane-disulphonic acid produced. | 1883. | G. SCHULTZ & E. STRENG.<br>ACTIENGESELLSCHAFT FÜR ANILINFABRIKATION.<br>Eng. Pat. $7550^{89}$.<br>Ger. Pat. $50782^{89}$.<br>Fr. Pat. $198417^{89}$. | **Appearance of dyestuff:** dull dark green powder.—**In water or alcohol:** green solution.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes brownish yellow.—**On addition of caustic soda to the aqueous solution:** blackish green precipitate.—**With barium chloride:** green precipitate.—**In conc. sulphuric acid:** yellow solution; on dilution with water, yellowish red, yellowish green, and finally green.—**Dyes:** silk and wool green from an acid bath. |
| Condensation of benzaldehyde with methylbenzylaniline, sulphonation of the product, and oxidation of the sulphonic acid. | 1879. | BAD. ANIL. & SODA FABRIK. | **Appearance of dyestuff:** brownish black powder.—**In water or alcohol:** green solution.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes yellowish brown.—**On addition of caustic soda to the aqueous solution:** decolorised with formation of a dull violet precipitate.—**With barium chloride or picric acid:** no precipitate.—**In conc. sulphuric acid:** yellow solution; green on dilution with water.—**Dyes:** wool and silk green from an acid bath. Fast to light but not to milling; sensitive to dilute alkalies but not to dilute acids. |
| Condensation of benzaldehyde with benzylethylaniline, sulphonation of the diethyldibenzyldiamidotriphenylmethane obtained, and oxidation of the sulphonic acid. | 1879. | KÖHLER.<br>BAD. ANIL. & SODA FABRIK.<br>FR. BAYER & CO.<br>P. FRIEDLÄNDER.<br>Ber. **22**, 588.<br>O. MÜHLHÄUSER.<br>Ding. Pol. J. **263**, 249, 295.<br>J. Soc. Chem. Ind. 1887, 433; 1890, 50. | **Appearance of dyestuff:** bright green dull powder.—**In water:** green solution.—**In alcohol:** soluble.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes yellowish brown.—**On addition of caustic soda to the aqueous solution:** decolorised with formation of dull violet precipitate.—**With barium chloride or picric acid:** no precipitate.—**In conc. sulphuric acid:** yellow solution; green on dilution with water.—**Dyes:** silk and wool green from an acid bath; fastness the same as preceding. |
| Condensation of benzaldehyde-*o*-sulphonic acid with ethylbenzylaniline-sulphonic acid and oxidation of the leuco product. | 1896. | SANDMEYER.<br>J. R. GEIGY & CO.<br>Eng. Pat. $5068^{95}$.<br>Am. Pat. 564801.<br>Ger. Pat. $89397^{96}$.<br>Fr. Pat. 254742.<br>J. Soc. Dyers, 1896, 154. | **Appearance of dyestuff:** dark blue bronzy powder.—**In water:** very soluble with greenish blue colour.—**In alcohol:** soluble.—**On addition of hydrochloric acid to the aqueous solution:** becomes first green then yellow.—**On addition of caustic soda:** no change; on boiling violet.—**In conc. sulphuric acid:** pale yellow solution; green and greenish blue on dilution.—**Dyes:** wool and silk from an acid bath greenish blue in level shades, fast to alkalies. |
| Condensation of *o*-chloro-*m*-nitro-benzaldehyde with ethylbenzylaniline-sulphonic acid and oxidation of the leuco product. | 1899. | WEILER-TER-MEER. | **Appearance of dyestuff:** bluish green powder.—**In water:** easily soluble with bluish green colour.—**In alcohol:** easily soluble.—**On addition of hydrochloric acid:** green precipitate.—**On addition of caustic soda:** dull green precipitate.—**In conc. sulphuric acid:** yellow solution; on dilution yellowish green precipitate, becoming bluish green.—**Dyes:** wool and silk bluish green from an acid bath. |
| Condensation of *o*-chlorobenzaldehyde with ethylbenzylaniline-sulphonic acid and oxidation of the leuco product. | 1899. | WEILER-TER-MEER. | **Appearance of dyestuff:** bluish green powder.—**In water:** easily soluble, with bluish green colour.—**In alcohol:** easily soluble.—**On addition of hydrochloric acid:** green precipitate.—**On addition of caustic soda:** olive green precipitate, becoming dirty brown.—**Dyes:** wool and silk bluish green from an acid bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 439 | **Cyanol extra.**<br>[*C.*]<br>**Acid Blue 6 G.**<br>[*C.*] | Sodium salt of *m*-oxy-diethyl-diamido-phenyl-ditolyl-carbinol-di-sulphonic acid. | $C_{25}H_{28}N_2S_2O_8Na_2$ |  $\left.\begin{array}{r}HO{[3]}\\ NaO_3S{[6]}\\ NaO_3S{[4]}\end{array}\right\}C_6H_2{[1]}-C\left\langle\begin{array}{l}{[1]}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}NH\cdot C_2H_5\end{array}\right.\\ OH\\ {[1]}C_6H_3\left\{\begin{array}{l}{[3]}CH_3\\ {[4]}NH\cdot C_2H_5\end{array}\right.\end{array}\right.$ |
| 440 | **Patent Blue** [*]<br>**V, N, superfine, & extra.** [*M.*]<br>**New Patent Blue B & 4 B.** [*By.*] | Calcium, magnesium or sodium salt of the disulphonic acid of *m*-oxy-tetra-alkyl-diamido-triphenyl-carbinol. | $C_{27}H_{31}N_2S_2O_7Na$ |  $C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(C_2H_5)_2\\ {[1]}C_6H_2\left\{\begin{array}{l}{[3]}OH\\ {[4]}SO_3Na\\ {[6]}SO_3\end{array}\right.\\ {[1]}C_6H_4{[4]}:N(C_2H_5)_2\end{array}\right.$ |
| 441 | **Cyanine B.**<br>[*M.*] | | | Unknown. |
| 442 | **Patent Blue A.**<br>[*M.*] | Calcium salt of the disulphonic acid of *m*-oxy-diethyl-dibenzyl-diamido-triphenyl-carbinol. | $(C_{37}H_{35}N_2S_2O_7)_2Ca$ |  $C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(C_2H_5)CH_2\cdot C_6H_5\\ {[1]}C_6H_4{[4]}:N(C_2H_5)CH_2\cdot C_6H_5\\ {[1]}C_6H_2\left\{\begin{array}{l}{[6]}SO_3\\ {[4]}SO_3\tfrac{1}{2}Ca\\ {[3]}OH\end{array}\right.\end{array}\right.$ |
| 443 | **Chrome Green.**<br>[*By.*] | Tetramethyldiamido-triphenyl-carbinol-*m*-carboxylic acid. | $C_{24}H_{25}N_2O_3$ |  $HO-C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(CH_3)_2\\ {[1]}C_6H_3{[3]}CO_2H\\ {[1]}C_6H_4{[4]}N(CH_3)_2\end{array}\right.$ |
| 444 | **Chrome Violet.**[†]<br>[*By.*] | Tetramethyldiamido-oxy-triphenyl-carbinol-*m*-carboxylic acid. | $C_{24}H_{25}N_2O_4$ |  $HO-C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(CH_3)_2\\ {[1]}C_6H_3\left\{\begin{array}{l}{[3]}CO_2H\\ {[4]}OH\end{array}\right.\\ {[1]}C_6H_4{[4]}N(CH_3)_2\end{array}\right.$ |
| 445 | **Azo Green.**<br>[*By.*] | Tetramethyldiamido-triphenyl-carbinol-azo-salicylic acid. | $C_{30}H_{30}N_4O_4$ |  $HO-C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(CH_3)_2\\ {[1]}C_6H_4{[3]}N=N{[1]}C_6H_3\left\{\begin{array}{l}{[4]}OH\\ {[3]}CO_2H\end{array}\right.\\ {[1]}C_6H_4{[4]}N(CH_3)_2\end{array}\right.$ |
| 446 | **Fast Green.**<br>[*By.*]<br>**Fast Green extra.**<br>[*By.*]<br>**Fast Green extra, bluish.** [*By.*] | Sodium salt of tetramethyldibenzyl-pseudorosaniline-disulphonic acid. | $C_{37}H_{37}N_3O_7S_2Na_2$ |  $HO-C\left\langle\begin{array}{l}{[1]}C_6H_4{[4]}N(CH_3)_2\\ {[1]}C_6H_4{[4]}N(CH_3)_2\\ {[1]}C_6H_4{[3]}N(CH_2\cdot C_6H_4\cdot SO_3Na)_2\end{array}\right.$ |

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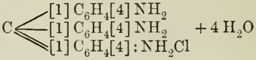
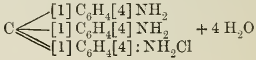
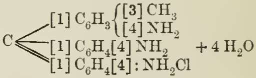
[*] **Ketone Blue G** and **Ketone Blue R** [*M.*] are also dyestuffs of the same

[†] Colours of the same group are **Chrome Blue** [*By.*] and **Turkey Blue** [*By.*], the former obtained by condensation of the tetramethyldiamidobenzhydrol

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of *m*-oxybenzaldehyde with monoethyl-*o*-toluidine, sulphonation of the leuco base, and oxidation of the product. | 1891. | Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. 15143$^{91}$.<br>Ger. Pat. 73717$^{91}$.<br>Am. Pat. 472091.<br>Fr. Pat. 215835. | **Appearance of dyestuff**: dark blue powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: solution becomes green, then yellow.—**On addition of caustic soda**: dichroic green and red solution; on boiling becomes red.—**In conc. sulphuric acid**: yellow solution; on dilution yellowish green and then blue.—**Dyes**: wool and silk from an acid bath pure blue in level shades which are fast to light, washing, alkali, and acid, moderately fast to milling (substitute for indigo carmine). |
| (1) Condensation of *m*-nitrobenzaldehyde with diethylaniline, reduction of the *m*-nitro-compound to the *m*-amido-compound, conversion into the *m*-oxy-compound by treatment with nitrous acid, sulphonation of the product, and oxidation of the leuco-sulphonic acid.<br>(2) Condensation of *m*-oxybenzaldehyde with diethylaniline, sulphonation of the leuco base, and oxidation of the product. | 1888. | Herrmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pats. 12796$^{88}$ & 14822$^{88}$.<br>Ger. Pats. 46384$^{88}$; 50286$^{89}$; 48523$^{88}$; 50293$^{89}$; 50440$^{89}$; 55621$^{90}$; 66791$^{92}$; 71156$^{92}$; & 74014$^{93}$.<br>Am. Pats. 412613; 412614, reissue 11078; 412615, reissue 11077.<br>Chem. Ztg. 1889, 1702.<br>J. Soc. Dyers and Colorists, 1889, 106.<br>Ann. 294, 376. | **Appearance of dyestuff**: copper red or blue powder.—**In water**: blue solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes green and finally yellow.—**On addition of caustic soda to the aqueous solution**: in the cold no change, on boiling the colour becomes violet.—**In conc. sulphuric acid**: yellowish solution; deep yellow and finally green on dilution with water.—**Dyes**: wool greenish blue in level shades fairly fast to alkalies and light (substitute for indigo carmine). |
| Oxidation of Patent Blue with ferric salts or chromic acid. | 1891. | Herrmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 7964$^{91}$.<br>Ger. Pat. 60961$^{91}$.<br>Fr. Pat. 213231. | **Appearance of dyestuff**: dark blue powder.—**In water**: indigo blue solution.—**On addition of hydrochloric acid**: solution green, then yellow.—**On addition of caustic soda**: no change; on warming violet, on cooling dark green.—**In conc. sulphuric acid**: brownish yellow solution, becoming yellow, green, and finally blue on dilution.—**Dyes**: wool indigo blue, gives level shades, and is faster than Patent Blue to light and alkalies. |
| Sulphonation and oxidation of the *m*-oxy-leuco base, obtained either by condensation of *m*-oxybenzaldehyde with ethylbenzylaniline, or by condensation of *m*-nitrobenzaldehyde with ethylbenzylaniline followed by reduction of the nitro-leuco base and treatment with nitrous acid. | 1888. | Herrmann.<br>Ger. Pat. 46384$^{88}$.<br>See also under Patent Blue V. | **Appearance of dyestuff**: copper red powder.—**In water**: easily soluble, with blue colour.—**In alcohol**: sparingly soluble.—**On addition of hydrochloric acid**: green coloration and precipitate.—**On addition of caustic soda**: no change; on warming, violet.—**In conc. sulphuric acid**: yellow solution; on dilution green followed by precipitation.—**Dyes**: wool greenish blue, tolerably fast to milling. |
| Condensation of tetramethyldiamido-benzhydrol with benzoic acid and subsequent oxidation. | 1890. | Runkel.<br>Fr. Bayer & Co.<br>Eng. Pat. 14621$^{90}$.<br>Ger. Pat. 60606$^{90}$.<br>Fr. Pat. 208330$^{90}$.<br>Am. Pat. 501104. | **Appearance of dyestuff**: dark brown powder.—**In water**: greenish blue solution.—**In alcohol**: bluish green solution.—**On addition of hydrochloric acid**: yellowish orange solution.—**On addition of caustic soda**: solution decolorised.—**In conc. sulphuric acid**: yellowish orange solution; no change on dilution.—**Dyes**: chrome mordanted wool green, tolerably fast to milling, but not fast to light. Chiefly employed in cotton printing. |
| Condensation of tetramethyldiamido-benzhydrol with salicylic acid and subsequent oxidation. | 1890. | Runkel.<br>Fr. Bayer & Co.<br>Eng. Pat. 14621$^{90}$.<br>Am. Pat. 476414.<br>Ger. Pat. 58483$^{90}$. | **Appearance of dyestuff**: black powder.—**In water**: insoluble.—**In alcohol**: sparingly soluble, with reddish violet colour.—**In hydrochloric acid**: reddish brown solution.—**In caustic soda**: reddish violet solution and blackish precipitate.—**In conc. sulphuric acid**: yellowish brown solution; reddish brown on dilution.—**Dyes**: chromed wool violet, tolerably fast to milling, but not to light. Chiefly used in cotton printing. |
| Combination of the diazo compound of *m*-amido-tetramethyl-diamido-triphenylmethane with salicylic acid, and oxidation of the product. | 1888. | O. Sohst & F. Runkel.<br>Fr. Bayer & Co.<br>Eng. Pat. 3398$^{90}$.<br>Ger. Pat. 57452$^{89}$.<br>J. Soc. Chem. Ind. 1892, 31. | **Appearance of dyestuff**: dark green paste.—**In water**: sparingly soluble with a green colour.—**In alcohol**: sparingly soluble with a green colour.—**On addition of hydrochloric acid to the diluted paste**: colour becomes brownish red.—**On addition of caustic soda**: clear solution on warming.—**In conc. sulphuric acid**: reddish brown solution; reddish flocculent precipitate on dilution with water.—**Dyes**: chromed wool green. |
| Action of *m*-nitrobenzaldehyde upon dimethylaniline, reduction of the condensation-product, benzylation, sulphonation, and finally oxidation of the leuco-sulphonic acid obtained. | 1885. | H. Hassenkamp.<br>Fr. Bayer & Co.<br>Ger. Pat. 37067$^{85}$.<br>J. Soc. Chem. Ind. 1892, 30. | **Appearance of dyestuff**: dark bluish green crystalline powder.—**In water**: greenish blue solution.—**In alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes yellow; greenish yellow on dilution with water.—**On addition of caustic soda to the aqueous solution**: decolorised on warming.—**In conc. sulphuric acid**: yellowish red solution; becomes nearly colourless on dilution with water, with great dilution greenish blue.—**Dyes**: wool bluish green from an acid bath. |

group (see Ger. Pat. 65952). They dye wool fast to acids and washing.

with α-oxynaphthoic acid, the latter by condensation of the same hydrol with *p*-nitrotoluene. **Chrome Violet** [*G.*] is the **tricarboxylic** acid of aurine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 447 | **Para-fuchsine.**<br>**Para-magenta.**<br>[*H.*] | Hydrochloride of pararosaniline.<br>Hydrochloride of triamido-triphenyl-carbinol. | $C_{19}H_{26}N_3ClO_4$ |  $C\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]:NH_2Cl\end{array}\right. + 4\,H_2O$ |
| 448 | **Magenta.***<br>[*R.H.*]<br>**Roseine.**<br>[*B.S.S.*]<br>**Fuchsine.**<br>[*B.*] [*By.*] [*M.*] [*C.*]<br>**Aniline Red.**<br>*Obsolete names:*<br>**Rubine.**<br>**Azaleïne.**<br>**Solferino.**<br>**Erythrobenzin.**<br>**Fuchsiacine.**<br>**Harmaline.**<br>**Rubianite.** | Mixture of hydrochloride or acetate of pararosaniline (triamidotriphenyl-carbinol) and rosaniline (triamidodiphenyltolyl-carbinol). | *Hydrochlorides:*<br>$C_{19}H_{26}N_3ClO_4$<br>$C_{20}H_{28}N_3ClO_4$<br>*Acetates:*<br>$C_{21}H_{21}N_3O_2$<br>$C_{22}H_{23}N_3O_2$ | *Hydrochlorides:*<br> $C\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]:NH_2Cl\end{array}\right. + 4\,H_2O$<br>*and*<br> $C\left\langle\begin{array}{l}[1]\,C_6H_3\left\{\begin{array}{l}[3]\,CH_3\\ [4]\,NH_2\end{array}\right.\\ [1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]:NH_2Cl\end{array}\right. + 4\,H_2O$ |

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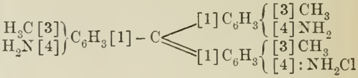
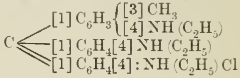
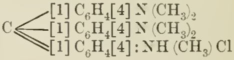
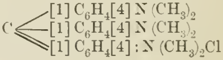
* Impure kinds of magenta containing phosphine, etc., come into commerce as

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Oxidation of a mixture of aniline and *p*-toluidine with arsenic acid.<br>(*b*) Heating nitrobenzene and *p*-nitrotoluene with aniline, *p*-toluidine, iron, and hydrochloric acid.<br>(*c*) Heating diamidodiphenylmethane (or formaldehyde-anilide) with aniline hydrochloride and aniline in presence of an oxidising agent.<br>(*d*) Oxidation of triamidotriphenylmethane in acetone or alcoholic solution. | 1858.<br>1869.<br>1889. | A. W. Hofmann.<br>Jahresber. 1858, 351; Jour. Pr. Chem. (1859) **77**, 190; (1862) **87**, 226.<br>Rosenstiehl.<br>Bull. de Mulhouse **36**, 264; Ding. Pol. J. **181**, 389.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 20678$^{89}$.<br>Ger. Pat. 61146.<br>*Theory:*<br>Caro & Graebe.<br>Ber. (1878) **11**, 1117.<br>E. & O. Fischer.<br>Ann. (1878) **194**, 242; Ber. (1878) **11**, 1079; (1880) **13**, 2204.<br>*Methods of formation:*<br>G. Schultz.<br>Chemie des Steinkohlentheers. 2nd edit. **2**, 395.<br>O. Mühlhäuser.<br>Die Technik der Rosanilinfarbstoffe. | **Appearance of dyestuff**: cantharides-glistening crystals.—**In water**: sparingly soluble cold, more readily hot.—**In alcohol**: easily soluble to a crimson solution.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes yellow.—**On addition of caustic soda**: reddish crystalline precipitate of the base.—**In conc. sulphuric acid**: yellow solution; colourless on dilution with water.—**Dyes**: wool, silk, and leather magenta red direct, cotton after mordanting with tannin and tartar emetic. |
| (*a*) Oxidation of a mixture of aniline, *o*-toluidine and *p*-toluidine by means of arsenic acid (*arsenic acid method*).<br>(*b*) Heating a mixture of aniline, *o*-toluidine, and *p*-toluidine, with nitrobenzene, *o*-nitrotoluene and *p*-nitrotoluene in presence of iron and hydrochloric acid (*nitrobenzol method*).<br>(*c*) Condensation of formaldehyde with aniline and *o*-toluidine and oxidation (*formaldehyde method*). | 1856.<br>1858.<br>1859.<br>1860.<br>1861.<br>1869. | Natanson.<br>(from aniline and ethylene chloride)<br>Ann. (1856) **98**, 297.<br>A. W. Hofmann.<br>(from aniline and carbon tetrachloride)<br>Jahresber. (1858) 353; Jour. Pr. Chem. (1859) **77**, 190; (1862) **87**, 226.<br>Verguin.<br>(from toluidine-containing aniline and stannic chloride)<br>Renard Frères et Franc in Lyon.<br>Fr. Pat. of 8th April 1859.<br>Ding. Pol. J. (1859) **154**, 236 & 397.<br>Gerber & Keller.<br>(from toluidine-containing aniline and mercuric nitrate)<br>Fr. Pat. of 29th October 1859.<br>H. Medlock.<br>(from toluidine-containing aniline and arsenic acid)<br>Eng. Pat. of 18th January 1860.<br>Ding. Pol. J. (1860) **158**, 146.<br>E. C. Nicholson.<br>Eng. Pat. of 26th January 1860.<br>Girard & De Laire.<br>Fr. Pat. of 26th May 1860.<br>Laurent & Casthelaz.<br>(from nitrotoluene-containing nitrobenzene, iron, and hydrochloric acid)<br>Fr. Pat. of 10th December 1861.<br>Wagner's Jahresber. **8**, 567.<br>Coupier.<br>(from nitrobenzene, nitrotoluene, aniline, toluidine, iron, and hydrochloric acid)<br>Wagner's Jahresber. (1869) **15**, 568; Ber. (1873) **6**, 25, 423, 1072.<br>*Methods of formation and manufacture:*<br>G. Schultz.<br>Chemie des Steinkohlentheers. 2nd Edit. II., 404.<br>O. Mühlhäuser.<br>Technik der Rosanilinfarbstoffe.<br>Ding. Pol. J. (1887) **266**, 455, 503, 547.<br>P. Schoop.<br>Ding. Pol. J. (1885) **258**, 276.<br>J. Soc. Chem. Ind. 1886, 163; 1888, 118.<br>*Theory:* see references under Parafuchsine. | **Appearance of dyestuff**: the hydrochloride forms cantharides-glistening crystals, the acetate fused green glistening lumps, the sulphate a fine green glistening crystalline powder.—**In water**: red solution.—**In alcohol**: red solution.—**On addition of hydrochloric acid to the aqueous solution**: yellow.—**On addition of caustic soda to the aqueous solution**: nearly decolourised with precipitation of the base.—**In conc. sulphuric acid**: yellowish brown solution, nearly colourless on dilution with water.—**Dyes**: silk, wool, and leather bluish red direct, cotton after having been mordanted with tannin and tartar emetic. |

**Maroon, Grenat, Geranium, Cerise, Ponceau, Grenadine, Russian Red**, etc.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 449 | **New Magenta.**<br>[*M.*] [*O.*]<br>**New Fuchsine.**<br>**Isorubine.**<br>[*A.*] | Hydrochloride of triamido-tritolyl-carbinol. | $C_{22}H_{24}N_3Cl$ |  $\left.\begin{matrix}H_3C\,{[3]}\\H_2N\,{[4]}\end{matrix}\right\}C_6H_3[1]-C\begin{matrix}\diagup [1]\,C_6H_3\left\{\begin{matrix}{[3]}\,CH_3\\{[4]}\,NH_2\end{matrix}\right.\\ \diagdown [1]\,C_6H_3\left\{\begin{matrix}{[3]}\,CH_3\\{[4]}:NH_2Cl\end{matrix}\right.\end{matrix}$ |
| 450 | **Hofmann Violet.**<br>[*B.S.S.*]<br>**Iodine Violet.**<br>**Dahlia.**<br>**Primula.**<br>**Red Violet 5 R extra.** [*B.*]<br>**Violet 5 R.** [*By.*]<br>**Violet R.** [*Mo.*]<br>**Violet R R.** [*Mo.*] | Mixture of the hydrochlorides or acetates of the mono- di- or tri-methyl- (or ethyl)-rosanilines and pararosanilines. | *Hydrochloride of triethylrosaniline :*<br>$C_{26}H_{32}N_3Cl$ | *Hydrochloride of triethylrosaniline :*<br> $C\begin{matrix}\diagup [1]\,C_6H_3\left\{\begin{matrix}{[3]}\,CH_3\\{[4]}\,NH\,(C_2H_5)\end{matrix}\right.\\ -[1]\,C_6H_4[4]\,NH\,(C_2H_5)\\ \diagdown [1]\,C_6H_4[4]:NH\,(C_2H_5)\,Cl\end{matrix}$ |
| 451 | **Methyl Violet B.**<br>[*B.*] [*By.*] [*A.*]<br>[*C.*] [*M.*]<br>**Paris Violet.**<br>**Direct Violet.**<br>**Violet de Methyl-aniline.**<br>**Dahlia.**<br>**Pyoktanine.*** | *Chiefly :*<br>Hydrochloride of penta- and hexa-methyl-pararos-aniline. | $C_{24}H_{28}N_3Cl$ |  $C\begin{matrix}\diagup [1]\,C_6H_4[4]\,N\,(CH_3)_2\\ -[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ \diagdown [1]\,C_6H_4[4]:NH\,(CH_3)\,Cl\end{matrix}$ |
| 452 | **Crystal Violet.**<br>[*B.*] [*K.S.*]<br>**Crystal Violet 5 BO.** [*I.*]<br>**Crystal Violet O.**<br>[*M.*]<br>**Violet C.**<br>[*P.*]<br>**Violet 7 B extra.**<br>[*Mo.*] | Hydrochloride of hexamethyl-pararosaniline. | *Bronzy crystals :*<br>$C_{25}H_{30}N_3Cl+8H_2O$<br>*Cantharides-glistening crystals :*<br>$C_{25}H_{30}N_3Cl$ |  $C\begin{matrix}\diagup [1]\,C_6H_4[4]\,N\,(CH_3)_2\\ -[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ \diagdown [1]\,C_6H_4[4]:N\,(CH_3)_2Cl\end{matrix}$ |

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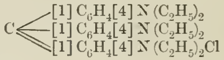
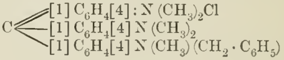
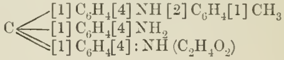
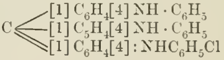
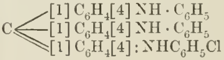
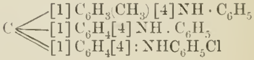
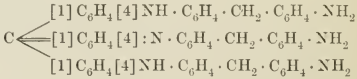
* For medicinal

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating diamidoditolylmethane (from *o*-toluidine and formaldehyde) with *o*-toluidine hydrochloride in presence of an oxidising agent. | 1889. | Homolka.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $2067^{89}$.<br>Am. Pat. $471638^{89}$.<br>Ger. Pat. $59775^{89}$.<br>Fr. Pat. $202769^{89}$. | **Appearance of dyestuff**: beetle green powder.—**In water**: more soluble than ordinary magenta.—**In alcohol**: easily soluble.—**On addition of hydrochloric to aqueous solution**: yellow; red again on dilution.—**On addition of caustic soda**: light red crystalline precipitate on boiling (base).—**In conc. sulphuric acid**: yellow solution; red on dilution.—**Dyes**: wool, silk, leather, and tannined cotton red, rather brighter and bluer than magenta but not faster. |
| Action of methyl (or ethyl) chloride, bromide, or iodide upon rosaniline and pararosaniline. | 1863. | A. W. Hofmann.<br>Comp. rend. **54**, 428; **56**, 945, 1033; **57**, 1131. Jahresber. (1862) 347.<br>G. Schultz.<br>Chemie des Steinkohlentheers. 2nd. edit. vol. ii. p. 467. | (*a*) *Red shades* (Red violet 5 R extra [B.]):<br>**Appearance of dyestuff**: green crystalline powder.—**In water**: magenta red solution.—**On addition of hydrochloric acid**: colour becomes yellowish brown.—**On addition of caustic soda**: brown precipitate.—**In conc. sulphuric acid**: yellowish brown solution; no change on dilution.—**Dyes**: wool bluish red.<br>(*b*) *Blue shades* (Hofmann's violet):<br>**Appearance of dyestuff**: green glistening lumps.—**In water**: easily soluble with bluish violet colour.—**On warming with zinc dust**: decolourised.—**On addition of hydrochloric acid to the aqueous solution**: first green then yellow.—**On addition of caustic soda**: brownish red precipitate.—**In conc. sulphuric acid**: brownish yellow solution; becomes olive-green, green, and finally blue, on dilution with water.—**Dyes**: wool, silk, and mordanted cotton violet. |
| Oxidation of dimethylaniline with cupric chloride. | 1861. | Ch. Lauth.<br>Mon. Scien. (1861) 336.<br>Poirrier & Chappat.<br>Fr. Pat. $71970^{66}$.<br>Mon. Scien. 1866, 1033.<br>Wagner's Jahresber. **12**, 551.<br>A. W. Hofmann.<br>Ber. (1873) **6**, 359.<br>E. & O. Fischer.<br>Ber. (1878) **11**, 2098; (1879) **12**, 2350.<br>Ann. (1878) **194**, 295.<br>O. Fischer & L. Germann.<br>Ber. (1883) **16**, 710.<br>H. Wichelhaus<br>Ber. (1883) **16**, 2005.<br>O. Fischer & G. Körner.<br>Ber. (1883) **16**, 2904; (1884) **17**, 98.<br>O. Mühlhäuser.<br>Ding. Pol. J. **264**, 37.<br>J. Soc. Chem. Ind. 1887, 434. | **Appearance of dyestuff**: glistening metallic-green lumps or powder.—**In water**: violet solution.—**In alcohol or amyl alcohol**: easily soluble.—**On addition of hydrochloric acid to the aqueous solution**: the colour turns first green then deep yellowish brown.—**On addition of caustic soda to the aqueous solution**: brownish red coloration and precipitate.—**In conc. sulphuric acid**: yellow solution, becoming yellowish green, greenish blue, and finally violet on dilution with water.—**Dyes**: silk and wool violet direct, cotton after mordanting with tannin and tartar-emetic. |
| (*a*) Action of dimethylaniline upon tetramethyl-diamidobenzophenone chloride.<br>(*b*) Direct action of carbonyl chloride in presence of zinc chloride upon dimethylaniline.<br>(*c*) Condensation of tetramethyldiamidobenzhydrol with dimethylaniline and oxidation of the leuco-base. | 1883. | A. Kern.<br>(from tetramethyldiamidobenzhydrol)<br>H. Caro.<br>(from tetramethyldiamidobenzophenone)<br>Gesellschaft für Chem. Industrie in Basel, and Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $4428^{83}$; $11030^{84}$; $4850^{84}$; $5038^{84}$; $12022^{86}$.<br>Am. Pats. 290891; 290892; 290856.<br>Ger. Pats. $26016^{83}$; $27032^{83}$; $27789^{83}$; $29943^{84}$ (addn.); $29962^{84}$ (addn.).<br>Fr. Pats. $157430^{83}$; $160090^{84}$.<br>Kern & Sandoz.<br>Ger. Pat. $64270^{91}$.<br>O. Fischer & L. Germann.<br>Ber. (1883) **16**, 706.<br>O. Fischer & G. Körner.<br>Ber. (1883) **16**, 2904.<br>A. W. Hoffmann.<br>Ber. (1885) **18**, 767.<br>J. Soc. Chem. Ind. 1885, 395. | **Appearance of dyestuff**: bronzy or cantharides-glistening crystals.—**In water**: violet solution.—**In alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes first blue, then green, and finally yellow.—**On addition of caustic soda to the aqueous solution**: violet precipitate.—**In conc. sulphuric acid**: yellow solution; becoming green, blue, and finally violet, on dilution with water.—**Dyes**: silk and wool violet direct, cotton after having been mordanted with tannin and tartar-emetic. |

purposes (E. Merck).

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 453 | **Ethyl Violet.**<br>[*B.*] [*I.*]<br>**Ethyl Purple 6 B.** | Hydrochloride of hexaethylpararosaniline. | $C_{31}H_{42}N_3Cl$ |  $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,N\,(C_2H_5)_2\\ [1]\,C_6H_4[4]\,N\,(C_2H_5)_2\\ [1]\,C_6H_4[4]\,N\,(C_2H_5)_2Cl\end{array}\right.$ |
| 454 | **Benzyl Violet.**<br>**Paris Violet 6 B.**<br>**Methyl Violet 6 B.**<br>**Methyl Violet 6 B extra.** [*A.*] [*C.*] [*M.*]<br>**Violet 5 B.** [*By.*]<br>**Violet 6 B.** [*By.*] | Chiefly a mixture of the hydrochlorides of benzylpentamethylpararosaniline and hexamethylpararosaniline. | *Benzylpentamethylpararosaniline hydrochloride:*<br>$C_{31}H_{34}N_3Cl$ |  $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4[4]:N\,(CH_3)_2Cl\\ [1]\,C_6H_4[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4[4]\,N\,(CH_3)\,(CH_2\cdot C_6H_5)\end{array}\right.$ |
| 455 | **Regina Purple.**<br>[*B.S.S.*]<br>**Regina Violet.**<br>**Violet impérial rouge.**<br>**Violet phenylique.** | Acetate of monophenyl or mono-*o*-tolyl-rosaniline mixed with the corresponding derivatives of pararosaniline. | *Acetate of o-tolylpararosaniline:*<br>$C_{28}H_{27}N_3O_2$ | *Acetate of o-tolyl-pararosaniline:*<br> $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,NH\,[2]\,C_6H_4[1]\,CH_3\\ [1]\,C_6H_4[4]\,NH_2\\ [1]\,C_6H_4[4]:NH\,(C_2H_4O_2)\end{array}\right.$ |
| 456 | **Diphenylamine Blue, spirit-soluble, or opal.**<br>**Bavarian Blue spirit-soluble.**<br>**XL Opal Blue.**<br>[*B.S.S.*] | Hydrochloride of triphenylpararosaniline. | $C_{37}H_{30}N_3Cl$ |  $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,NH\cdot C_6H_5\\ [1]\,C_5H_4[4]\,NH\cdot C_6H_5\\ [1]\,C_6H_4[4]:NHC_6H_5Cl\end{array}\right.$ |
| 457 | **Aniline Blue, spirit-soluble.***<br>**Opal Blue.**<br>[*B.S.S.*] [*C.*]<br>**Spirit Blue.** [*B.S.S.*] [*B.*] [*By.*] [*L.*]<br>**Gentian Blue 6 B.** [*A.*]<br>**Fine Blue.**<br>**Hessian Blue.** [*L.*]<br>**Bleu lumière.**<br>**Bleu-de-nuit.** | Hydrochloride, sulphate, or acetate of triphenylrosaniline and triphenylpararosaniline. | *Hydrochloride:*<br>$C_{37}H_{30}N_3Cl$ and $C_{38}H_{32}N_3Cl$<br>*Sulphate:*<br>$C_{74}H_{60}N_6SO_4$ and $C_{76}H_{64}N_6SO_4$<br>*Acetate:*<br>$C_{39}H_{33}N_3O_2$ and $C_{40}H_{35}N_3O_2$ | *Hydrochloride:*<br> $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4[4]\,NH\cdot C_6H_5\\ [1]\,C_6H_4[4]\,NH\cdot C_6H_5\\ [1]\,C_6H_4[4]:NHC_6H_5Cl\end{array}\right.$<br>*and*<br> $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_3(CH_3)\,[4]\,NH\cdot C_6H_5\\ [1]\,C_6H_4[4]\,NH\,.\,C_6H_5\\ [1]\,C_6H_4[4]:NHC_6H_5Cl\end{array}\right.$ |
| 458 | **Pacific Blue.**<br>[*H.*] |  | $C_{58}H_{49}N_6$ | *Base:*<br> $\mathrm{C}\left\langle\begin{array}{l}[1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH_2\\ [1]\,C_6H_4\,[4]:N\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH_2\\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH_2\end{array}\right.$ |

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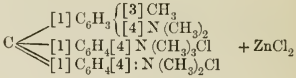
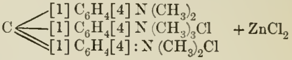
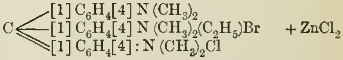
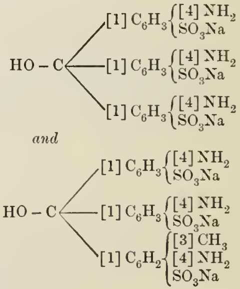
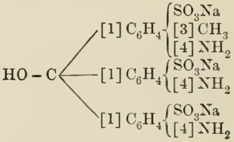
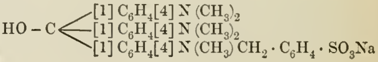
* The earliest blues, obtained without employment of acetic or benzoic acid and consequently incompletely phenylated and of red shade, came into dependent upon the degree of phenylation and is indicated by the suffix **3 R**, **6 B**, etc.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Action of diethylaniline upon tetraethyldiamidobenzophenone chloride.<br>(*b*) Direct action of carbonyl chloride upon diethylaniline in presence of zinc chloride.<br>(*c*) Oxidation of a mixture of tetraethyldiamidodiphenylmethane and diethylaniline with copper sulphate. | 1883. | A. KERN.<br>(from tetraethyldiamidobenzhydrol)<br>H. CARO.<br>(from tetraethyldiamidobenzophenone chloride)<br>GESELLSCHAFT FÜR CHEM. INDUSTRIE in BASEL and BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $4428^{83}$ ; $5038^{84}$ ; $11030^{84}$.<br>Am. Pats. 290856 ; 290891 ; 290892 ; 290893.<br>Ger. Pats. $26016^{83}$ ; $27032^{83}$ ; $27789^{83}$ ; $29943^{84}$ (addn.) ; $29962^{84}$ (addn.). | **Appearance of dyestuff:** green crystalline powder.—**In water:** easily soluble with a violet blue colour.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes reddish yellow.—**On addition of caustic soda to the aqueous solution:** grayish violet precipitate, which on heating melts together to a brown oil leaving the solution colourless.—**In conc. sulphuric acid:** brownish yellow solution; becomes green on great dilution with water.—**Dyes:** silk and wool bluish violet direct, cotton after mordanting with tannin and tartar-emetic. |
| Action of benzyl chloride upon methyl violet. | 1868. | CH. LAUTH.<br>O. FISCHER & G. KÖRNER.<br>Ber. (1883) **16**, 2910.<br>O. MÜHLHÄUSER.<br>Ding. Pol. J. **270**, 179.<br>J. Soc. Chem. Ind. 1889, 40. | **Appearance of dyestuff:** metallic glistening lumps or powder.—The reactions are the same as those of methyl violet B. |
| Action of the "echappés" of the magenta-melt (arsenic acid method) upon rosaniline base, in presence of acetic acid, at about 120° C. | 1860. | GIRARD & DE LAIRE.<br>Traité des dérivés de la houille, p. 594.<br>Eng. Pat. of 12th January 1861.<br>Fr. Pats. of 6th July 1860 and of 2nd January 1861.<br>LA FUCHSINE.<br>SIMPSON, MAULE, & NICHOLSON. | **Appearance of dyestuff:** green powder.—**In water:** easily soluble with reddish violet colour.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes brown, on dilution with water blue.—**On addition of caustic soda to the aqueous solution:** brown precipitate.—**In conc. sulphuric acid:** brown solution; brown on dilution with water.—**On warming with sulphuric acid and alcohol:** acetic ether is evolved.—**Dyes:** wool reddish violet direct. |
| (*a*) Action of oxalic acid upon diphenylamine (nearly obsolete).<br>(*b*) Heating pararosaniline with aniline and benzoic acid. | 1866. | GIRARD & DE LAIRE.<br>Traité des dérivés de la houille, p. 591.<br>Eng. Pats. $1093^{66}$ and $2686^{66}$.<br>Fr. Pat. of 21st May 1866.<br>A. HAUSDÖRFER.<br>Ber. (1890) **23**, 1962. | **Appearance of dyestuff:** brown powder.—**In water:** insoluble.—**In alcohol:** sparingly in the cold, more easily hot.—**In conc. sulphuric acid:** brownish yellow solution; blue precipitate on dilution with water. |
| Action of aniline, in presence of acetic or benzoic acid, upon rosaniline (containing some pararosaniline). | 1860.<br>1862. | GIRARD & DE LAIRE.<br>Fr. Pats. of 6th July 1860 and 2nd January 1861.<br>Ding. Pol. J. **162**, 297 ; **170**, 58.<br>E. C. NICHOLSON.<br>Eng. Pat. of 24th June 1862.<br>A. W. HOFMANN.<br>Ann. (1864) **132**, 160. | **Appearance of dyestuff:** the hydrochloride forms a bronzy powder, the sulphate or acetate a bluish violet powder.—**In water:** insoluble.—**In alcohol:** the acetate is easily soluble, the hydrochloride and sulphate much less readily.—**On addition of hydrochloric acid to the alcoholic solution:** no change.—**On addition of caustic soda to the alcoholic solution:** colour becomes brownish red.—**In conc. sulphuric acid:** brownish yellow solution; blue precipitate on dilution with water.—**Dyes:** silk and wool greenish blue. |
| Heating pararosaniline with diamidodiphenyl-methane at 160° in presence of benzoic acid. | 1896. | DEAN.<br>READ HOLLIDAY & SONS. | **Appearance of dyestuff:** powder or crystals with coppery lustre.—**In water:** blue solution.—**On addition of hydrochloric acid:** solution becomes greenish yellow.—**On addition of caustic soda or salt:** precipitation.—**Dyes:** wool and unmordanted cotton greenish blue. |

commerce as **Bleu de Paris** and **Bleu de Lyon**. The shade of the various brands of rosaniline blues (spirit blues, alkali blues, and soluble blues) is chiefly
The hydrochloride of tri-*p*-tolyl-rosaniline comes into commerce as **Greenish Blue** [*M.*].

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 459 | **Iodine Green.**<br>**Night Green.**<br>**Pomona Green.**<br>**Vert lumière.**<br>(No longer in commerce.) | Zinc-double-chloride of heptamethyl-rosaniline chloride. | $C_{27}H_{35}N_3Cl_4Zn$ |  |
| 460 | **Methyl Green.**<br>[*By.*]<br>**Paris Green.**<br>**Vert Etincelle.**<br>[*Mo.*]<br>**Light Green.**<br>**Vert de methyl-aniline.**<br>**Vert lumière.**<br>**Double Green.**<br>[*K.*]<br>**Green Powder.** | Zinc-double-chloride of heptamethyl-pararosaniline-chloride. | $C_{26}H_{33}N_3Cl_4Zn$ |  |
| 461 | **Ethyl Green.**<br>**Methyl Green.** | Zinc-double-chloride of ethylhexamethyl-pararosaniline-bromide. | $C_{27}H_{35}N_3Cl_3Br\ Zn$ |  |
| 462 | **Acid Magenta.**<br>[*B.*]<br>**Fuchsine S.**<br>[*B.*]<br>**Acid Fuchsine.** *<br>[*M.*]<br>**Acid Roseine.**<br>**Acid Rubine.**<br>**Rubine S.** [*A.*] | Mixture of the sodium or ammonium salts of the trisulphonic acids of rosaniline and pararosaniline. | *Sodium salts:*<br>$C_{19}H_{16}N_3O_{10}S_3Na_3$<br>$C_{20}H_{18}N_3O_{10}S_3Na_3$ |  |
| 463 | **Red Violet 5 R S.** [*B.*] | Sodium salt of ethylrosaniline-sulphonic acid. | *Chiefly:*<br>$C_{22}H_{22}N_3O_{10}S_3Na_3$ |  |
| 464 | **Acid Violet 4 B N.** [*B.*]<br>**Acid Violet 6 B.** [*By.*]<br>**Acid Violet 7 B.**<br>[*L.*]<br>**Acid Violet N.**<br>[*M.*] | Sodium salt of benzyl-penta-methyl-tri-amido-triphenyl-carbinol sulphonic acid. | $C_{31}H_{34}N_3O_4SNa$ |  |

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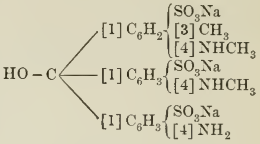
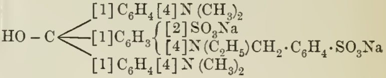
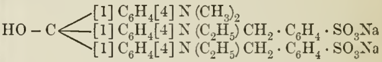
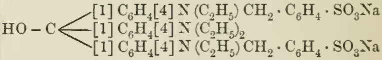
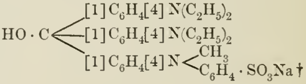
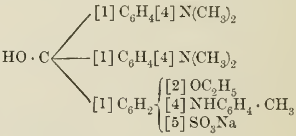
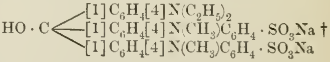
* Impure kinds of acid magenta come into commerce as **Maroon S** [*B.*].

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of methyl iodide or methyl chloride upon rosaniline or upon Hofmann violet. | 1866. | J. Keisser.<br>Fr. Pat. of 18th April 1866.<br>La Fuchsine.<br>Mon. Scien. 1867, 536.<br>Wagner's Jahresber. (1867) **13**, 597.<br>A. W. Hofmann & C. H. Girard.<br>Ber. (1869) **2**, 442.<br>H. Appenzeller.<br>Ber. (1873) **6**, 965. | **Appearance of dyestuff**: dark green hard lumps.—**In water**: easily soluble with a bluish green colour; a drop of this solution dried upon paper turns violet when strongly heated.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes reddish yellow.—**On addition of caustic soda to the aqueous solution**: decolourised.—**In conc. sulphuric acid**: reddish yellow solution; pale yellowish green on dilution with water.—**On heating with conc. sulphuric acid**: evolves iodine vapours if prepared with methyl iodide.—**Dyes**: silk green. |
| Action of methyl chloride upon methyl violet in amyl-alcoholic solution. | 1871.<br>1873. | Ch. Lauth & Baubigny.<br>(from methyl violet and methyl nitrate)<br>Ber. (1873) **6**, 825.<br>Monnet & Reverdin.<br>(from methyl violet and methyl chloride)<br>Mon. Scien. (1878) 124.<br>A. W. Hofmann.<br>Ber. (1873) **6**, 363.<br>E. & O. Fischer.<br>Ber. (1879) **12**, 2351. | **Appearance of dyestuff**: green crystals.—**In water**: easily soluble with a bluish green colour; a spot of the solution dried on paper becomes violet on heating strongly.—**In amyl alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes reddish yellow; on dilution with water it changes to yellowish green.—**On addition of caustic soda to the aqueous solution**: decolourised.—**In conc. sulphuric acid**: reddish yellow solution; yellowish green on dilution with water.—**Dyes**: silk green from a soap bath. |
| Action of ethyl bromide upon methyl violet. | 1866. | Holliday.<br>Eng. Pat. of 1st May 1866. | **Appearance of dyestuff**: moss-green crystalline powder.—**In water**: easily soluble with greenish blue colour.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes first green and then yellow.—**On addition of caustic soda**: decolourised.—**In conc. sulphuric acid**: yellowish solution; becomes green on great dilution with water.—**Dyes**: wool mordanted with sodium thiosulphate and sulphuric acid or zinc acetate, silk, and cotton mordanted with tannin, bluish green. |
| Action of fuming sulphuric acid upon magenta. | 1877. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Ber. (1878), 11, 1949.<br>Eng. Pat. 3731$^{79}$.<br>Am. Pat. 250201.<br>Ger. Pat. 2096$^{77}$.<br>Fr. Pat. 122721$^{78}$.<br>Read Holliday & Co.<br>Am. Pat. 250247.<br>E. Jacobsen.<br>Ber. (1880) 13, 294.<br>Eng. Pat. 2828$^{79}$.<br>Ger. Pat. 8764$^{79}$.<br>P. Schoop.<br>Chem. Zeit. **11**, 572<br>J. Soc. Chem. Ind. 1887, 592. | **Appearance of dyestuff**: metallic green glistening granules or powder.—**In water**: easily soluble to a crimson solution.—**In alcohol**: nearly insoluble.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: almost completely decolourised.—**In conc. sulphuric acid**: yellow solution; red on dilution with water.—**Dyes**: wool and silk red from an acid bath; not employed for cotton. |
| Action of fuming sulphuric acid upon ethylrosaniline. | 1877. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 3731$^{77}$.<br>Am. Pats. 204797 & 204798$^{78}$.<br>Ger. Pat. 2096$^{77}$. | **Appearance of dyestuff**: brownish violet metallic glistening lumps.—**In water**: easily soluble with magenta red colour.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: colour becomes light brownish yellow.—**In conc. sulphuric acid**: yellow solution; magenta red on dilution with water.—**Dyes**: wool bluish red from an acid bath. |
| (*a*) Sulphonation of the benzyl-pentamethyl-pararosaniline obtained by condensation of benzylmethylaniline with tetramethyldiamido-benzophenone chloride.<br>(*b*) Oxidation of benzyl-pentamethyl-paraleucaniline-sulphonic acid. | 1883.<br>1884. | Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 5038$^{84}$.<br>Ger. Pat. 27789$^{83}$.<br>H. Hassenkamp.<br>Fr. Bayer & Co.<br>Eng. Pat. 7645$^{85}$.<br>Am. Pats. 331964 & 331965.<br>Ger. Pat. 31509$^{84}$. | **Appearance of dyestuff**: bluish violet powder.—**In water**: bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate, soluble in excess to an olive solution, which becomes green and finally blue on dilution with water.—**On addition of caustic soda to the aqueous solution**: blue flocculent precipitate, on warming a colourless solution.—**In conc. sulphuric acid**: yellow solution, becoming olive, then green and finally blue, on dilution with water.—**Dyes**: wool bluish violet. |

**Grenat S** [*B.*], **Acid Cerise** [*M.*], **Cardinal Red S**, **Acid Maroon**, etc.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 465 | **Red Violet 4 R S.** [*B.*]<br>**Acid Violet 4 R S.** [*M.*] | Sodium salt of dimethylrosaniline-trisulphonic acid. | $C_{22}H_{22}N_3O_{10}S_3Na_3$ |  $HO-C\begin{cases}[1]\,C_6H_2\begin{cases}SO_3Na\\ {[3]}\,CH_3\\ {[4]}\,NHCH_3\end{cases}\\ {[1]}\,C_6H_3\begin{cases}SO_3Na\\ {[4]}\,NHCH_3\end{cases}\\ {[1]}\,C_6H_3\begin{cases}SO_3Na\\ {[4]}\,NH_2\end{cases}\end{cases}$ |
| 466 | **Fast Acid Violet 10 B.** [*By.*] | Sodium salt of benzylethyl-tetramethyl-pararosaniline-disulphonic acid. | $C_{32}H_{35}N_3O_7S_2Na_2$ |  $HO-C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ {[1]}\,C_6H_3\begin{cases}[2]\,SO_3Na\\ {[4]}\,N\,(C_2H_5)CH_2\cdot C_6H_4\cdot SO_3Na\end{cases}\\ {[1]}\,C_6H_4\,[4]\,N\,(CH_3)_2\end{cases}$ |
| 467 | **Acid Violet 6 B.** [*A.*] | Sodium salt of dimethyldibenzyl-triamido-triphenyl-carbinol-disulphonic acid. | $C_{39}H_{41}N_3O_7S_2Na_2$ |  $HO-C\begin{cases}[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ {[1]}\,C_6H_4[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na\\ {[1]}\,C_6H_4[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na\end{cases}$ |
| 468 | **Formyl Violet * S 4 B.** [*C.*]<br>**Acid Violet 6 B.** [*G.*]<br>**Acid Violet 4 B extra.** [*By.*] | Sodium salt of tetraethyldibenzyl-triamido-triphenyl-carbinol-disulphonic acid. | $C_{41}H_{45}N_3O_7S_2Na_2$ |  $HO-C\begin{cases}[1]\,C_6H_4[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na\\ {[1]}\,C_6H_4[4]\,N\,(C_2H_5)_2\\ {[1]}\,C_6H_4[4]\,N\,(C_2H_5)\,CH_2\cdot C_6H_4\cdot SO_3Na\end{cases}$ |
| 469 | **Alkali Violet 6 B.** [*B.*] [*I.*] | Sodium salt of tetraethyl-monomethylphenyl-pararosaniline-monosulphonic acid. | $C_{34}H_{40}N_3O_4SNa$ |  $HO\cdot C\begin{cases}[1]\,C_6H_4[4]\,N(C_2H_5)_2\\ {[1]}\,C_6H_4[4]\,N(C_2H_5)_2\\ {[1]}\,C_6H_4[4]\,N\begin{cases}CH_3\\ C_6H_4\cdot SO_3Na\,\dagger\end{cases}\end{cases}$ |
| 470 | **Acid Violet 6 B N.** [*I.*] [*B.*] | Sodium salt of tetramethyl-*p*-tolyl-triamido-ethoxy-triphenyl-carbinol-sulphonic acid. | $C_{32}H_{36}N_3O_5SNa$ |  $HO\cdot C\begin{cases}[1]\,C_6H_4[4]\,N(CH_3)_2\\ {[1]}\,C_6H_4[4]\,N(CH_3)_2\\ {[1]}\,C_6H_2\begin{cases}[2]\,OC_2H_5\\ {[4]}\,NHC_6H_4\cdot CH_3\\ {[5]}\,SO_3Na\end{cases}\end{cases}$ |
| 471 | **Acid Violet 7 B.** [*I.*] [*B.*] | Sodium salt of diethyl-dimethyl-diphenyl-triamido-triphenyl-carbinol-disulphonic acid. | $C_{37}H_{37}N_3O_7S_2Na_2$ |  $HO\cdot C\begin{cases}[1]\,C_6H_4[4]\,N(C_2H_5)_2\\ {[1]}\,C_6H_4[4]\,N(CH_3)C_6H_4\cdot SO_3Na\,\dagger\\ {[1]}\,C_6H_4[4]\,N(CH_3)C_6H_4\cdot SO_3Na\end{cases}$ |

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* Formyl Violet 6 B and 10 B [*C.*] are

† The position of the sulphonic groups in these two colours is uncertain ; their greater stability to alkalies

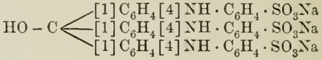
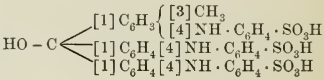
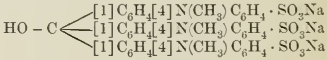
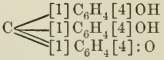
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of fuming sulphuric acid upon dimethylrosaniline. | 1877. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Ber. (1878) 11, 1949.<br>Eng. Pat. 3731$^{77}$.<br>Am. Pats. 204797 & 204798$^{78}$.<br>Ger. Pat. 2096$^{77}$. | **Appearance of dyestuff**: reddish violet powder.—**In water**: easily soluble with magenta red colour.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On warming the aqueous solution with caustic soda**: colour becomes pale reddish yellow.—**In conc. sulphuric acid**: brownish yellow solution; magenta red on dilution with water.—**Dyes**: wool from an acid bath a bluer shade than acid-magenta. |
| Condensation of tetramethyl-diamido-benzhydrol with ethylbenzylaniline-disulphonic acid. | 1892. | Hassenkamp.<br>Fr. Bayer & Co. | **Appearance of dyestuff**: gray powder.—**In water**: easily soluble, with reddish violet colour.—**On addition of hydrochloric acid**: lemon yellow solution.—**On addition of caustic soda**: no change; pink on warming.—**In conc. sulphuric acid**: orange yellow solution; on dilution with large amount of water, green.—**Dyes**: wool from an acid bath violet blue in very level shades, of good fastness to alkalies and moderately fast to light. |
| Condensation of dimethyl-*p*-amido-benzaldehyde with ethylbenzylaniline-sulphonic acid and oxidation of the product. | 1889. | Actiengesellschaft für Anilinfabrikation.<br>Eng. Pat. 7550$^{89}$.<br>Ger. Pat. 50782$^{89}$.<br>Fr. Pat. 198415$^{89}$. | **Appearance of dyestuff**: bluish violet powder.—**In water or alcohol**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish green solution.—**On addition of caustic soda to the aqueous solution**: colour becomes light blue, colourless with an excess.—**In conc. sulphuric acid**: yellowish brown solution; becomes dark brown and then bluish green on dilution with water.—**Dyes**: wool bluish violet from an acid bath. |
| Action of formaldehyde upon ethylbenzylaniline-sulphonic acid, oxidation of the diethyl-dibenzyl-diphenylmethane-disulphonic acid to diethyldibenzyl-diphenylbenzhydrol-disulphonic acid, condensation of the latter with diethylaniline, and oxidation of the leuco-acid obtained. | 1890.<br>1890. | T. Sandmeyer.<br>J. R. Geigy & Co.<br>Eng. Pat. 21284$^{90}$.<br>Ger. Pat. 59811$^{90}$.<br>A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. 857$^{91}$.<br>Ger. Pat. 62339$^{90}$.<br>Am. Pat. 464538. | **Appearance of dyestuff**: violet powder.—**In water or alcohol**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: violet blue precipitate, which redissolves in an excess to a green, in a large excess to a yellow solution.—**On addition of caustic soda to the aqueous solution**: no change; on warming decolorised.—**In conc. sulphuric acid**: orange yellow solution; becoming green and finally blue on dilution with water.—**Dyes**: wool violet from an acid bath. |
| Sulphonation of the product of condensation of methyldiphenylamine and tetraethyldiamido-benzophenone. | 1886. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 5038$^{84}$.<br>Am. Pat. 353264$^{86}$.<br>Ger. Pat. 27789$^{83}$.<br>Fr. Pat. 160090. | **Appearance of dyestuff**: bluish violet powder.—**In water**: bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish violet precipitate, soluble in an excess to a yellowish red solution.—**On addition of caustic soda to the aqueous solution**: blue precipitate.—**In conc. sulphuric acid**: yellowish red solution; dull green precipitate on dilution with water.—**Dyes**: wool from an alkaline, neutral, or acid bath, a bluish violet fast to milling. |
| Sulphonation of tetramethyl-*p*-tolyl-ethoxy-tri-phenyl-carbinol obtained by condensation of tetra-methyl-diamido-benzophenone chloride with *m*-ethoxy-phenol-*p*-tolyl-amine. | 1891. | C. L. Müller.<br>Société pour l'Industrie Chimique à Bâle.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 11275$^{91}$.<br>Am. Pat. 501434$^{93}$.<br>Ger. Pat. 62539$^{91}$.<br>Fr. Pat. 214571$^{91}$. | **Appearance of dyestuff**: dark violet powder.—**In water**: violet blue solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: slowly decolorised.—**In conc. sulphuric acid**: brownish yellow solution; green and finally blue on dilution with water.—**Dyes**: wool and silk bluish violet. |
| Action of diethyl-amido-benzoyl chloride upon methyl-diphenylamine and subsequent sulphonation. | 1884. | C. L. Müller.<br>Société pour l'Industrie Chimique à Bâle.<br>Bad. Anil. & Soda Fabrik.<br>Am. Pat. 353266$^{86}$. | **Appearance of dyestuff**: brownish violet powder.—**In water**: bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: bluish violet precipitate, soluble in excess with a yellowish green colour.—**On addition of caustic soda**: blue precipitate in the cold, colourless solution on warming.—**In conc. sulphuric acid**: brown solution; green and finally blue on dilution with water.—**Dyes**: wool bluish violet from an acid bath, moderately fast to alkalies. |

mixtures of S 4 B with Thiocarmine R.

would seem to indicate that the $HSO_3$ groups are situated in the ortho position to the methane carbon atom.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 472 | **Acid Violets 7 BS, 5 BNS, & 6 BNS.** [*K. S.*] | Sulphonic acid of β-naphthyl-penta-alkyl-rosaniline. | | |
| 473 | **Ketone Blue 4 BN.** [*M.*] | Sulphonic acid of ethoxytrimethyl-phenyl-triamido-triphenyl-carbinol. | | |
| 474 | **Acid Violet 7 BN.** [*M.*] | Sodium salt of tetramethyldiphenyl-rosaniline-disulphonic acid. | $C_{35}H_{33}N_3S_2O_7Na_2$ | $HO-C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)\,C_6H_4\cdot SO_3Na\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)\,C_6H_4\cdot SO_3Na\end{cases}$ |
| 475 | **Eriocyanine A.** [*G.*] | Sodium salt of tetramethyldibenzyl-rosaniline-disulphonic acid. | $C_{37}H_{37}N_3S_2O_7Na_2$ | $HO-C\begin{cases}[1]\,C_6H_3\begin{cases}SO_3Na\\ [4]\,N\,(CH_3)_2\end{cases}\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_3\begin{cases}[2]\,SO_3Na\\ [4]\,N\,(CH_2\cdot C_6H_5)_2\end{cases}\end{cases}$ |
| 476 | **Methyl Alkali Blue.** [*O.*] [*B.*] [*K.*] [*G.*] [*M.*]<br>**Bleu de Ciel Alkalin.** [*Ib.*]<br>**Alkali Blue D.** [*A.*]<br>**Alkali Blue 6 B.** [*I.*] [*H.*] | Sodium salt of triphenyl-*p*-rosaniline-monosulphonic acid. | $C_{37}H_{20}N_3SO_4Na$ | $HO-C\begin{cases}[1]\,C_6H_4\,[4]\,NHC_6H_5\\ [1]\,C_6H_4\,[4]\,NHC_6H_4\cdot SO_3Na\\ [1]\,C_6H_4\,[4]\,NHC_6H_5\end{cases}$ |
| 477 | **Alkali Blue.** [*B.S.S.*] [*A.*] [*B.*] [*By.*] [*C.*] [*L.*] [*M.*]<br>**Nicholson Blue.** [*B.S.S.*]<br>**Fast Blue.** [*B.S.S.*] | Mixture of the sodium salts of triphenyl-rosaniline-monosulphonic acid and triphenylpararosaniline-monosulphonic acid. | $C_{38}H_{32}N_3O_4SNa$<br>and<br>$C_{37}H_{30}N_3O_4SNa$ | *Rosaniline derivative:*<br>$HO-C\begin{cases}[1]\,C_6H_3\begin{cases}[3]\,CH_3\\ [4]\,NH\cdot C_6H_4\cdot SO_3Na\end{cases}\\ [1]\,C_6H_4\,[4]\,NHC_6H_5\\ [1]\,C_6H_4\,[4]\,NHC_6H_5\end{cases}$ |
| 478 | **Bavarian Blue D S F.** [*A.*]<br>**Methyl Blue water soluble.** [*G.*]<br>**Navy Blue B.** [*I.*]<br>**Methyl Blue for silk M L B.** [*M.*] | Sodium salt of triphenyl-pararosaniline-disulphonic acid with some trisulphonic acid. | $C_{37}H_{27}N_3O_6S_2Na_2$ | $HO-C\begin{cases}[1]\,C_6H_4\,[4]\,NH\cdot C_6H_5\\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3Na\\ [1]\,C_6H_4\,[4]\,NHC_6H_4\cdot SO_3Na\end{cases}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of tetra-alkyl-diamidobenzophenone with alkyl-phenyl-β-naphthylamine, and subsequent sulphonation of the product. | 1895. | A. Steiner.<br>Sandoz & Co., Basle.<br>Eng. Pat. $30015^{96}$.<br>Am. Pat. 603016.<br>Fr. Pat. 257887.<br>Ger. Pat. 96402. | **Appearance of dyestuff**: dark violet powder —**In water**: violet solution.—**On addition of hydrochloric acid**: violet precipitate, dissolving in an excess to a green to yellowish brown solution.—**On addition of caustic soda**: solution blue; on warming lighter.—**In conc. sulphuric acid**: yellowish brown solution; green and then blue on dilution.—**Dyes**: wool a pure bluish violet fast to alkalies. |
| Condensation of ethoxy-dimethylamidobenzophenone with methyldiphenylamine and sulphonation of the product. | 1890. | Fuchs & Kees.<br>Meister, Lucius, & Brüning. | **Appearance of dyestuff**: reddish violet lumps.—**In water**: easily soluble, with blue colour.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid**: decolorised.—**On addition of caustic soda**: brownish red solution.—**In conc. sulphuric acid**: yellow solution; green on dilution.—**Dyes**: wool and silk very level shades of blue. |
| Condensation of dimethyl-amidobenzoic acid with methyldiphenylamine-sulphonic acid. | 1885. | Fuchs & Hörmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $4961^{84}$.<br>Ger. Pat. $34463^{84}$. | **Appearance of dyestuff**: blue violet powder.—**In water**: easily soluble, with blue colour.—**On addition of hydrochloric acid**: green solution; blue on dilution.—**On addition of caustic soda**: decolorised on heating.—**In conc. sulphuric acid**: orange yellow solution; blue on dilution.—**Dyes**: wool and silk bluish violet from an acid bath. |
| Condensation of tetramethyl-diamidobenzhydrol-sulphonic acid with dibenzylaniline-sulphonic acid and oxidation of the leuco product. | 1895. | J. R. Geigy & Co. | **Appearance of dyestuff**: reddish brown coppery powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: yellowish green, brown with large excess.—**On addition of caustic soda**: no change; reddish violet on heating.—**In conc. sulphuric acid**: light brown, on dilution becoming light green and then light blue.—**Dyes**: wool a bright reddish blue from acid bath. |
| Sulphonation of triphenyl-*p*-rosaniline (No. 456). | | E. C. Nicholson.<br>K. Oehler. | **Appearance of dyestuff**: blue powder.—**In water**: insoluble cold, easily soluble hot.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: reddish brown solution.—**In conc. sulphuric acid**: reddish brown solution; blue precipitate on dilution.—**Dyes**: wool from an alkaline bath, the blue colour being developed on passing through dilute acid. |
| Action of conc. sulphuric acid upon opal blue (No. 457). | 1862. | E. C. Nicholson.<br>Eng. Pat. 1857 of 1st June 1862.<br>Gilbee.<br>Eng. Pat. of 3rd July 1862.<br>C. Bulk.<br>Ber. (1872) 5, 417. | **Appearance of dyestuff**: light or dark blue powder.—**In water**: sparingly soluble cold, easily hot with a blue colour.—**In alcohol**: somewhat soluble.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**On addition of caustic soda to the aqueous solution**: colour becomes reddish brown.—**In conc. sulphuric acid**: brownish red solution; blue on dilution with water.—**Dyes**: wool from a boiling bath made alkaline with borax, the colour being subsequently developed by passing through weak acid. |
| Sulphonation of triphenyl-*p*-rosaniline (No. 456). | 1862. | E. C. Nicholson.<br>Kalle.<br>Zeits. f. chem. Grossgew. 1, 189. | **Appearance of dyestuff**: indigo blue powder.—**In water**: easily soluble, with blue colour.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes more intense.—**On addition of caustic soda to the aqueous solution**: colour becomes brownish red.—**In conc. sulphuric acid**: yellowish brown solution; blue on dilution with water.—**Dyes**: silk blue from a "killed" soap bath. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 479 | **Methyl Blue.** [*O.*] [*K.*] [*C.*] [*M.*] [*B.*]<br>**Brilliant Cotton Blue, greenish.** [*By.*]<br>**XL Soluble Blue.** [*B.S.S.*]<br>**Diphenylamine Blue.** [*K.S.*]<br>**Bavarian Blue D B F.** [*A.*]<br>**Soluble Blue 8 B and 10 B.** [*B.S.S.*]<br>**Helvetia Blue.** [*G.*] | Sodium salt of triphenyl-pararosaniline-trisulphonic acid. | $C_{37}H_{26}N_3O_9S_3Na_3$ |  $HO-C \begin{cases} [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3Na \\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3Na \\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3Na \end{cases}$ |
| 480 | **Soluble Blue.*** [*B.S.S.*]<br>**Water Blue.** [*B.*] [*By.*]<br>**Water Blue 6 B extra.** [*A.*]<br>**China Blue.** [*B.S.S.*] [*A.*] [*By.*]<br>**London Blue extra.** [*B.S.S.*]<br>**Cotton Blue.** [*L.*]<br>**Bleu Marine.** | Sodium, ammonium or calcium salt of the trisulphonic acid (with some disulphonic acid) of triphenylrosaniline and triphenyl-pararosaniline. | *Free acid :*<br>$C_{38}H_{31}N_3O_9S$<br>and<br>$C_{37}H_{29}N_3O_9S$ | *Rosaniline derivative, free acid :*<br> $HO-C \begin{cases} [1]\,C_6H_3 \begin{cases} [3]\,CH_3 \\ [4]\,NH\cdot C_6H_4\cdot SO_3H \end{cases} \\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3H \\ [1]\,C_6H_4\,[4]\,NH\cdot C_6H_4\cdot SO_3H \end{cases}$ |
| 481 | **Alkali Blue X G.** [*B.S.S.*]<br>**Soluble Blue X G.** [*B.S.S.*]<br>**Non-mordant Cotton Blue.** [*B.S.S.*] | Sodium salts of sulphonic acids of $\beta$-naphthylated rosaniline. | | |
| 482 | **Höchst New Blue.** [*M.*] | Calcium salt of the di- and tri-sulphonic acids of trimethyl-triphenyl-para-rosaniline. | *Trisulphonic acid :*<br>$C_{40}H_{34}N_3O_{10}S_3Na_3$ | *Trisulphonic acid :*<br> $HO-C \begin{cases} [1]\,C_6H_4[4]\,N(CH_3)\,C_6H_4\cdot SO_3Na \\ [1]\,C_6H_4[4]\,N(CH_3)\,C_6H_4\cdot SO_3Na \\ [1]\,C_6H_4[4]\,N(CH_3)\,C_6H_4\cdot SO_3Na \end{cases}$ |
| 483 | **Aurine.**<br>**Rosolic Acid.**<br>**Yellow Coralline.**<br>(Sodium salt) | Mixture of aurine (trioxytriphenyl-carbinol), oxydised aurine, methylaurine, and pseudorosolic acid (coralline-phthalin). The pseudorosolic acid forms the chief constituent of coml. aurine. | *Aurine :*<br>$C_{19}H_{14}O_3$<br>*Oxy-aurine :*<br>$C_{19}H_{16}O_6$<br>*Methylaurine :*<br>$C_{20}H_{16}O_3$<br>*Pseudorosolic acid :*<br>$C_{20}H_{16}O_4$ | *Aurine :*<br> $C \begin{cases} [1]\,C_6H_4\,[4]\,OH \\ [1]\,C_6H_4\,[4]\,OH \\ [1]\,C_6H_4\,[4]:O \end{cases}$ |

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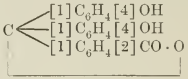
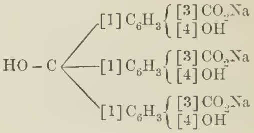
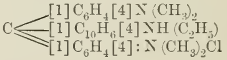
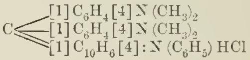
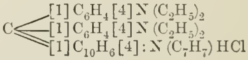
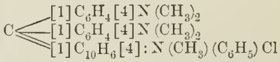
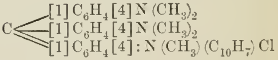
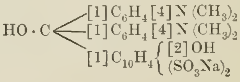
* The name "Soluble Blue" was originally applied to the Alkali Blues, but was subsequently transferred to the higher

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Sulphonation of triphenyl-*p*-rosaniline (No. 456).<br>(*b*) Condensation of formaldehyde with diphenylamine-sulphonic acid (2 mols.), and oxidation of the product with a third mol. of diphenylamine-sulphonic acid. | 1862.<br>1866.<br>1892. | E. C. NICHOLSON.<br>Eng. Pat. of 24th June 1862.<br>GIRARD & DE LAIRE.<br>T. SANDMEYER.<br>J. R. GEIGY & Co.<br>Eng. Pat. $12720^{92}$.<br>Ger. Pat. 73092.<br>Fr. Pat. 223032. | **Appearance of dyestuff**: dark blue powder.—**In water**: blue solution.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: colour becomes reddish brown.—**In conc. sulphuric acid**: reddish brown solution; blue on dilution with water.—**Dyes**: silk and mordanted cotton blue. |
| Action of conc. sulphuric acid upon opal blue (No. 457). | 1862. | E. C. NICHOLSON.<br>Eng. Pat. 1857 of 1st June 1862.<br>SIMPSON, MAULE, & NICHOLSON.<br>C. BULK.<br>Ber. (1872) **5**, 419. | **Appearance of dyestuff**: blue glistening powder, or coppery flakes.—**In water**: blue solution.—**In alcohol**: nearly insoluble.—**On addition of hydrochloric acid to the aqueous solution**: colour not altered, more or less precipitate of disulphonic acid.—**On addition of caustic soda to the aqueous solution**: colour becomes brownish red.—**In conc. sulphuric acid**: dark reddish yellow solution; blue solution and precipitate on dilution with water.—**Dyes**: silk and mordanted cotton blue. |
| Action of conc. sulphuric acid upon the β-naphthylated rosaniline obtained by heating rosaniline with β-naphthylamine. | 1883. | R. MELDOLA.<br>Chem. News, 23rd & 30th March 1883.<br>BROOKE, SIMPSON, & SPILLER. | *Alkali blue X G:*<br>**Appearance of dyestuff**: grayish black lumps.—**In water**: greenish blue solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: violet black solution and precipitate, on heating the precipitate gums together leaving a colourless solution.—**In conc. sulphuric acid**: reddish brown solution; blue precipitate on dilution.—**After reduction with zinc dust**: colour does not return on paper.—**Dyes**: like an ordinary alkali blue but is greener in shade.<br>*Soluble blue X G:*<br>**Appearance of dyestuff**: flakes with reddish metallic lustre.—**In water**: blue solution.—**On addition of hydrochloric acid**: complete precipitation, blue precipitate.—**On addition of caustic soda**: dull claret colour.—**In conc. sulphuric acid**: reddish brown solution; blue precipitate on dilution with water.—**After reduction with zinc dust**: colour does not return on paper.—**Dyes**: cotton and silk from an acid bath. |
| Sulphonation of trimethyltriphenyl-pararosaniline obtained by the action of $COCl_2$ upon methyldiphenylamine. | 1884. | MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $4961^{84}$.<br>Ger. Pat. $34463^{84}$. | **Appearance of dyestuff**: dark blue powder.—**In water**: easily soluble with a blue colour.—**In alcohol**: very sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution**: a portion of the sulphonic acid precipitates.—**On addition of caustic soda to the aqueous solution**: the blue colour disappears.—**In conc. sulphuric acid**: brownish red solution.—**Dyes**: wool blue from an acid bath. |
| Action of oxalic acid and conc. sulphuric acid upon phenol. | 1834.<br>1859.<br>1866. | F. RUNGE.<br>(from crude carbolic acid.)<br>Berz. Jahresber. **15**, 423.<br>J. KOLBE & SCHMITT.<br>J. PERSOZ.<br>(from phenol and oxalic acid.)<br>H. CARO & WANKLYN.<br>(from rosaniline.)<br>Zeits. f. Chem. (1866) **2**, 563.<br>DALE & SCHORLEMMER.<br>Ann. (1873) **166**, 279.<br>C. GRAEBE & H. CARO.<br>Ann. (1875) **179**, 184.<br>K. ZULKOWSKY.<br>Ann. **194**, 109, 122; **202**, 179.<br>Ber. (1878) **11**, 391. | *Aurine:*<br>**Appearance of dyestuff**: yellowish brown lumps, with greenish fracture.—**In water**: insoluble.—**In alcohol**: golden yellow solution.—**On addition of hydrochloric acid to the alcoholic solution**: no change.—**On addition of caustic soda to the alcoholic solution**: cherry red colour.—**In conc. sulphuric acid**: yellow solution.—**Employment**: for colouring spirit varnishes and lacquers.<br>*Yellow Coralline:*<br>**Appearance of dyestuff**: metallic green glistening lumps.—**In water**: soluble with red colour.—**In alcohol**: magenta red solution.—**On addition of hydrochloric acid**: yellow solution and flocculent precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: yellow solution; yellow solution and precipitate on dilution with water.—**Employment**: for preparation of red lakes for paper staining. |

sulphonic acids. Lower qualities of Alkali Blue appear in commerce as **Guernsey Blue**, of soluble-blue as **Serge Blue**, etc.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 484 | **Coralline.**<br>**Aurine R.**<br>**Red Coralline.**<br>**Pæonine.** | | | |
| 485 | **Phenol Phthaleïne.** | Lactone of dioxytri-phenyl-carbinol-carboxylic acid. | $C_{20}H_{14}O_4$ |  $C\begin{cases}[1]\,C_6H_4\,[4]\,OH\\ [1]\,C_6H_4\,[4]\,OH\\ [1]\,C_6H_4\,[2]\,CO\cdot O\end{cases}$ |
| 486 | **Chrome Violet.**<br>[*G.*] | Sodium salt of aurine-tricarboxylic acid. | $C_{22}H_{13}O_{10}Na_3$ |  $HO-C\begin{cases}[1]\,C_6H_3\begin{cases}[3]\,CO_2Na\\ [4]\,OH\end{cases}\\ [1]\,C_6H_3\begin{cases}[3]\,CO_2Na\\ [4]\,OH\end{cases}\\ [1]\,C_6H_3\begin{cases}[3]\,CO_2Na\\ [4]\,OH\end{cases}\end{cases}$ |
| 487 | **New Victoria Blue R.** [*By.*]<br>**Victoria Blue R.** [*B.*] [*I.*] | Hydrochloride of ethyltetramethyl-triamido-α-naphthyl-diphenyl-carbinol. | $C_{29}H_{32}N_3Cl$ |  $C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_6\,[4]\,NH\,(C_2H_5)\\ [1]\,C_6H_4\,[4]:N\,(CH_3)_2Cl\end{cases}$ |
| 488 | **Victoria Blue* B.** [*B.*] [*I.*] | Hydrochloride of phenyltetramethyl-triamido-diphenyl-α-naphthyl-carbinol. | $C_{33}H_{32}N_3Cl$ |  $C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_6\,[4]:N\,(C_6H_5)\,HCl\end{cases}$ |
| 489 | **Night Blue.**<br>[*B.*] [*I.*] | Hydrochloride of *p*-tolyltetraethyl-triamido-diphenyl-α-naphthyl-carbinol. | $C_{38}H_{42}N_3Cl$ |  $C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(C_2H_5)_2\\ [1]\,C_6H_4\,[4]\,N\,(C_2H_5)_2\\ [1]\,C_{10}H_6\,[4]:N\,(C_7H_7)\,HCl\end{cases}$ |
| 490 | **Victoria Blue 4 R.** [*B.*] [*I.*] | Hydrochloride of phenylpentamethyl-triamido-diphenyl-α-naphthyl-carbinol. | $C_{34}H_{34}N_3Cl$ |  $C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_6\,[4]:N\,(CH_3)\,(C_6H_5)\,Cl\end{cases}$<br>*Or*<br> $C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]:N\,(CH_3)\,(C_{10}H_7)\,Cl\end{cases}$ |
| 491 | **Wool Green S.**<br>[*I.*] [*B.*] | Sodium salt of tetramethyl-diamido-diphenyl-β-oxy-naphthyl-carbinol-di-sulphonic acid. | $C_{27}H_{26}N_2O_8S_2Na_2$ |  $HO\cdot C\begin{cases}[1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_6H_4\,[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_4\begin{cases}[2]\,OH\\ (SO_3Na)_2\end{cases}\end{cases}$ (?) |

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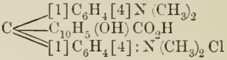
* New Green [*M.*] is obtained by condensing dimethyl-

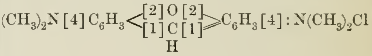
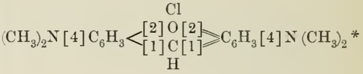
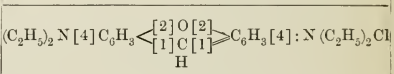
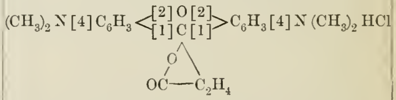
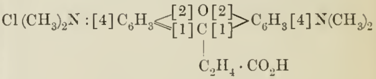
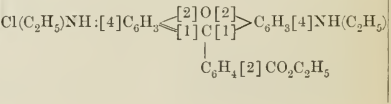
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of ammonia upon aurine. | | J. PERSOZ.<br>G. SCHULTZ.<br>Die Chemie des Steinkohlentheers. 2nd Edit. II. p. 515. | **Appearance of dyestuff:** reddish brown powder.—**In water:** insoluble cold, very sparingly on boiling with a cherry red colour.—**In alcohol:** reddish brown solution.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes yellow.—**On addition of caustic soda to the aqueous solution:** scarcely altered.—**In conc. sulphuric acid:** brownish yellow solution. |
| Heating phenol with phthalic anhydride and a dehydrating agent. | 1871. | AD. BAEYER.<br>Ber. (1871) 4, 658; (1876) **9**, 1230.<br>Ann. (1880) **202**, 68. | **Appearance of dyestuff:** white powder.—**In water:** insoluble.—**In aqueous caustic soda:** easily soluble with magenta red colour.—**On addition of hydrochloric acid to the alkaline solution:** decolorised.—**In conc. sulphuric acid:** yellowish solution; precipitated on dilution with water.—**Employment:** as an indicator in alkalimetry. |
| Action of formaldehyde, or methyl alcohol and sodium nitrite, upon a solution of salicylic acid in conc. sulphuric acid. | 1889. | TR. SANDMEYER.<br>J. R. GEIGY & CO.<br>Eng. Pat. $3333^{89}$.<br>Am. Pat. 410739.<br>Ger. Pat. $49970^{89}$.<br>Ber. **25**, 939.<br>J. Soc. Dyers and Colorists, 1889, 170. | **Appearance of dyestuff.:** chocolate powder.—**In water:** dark red solution.—**On addition of hydrochloric acid to the aqueous solution:** the free acid is precipitated.—**On addition of caustic soda to the aqueous solution:** light brown solution.—**In conc. sulphuric acid:** brown solution; separation of the colour acid on dilution with water.—**Employment:** for calico printing with a chrome mordant. Gives a reddish violet fast to soap. |
| (1) Condensation of tetramethyldiamido-benzhydrol with ethyl-α-naphthylamine, and oxidation of the leuco base.<br>(2) Action of tetramethyldiamidobenzophenone chloride upon ethyl-α-naphthylamine. | 1892. | NASTVOGEL.<br>FR. BAYER & CO. | **Appearance of dyestuff:** blue or gray powder.—**In water:** sparingly soluble cold, blue solution hot.—**On addition of hydrochloric acid:** yellowish brown solution, on dilution becoming green.—**On addition of caustic soda:** brown flocculent precipitate.—**In conc. sulphuric acid:** brownish yellow solution; bright green to blue on dilution.—**Dyes:** silk, wool, and tannined cotton blue. |
| (*a*) Action of phenyl-α-naphthylamine upon tetramethyldiamido-benzophenone chloride.<br>(*b*) Condensation of tetramethyldiamido-benzhydrol with phenyl-α-naphthylamine, conversion of the leuco base into its nitrosamine, oxidation and removal of the nitroso group. | 1883. | H. CARO & A. KERN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $5038^{84}$ & $12022^{86}$.<br>Am. Pat. $297414^{84}$.<br>Ger. Pats. $27789^{83}$ & $29962^{84}$.<br>Fr. Pat. $160090^{84}$.<br>FR. BAYER & CO.<br>Eng. Pat. $19062A^{91}$.<br>M. NATHANSON & P. MÜLLER.<br>Ber. (1889) **22**, 1888. | **Appearance of dyestuff:** bronzy glistening powder.—**In water:** sparingly soluble cold, moderately soluble hot.—**In alcohol:** easily soluble to a pure blue solution.—**On addition of hydrochloric acid to the aqueous solution:** blue precipitate, redissolving in excess to a green, or with a large excess to a yellowish brown solution.—**On addition of caustic soda to the aqueous solution:** dark reddish brown precipitate.—**In conc. sulphuric acid:** reddish yellow solution; becoming yellow, green, and finally blue on dilution with water.—**Dyes:** silk and wool blue from an acid bath; cotton either direct from an acetic acid bath or after previous mordanting with tannin and tartar emetic or with alum. |
| Action of *p*-tolyl-α-naphthylamine upon tetraethyldiamido-benzophenone chloride. | 1883. | H. CARO & A. KERN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $5038^{84}$ & $12022^{86}$.<br>Ger. Pat. $27789^{83}$. | **Appearance of dyestuff:** violet bronzy powder.—**In water:** bluish violet solution.—**In alcohol:** easily soluble.—**On addition of hydrochloric acid to the aqueous solution:** precipitate which dissolves in excess to a green, in a large excess to a yellowish brown solution.—**On addition of caustic soda to the aqueous solution:** pale reddish brown precipitate.—**In conc. sulphuric acid:** yellowish brown solution; becoming green and finally blue on dilution with water.—**Dyes:** like Victoria blue B but a greener shade. |
| Action of methyl-phenyl-α-naphthylamine upon tetramethyldiamido-benzophenone-chloride. | 1883. | H. CARO & A. KERN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $5038^{84}$ & $12022^{86}$.<br>Am. Pat. $308748^{84}$.<br>Ger. Pat. $27789^{83}$.<br>Fr. Pat. $160090^{84}$.<br>M. NATHANSON & P. MÜLLER.<br>Ber. (1889), **22**, 1891. | **Appearance of dyestuff:** bronzy glistening powder.—**In hot water:** bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution:** precipitate which dissolves in excess to a green, in a large excess to a yellowish brown solution.—**On addition of caustic soda to the aqueous solution:** violet brown precipitate.—**In conc. sulphuric acid:** yellowish brown solution; becoming green and finally blue on dilution with water.—**Dyes:** like Victoria blue B but a much redder shade. |
| Condensation of tetramethyldiamido-benzophenone chloride with β-naphthol and sulphonation of the product. | 1883. | BAD. ANIL. & SODA FABRIK.<br>Ger. Pat. $3121^{84}$.<br>J. Soc. Dyers & Colorists, 1893, 77. | **Appearance of dyestuff:** dark coppery powder.—**In water:** greenish blue solution.—**On addition of hydrochloric acid to the aqueous solution:** brown precipitate.—**On addition of caustic soda:** colour rather bluer, on boiling violet.—**In conc. sulphuric acid:** dull violet solution; becoming brown and finally green on dilution with water.—**Dyes:** silk and wool sea green shades, tolerably fast to alkalies, light, and milling. |

amido-benzophenone chloride with phenyl-α-naphthylamine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 492 | **Chrome Blue.**<br>[*By.*] | Tetramethyldiamido-oxy-diphenyl-naphthyl-carbinol-carboxylic acid. | $C_{28}H_{27}N_2O_3Cl$ |  $C\begin{cases}{[1]}C_6H_4[4]N(CH_3)_2\\ C_{10}H_5(OH)CO_2H\\ {[1]}C_6H_4[4]:N(CH_3)_2Cl\end{cases}$ |

## XI. XANTHENE

(Pyronines, Phthaleins,

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 493 | **Pyronine G.**<br>[*L.*] [*By.*]<br>**Casan Pink.**<br>[Gerber.] | Tetramethyldiamido-xanthenyl chloride. | $C_{17}H_{19}N_2OCl$ |  $(CH_3)_2N[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\underset{H}{C}[1]\end{matrix}\right\rangle C_6H_3[4]:N(CH_3)_2Cl$<br>*Or*<br> $(CH_3)_2N[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\overset{Cl}{\underset{H}{C}}[1]\end{matrix}\right\rangle C_6H_3[4]N(CH_3)_2$ * |
| 494 | **Pyronine B.**<br>[*L.*] [*By.*] | Tetraethyldiamido-xanthenyl chloride. | $C_{19}H_{23}N_2OCl$ |  $(C_2H_5)_2N[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\underset{H}{C}[1]\end{matrix}\right\rangle C_6H_3[4]:N(C_2H_5)_2Cl$ |
| 495 | **Acridine Red B, 2 B & 3 B.** [*L.*] | | | |
| 496 | **Rhodamine S.**<br>[*B.*] [*By.*] [*I.*] | Hydrochloride of dimethyl-*m*-amido-phenol-succineïne. | $C_{20}H_{23}N_2O_3Cl$ |  $(CH_3)_2N[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\underset{\underset{OC-C_2H_4}{O}}{C}[1]\end{matrix}\right\rangle C_6H_3[4]N(CH_3)_2HCl$<br>*Or*<br> $Cl(CH_3)_2N:[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\underset{C_2H_4\cdot CO_2H}{C}[1]\end{matrix}\right\rangle C_6H_3[4]N(CH_3)_2$ |
| 497 | **Rhodamine 6 G.**<br>[*B.*] [*I.*]<br>**Trianisoline.**<br>[*Mo.*] | Ethyl ether of sym. diethyl-rhodamine. | $C_{26}H_{27}N_2O_3Cl$ |  $Cl(C_2H_5)NH:[4]C_6H_3\left\langle\begin{matrix}{[2]}O[2]\\ {[1]}\underset{C_6H_4[2]CO_2C_2H_5}{C}[1]\end{matrix}\right\rangle C_6H_3[4]NH(C_2H_5)$ |

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* This and the following colouring matters of this group may be represented either as

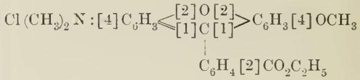
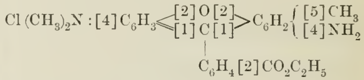
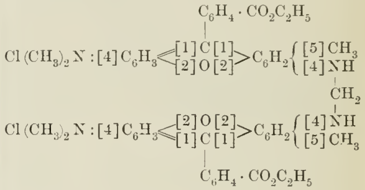
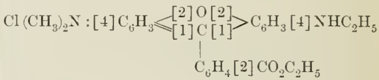
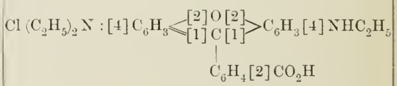
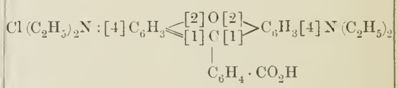
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of tetramethyldiamidobenzhydrol with α-oxynaphthoic acid and oxidation of the leuco product. | 1890. | RUNKEL.<br>FR. BAYER & Co.<br>Eng. Pat. $14621^{90}$.<br>Am. Pat. 476413.<br>Ger. Pat. 58483. | **Appearance of dyestuff**: brown paste.—**In water**: partially soluble with blue colour.—**In hydrochloric acid**: reddish brown solution.—**On addition of caustic soda**: little change.—**In conc. sulphuric acid**: dark bordeaux red solution; reddish brown on dilution.—**Dyes**: chromed wool blue, fairly fast to milling but not to light. Chiefly used for cotton printing. |

## COLOURING MATTERS.

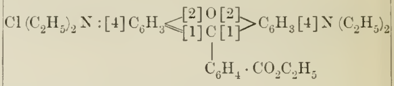
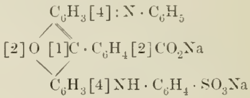
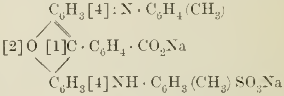
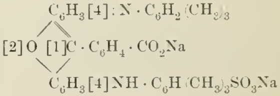
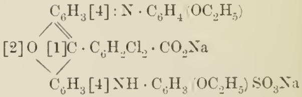
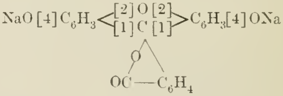
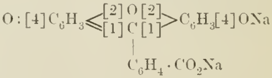
### Eosines, and Rhodamines.)

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Oxidation of tetramethyldiamidodiphenylmethane-oxide, obtained by condensation of formaldehyde with dimethyl-*m*-amidophenol. | 1889. | F. BENDER.<br>A. LEONHARDT & Co.<br>Eng. Pats. $13217^{89}$ & $18606^{91}$.<br>Ger. Pats. $59003^{90}$ & $63081^{90}$.<br>Am. Pat. 445684.<br>Fr. Pat. 200401.<br>FR. BAYER & Co.<br>Eng. Pat. $8673^{89}$.<br>Ger. Pat. $54190^{90}$.<br>Mon. Scien. 1890, 751.<br>J. Soc. Chem. Ind. 1892, 30. | **Appearance of dyestuff**: green glistening crystals.—**In water**: red solution with yellow fluorescence.—**In alcohol**: red solution with yellow fluorescence.—**On addition of much hydrochloric acid to the aqueous solution**: colour becomes bright orange.—**On addition of caustic soda to the aqueous solution**: pale red precipitate.—**In conc. sulphuric acid**: reddish yellow solution; becomes red on dilution with water.—**Dyes**: cotton, wool, and silk a beautiful crimson red, fairly fast to light but only moderately fast to soap. |
| Oxidation of tetraethyldiamidodiphenylmethane oxide, obtained by condensation of formaldehyde with tetraethyl-*m*-amidophenol. | 1889. | F. BENDER.<br>A. LEONHARDT & Co.<br>Eng. Pats. $13217^{89}$ & $18606^{91}$.<br>Ger. Pat. 59003.<br>FR. BAYER & Co.<br>Eng. Pat. $8673^{89}$.<br>Ger. Pat. $54190^{90}$.<br>Mon. Scien. 1890, 751. | The reactions are the same as those of pyronine G, but the shade of the colour is bluer and the fluorescence redder. |
| Oxidation of pyronine B with potassium permanganate. | 1891. | F. BENDER & M. KÄMMERER.<br>A. LEONHARDT & Co.<br>Ger. Pat. appl. L. $7176^{92}$. | **Appearance of dyestuff**: reddish powder.—**In water or alcohol**: red solution with greenish yellow fluorescence.—**On addition of much hydrochloric acid to the aqueous solution**: colour becomes orange.—**On addition of caustic soda to the aqueous solution**: reddish precipitate.—**In conc. sulphuric acid**: yellow solution; red on dilution with water.—**Dyes**: silk or mordanted cotton yellower shades of red than pyronine G or B. Fast to washing and moderately fast to light. |
| (*a* Heating succinic anhydride with dimethyl-*m*-amidophenol.<br>(*b*) Heating resorcinol-succineine with dimethylamine at 170°-200°. | 1888. | M. KAHN.<br>MAJERT.<br>R. GNEHM.<br>Am. Pats. 402436 & 425504.<br>FR. BAYER & Co.<br>Ger. Pat. $51983^{88}$, assigned to the BAD. ANIL. & SODA FABRIK.<br>Färberztg. (1890) **26**, 267.<br>SOC. CHEM. INDUSTRIE IN BASEL.<br>Eng. Pats. $2635^{89}$ & $10047^{90}$. | **Appearance of dyestuff**: dark crystalline powder.—**In water**: easily soluble with red colour and yellow fluorescence.—**On addition of caustic soda to the aqueous solution**: slowly decolorised.—**In conc. sulphuric acid**: yellow solution with green fluorescence; rose red solution on dilution with water.—**Dyes**: red upon unmordanted cotton or cotton mordanted with tannin and tartar emetic.—**Employment**: for dyeing half-silk materials, and for colouring paper-pulp and wood. |
| Etherification of sym. diethylrhodamine by means of alcohol and a mineral acid. | 1892. | BERNTHSEN.<br>Chem. Zeit. 1882, **16**, 1056.<br>J. SCHMID.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $9633^{92}$.<br>Am. Pat. $516584^{94}$.<br>Ger. Pats. $73880^{92}$ & $73573^{92}$.<br>Fr. Pat. $225341^{92}$. | **Appearance of dyestuff**: yellowish brown or red powder.—**In water**: readily soluble with red colour.—**On addition of hydrochloric acid**: red precipitate.—**On addition of caustic soda**: red precipitate of the base.—**In conc. sulphuric acid**: yellow solution; red on dilution.—**Dyes**: silk and mordanted cotton brilliant red or pink shades. |

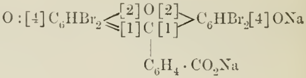
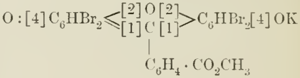
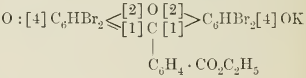
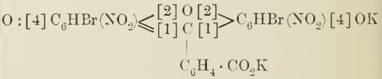
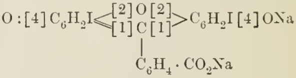
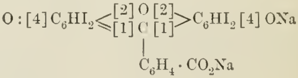
paraquinonoid or orthoquinonoid compounds: only the paraquinonoid formulæ will be given.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 498 | **Rhodamine 12 G M.**<br>[*Bl.*] | Ethyl ether of dimethylamido-ethoxy-rhodamine. | $C_{25}H_{24}NO_4Cl$ | <br>$\begin{array}{l}\mathrm{Cl\,(CH_3)_2\,N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_3\,[4]\,OCH_3}\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\,[2]\,CO_2C_2H_5}\end{array}$ |
| 499 | **Irisamine G.**<br>[*C.*] [*B.*]<br>**Rhodine 3 G.**<br>[*Bl.*] | Ethyl ether of unsym. dimethyl-homo-rhodamine. | $C_{25}H_{25}N_2O_3Cl$ | <br>$\begin{array}{l}\mathrm{Cl\,(CH_3)_2N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_2}\left\{\begin{matrix}[5]\,CH_3\\ {[4]}\,NH_2\end{matrix}\right.\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\,[2]\,CO_2C_2H_5}\end{array}$ |
| 500 | **Cotton Rhodine BS.** [*Bl.*] | Methylene derivative of dimethyl-homo-rhodamine ester. | $C_{51}H_{50}N_4O_6Cl_2$ | <br>$\begin{array}{l}\qquad\qquad\qquad\quad\mathrm{C_6H_4\cdot CO_2C_2H_5}\\ \qquad\qquad\qquad\quad\vert\\ \mathrm{Cl\,(CH_3)_2\,N:[4]\,C_6H_3}{<}\begin{matrix}[1]\,C\,[1]\\ {[2]}\,O\,[2]\end{matrix}{>}\mathrm{C_6H_2}\left\{\begin{matrix}[5]\,CH_3\\ {[4]}\,NH\end{matrix}\right.\\ \qquad\qquad\qquad\qquad\qquad\qquad\vert\\ \qquad\qquad\qquad\qquad\qquad\qquad\mathrm{CH_2}\\ \qquad\qquad\qquad\qquad\qquad\qquad\vert\\ \mathrm{Cl\,(CH_3)_2\,N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_2}\left\{\begin{matrix}[4]\,NH\\ {[5]}\,CH_3\end{matrix}\right.\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\cdot CO_2C_2H_5}\end{array}$ |
| 501 | **Rhodine 2 G.**<br>[*Bl.*] | Ethyl ester of dimethyl-ethyl-rhodamine. | $C_{26}H_{27}N_2O_3Cl$ | <br>$\begin{array}{l}\mathrm{Cl\,(CH_3)_2N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_3\,[4]\,NHC_2H_5}\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\,[2]\,CO_2C_2H_5}\end{array}$ |
| 502 | **Rhodamine G and G extra.**<br>[*B.*] [*I.*] | Chiefly triethyl-rhodamine. | | <br>$\begin{array}{l}\mathrm{Cl\,(C_2H_5)_2\,N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_3\,[4]\,NHC_2H_5}\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\,[2]\,CO_2H}\end{array}$ |
| 503 | **Rhodine 12 G F.**<br>[*Bl.*] | | | |
| 504 | **Rhodamine B.**<br>[*B.*] [*M.*] [*I.*]<br>**Rhodamine O.**<br>[*M.*]<br>**Safraniline.**<br>[*G.*] | Hydrochloride of diethyl-*m*-amido-phenol-phthaleïne. | $C_{28}H_{31}N_2O_3Cl$ | <br>$\begin{array}{l}\mathrm{Cl\,(C_2H_5)_2N:[4]\,C_6H_3}{<}\begin{matrix}[2]\,O\,[2]\\ {[1]}\,C\,[1]\end{matrix}{>}\mathrm{C_6H_3\,[4]\,N\,(C_2H_5)_2}\\ \qquad\qquad\qquad\quad\vert\\ \qquad\qquad\qquad\quad\mathrm{C_6H_4\cdot CO_2H}\end{array}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of dimethylamido-oxy-benzoylbenzoic acid upon mono- or di-methyl-resorcin, and etherification of the product. | 1900. | Brack.<br>Basle Chemical Co. | **Appearance of dyestuff**: reddish brown powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: light red precipitate.—**In conc. sulphuric acid**: yellow solution; yellowish red on dilution.—**Dyes**: silk and tannined cotton yellowish red. |
| Action of dimethylamido-oxy-benzoylbenzoic acid upon amido-*p*-cresol and etherification of the product. | 1895 | Müller.<br>Eng. Pat. 4985$^{95}$.<br>Am. Pat. 584119.<br>Fr. Pat. 245593. | **Appearance of dyestuff**: green crystalline powder.—**In water**: crimson red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: scarlet red precipitate.—**In conc. sulphuric acid**: yellow solution; red on dilution.—**Dyes**: tannined cotton, silk, and wool brilliant red. |
| Action of formaldehyde upon the ethyl ether of unsym. dimethyl-homo-rhodamine. | 1899. | Brack.<br>L. Cassella & Co.<br>Am. Pat. 643371.<br>Ger. Pat. 109883. | **Appearance of dyestuff**: reddish brown powder.—**In water**: bluish red solution.—**On addition of hydrochloric acid or caustic soda**: reddish brown precipitate.—**In conc. sulphuric acid**: yellowish brown solution; reddish brown precipitate on dilution.—**Dyes**: tannined cotton bright violet red. |
| Action of dimethylamido-oxy-benzoylbenzoic acid upon monoethyl-*m*-amidophenol, and etherification of the product. | 1895. | Müller.<br>Basle Chemical Works.<br>Eng. Pat. 4985$^{95}$.<br>Am. Pat. 584119.<br>Fr. Pat. 245593. | **Appearance of dyestuff**: green crystalline powder.—**In water**: crimson red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: scarlet red precipitate.—**In conc. sulphuric acid**: yellow solution; red on dilution.—**Dyes**: silk, wool, and tannined cotton brilliant red. |
| Heating Rhodamine B with aniline hydrochloride. | 1891. | Ceresole.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 14723$^{91}$.<br>Am. Pat. 516588.<br>Ger. Pat. 68325$^{91}$.<br>Fr. Pat. 215700$^{91}$. | **Appearance of dyestuff**: green glistening crystals.—**In water**: reddish violet solution with red fluorescence.—**On addition of hydrochloric acid**: yellow solution; red again on dilution.—**On addition of caustic soda**: no change when cold; on heating decolorised with precipitation of the base.—**In conc. sulphuric acid**: pale yellow solution; fluorescent red solution on adding water.—**Dyes**: silk, wool, and tannined cotton red of yellower shade than Rhodamine B. |
| Action of formaldehyde upon the etherified condensation-product from dimethyl-amido-benzoylbenzoic acid and resorcin. | 1898. | Brack.<br>Basle Chemical Works.<br>Eng. Pat. 18477$^{98}$.<br>Am. Pat. 613113.<br>Ger. Pat. 106720.<br>Fr. Pat. 280925. | **Appearance of dyestuff**. light red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: light red precipitate.—**In conc. sulphuric acid**: yellow solution; yellowish red on dilution.—**Dyes**:—tannined cotton and silk yellowish red. Chiefly used for printing on cotton and silk. |
| (*a*) Heating phthalic anhydride with diethyl-*m*-amidophenol.<br>(*b*) Action of diethylamine upon fluoresceïne chloride. | 1887. | M. Ceresole.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 15374$^{87}$.<br>Am. Pats. 377349 & 377350$^{88}$.<br>Ger. Pat. 44002$^{87}$.<br>Fr. Pat. 186697$^{87}$.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 9600$^{88}$.<br>Ger. Pat. 48367$^{88}$.<br>A. Bernthsen.<br>Chem. Zeit. (1892) 16, 1956.<br>J. Soc. Chem. Ind. 1893, 513. | **Appearance of dyestuff**: green crystals or reddish violet powder.—**In water or alcohol**: easily soluble with bluish red colour, and strong fluorescence in dilute solution; fluorescence of the alcoholic solution disappears on heating, and returns again on cooling.—**On addition of hydrochloric acid to the aqueous solution**: separation of green crystals of the hydrochloride, which dissolve in excess to a scarlet red solution which is turned bluer on dilution with water.—**On addition of caustic soda to the aqueous solution**: small quantity in the cold produces little change; larger quantity or heating the solution throws down a rose red precipitate, soluble in ether or benzene to a colourless solution.—**On heating with strong aqueous caustic soda**: smell of dimethylamine.—**In conc. sulphuric acid**: yellowish brown solution with evolution of hydrochloric acid; becomes scarlet red and finally bluish red on dilution with water.—**Dyes**: wool and silk fast shades of bluish red with strong fluorescence, tannined cotton violet red without fluorescence, oiled cotton with fluorescence. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 505 | **Rhodamine 3 B.**<br>[*B.*] [*I.*]<br>**Anisoline.**<br>[*Mo.*] | Ethyl ester of tetraethylrhodamine. | $C_{30}H_{35}N_2O_3Cl$ |  $Cl\,(C_2H_5)_2N:[4]\,C_6H_3<\begin{matrix}[2]\,O\,[2]\\ [1]\,C\,[1]\end{matrix}>C_6H_3\,[4]\,N\,(C_2H_5)_2$<br>$C_6H_4\cdot CO_2C_2H_5$ |
| 506 | **Fast Acid Violet B.** [*M.*]<br>**Violamine B.**<br>[*M.*] | Sodium salt of diphenyl-*m*-amidophenolphthaleinsulphonic acid. | $C_{34}H_{24}N_2O_6SNa_2$ |  $C_6H_3\,[4]:N\cdot C_6H_5$<br>$[2]\,O\ \ [1]\,C\cdot C_6H_4\,[2]\,CO_2Na$<br>$C_6H_3\,[4]\,NH\cdot C_6H_4\cdot SO_3Na$ |
| 507 | **Fast Acid Violet A 2 R.** [*M.*]<br>**Violamine R.**<br>[*M.*]<br>**Acid Violet 4 R.**<br>[*B.*] | Sodium salt of di-*o*-tolyl-*m*-amidophenolphthaleinsulphonic acid. | $C_{34}H_{24}N_2O_6SNa_2$ |  $C_6H_3\,[4]:N\cdot C_6H_4\,(CH_3)$<br>$[2]\,O\ \ [1]\,C\cdot C_6H_4\cdot CO_2Na$<br>$C_6H_3\,[4]\,NH\cdot C_6H_3\,(CH_3)\,SO_3Na$ |
| 508 | **Acid Rosamine A.**<br>[*M.*]<br>**Violamine G.**<br>[*M.*] | Sodium salt of di-mesidyl-*m*-amidophenolphthaleinsulphonic acid. | $C_{38}H_{32}N_2O_6SNa_2$ |  $C_6H_3\,[4]:N\cdot C_6H_2\,(CH_3)_3$<br>$[2]\,O\ \ [1]\,C\cdot C_6H_4\cdot CO_2Na$<br>$C_6H_3\,[4]\,NH\cdot C_6H\,(CH_3)_3SO_3Na$ |
| 509 | **Fast Acid Blue R.**<br>[*M.*]<br>**Violamine 3 B.**<br>[*M.*] | Sodium salt of di-*p*-ethoxy-phenyl-*m*-amidophenol-dichlorphthaleinsulphonic acid. | $C_{36}H_{26}N_2O_8SCl_2Na_2$ |  $C_6H_3\,[4]:N\cdot C_6H_4\,(OC_2H_5)$<br>$[2]\,O\ \ [1]\,C\cdot C_6H_2Cl_2\cdot CO_2Na$<br>$C_6H_3\,[4]\,NH\cdot C_6H_3\,(OC_2H_5)\,SO_3Na$ |
| 510 | **Uranine.**<br>[*B.*] [*A.*] [*L.*] [*M.*]<br>[*B.S.S.*]<br>**Fluoresceïne.** | Sodium or potassium salt of fluoresceïne. | $C_{20}H_{10}O_5Na_2$ |  $NaO\,[4]\,C_6H_3<\begin{matrix}[2]\,O\,[2]\\ [1]\,C\,[1]\end{matrix}>C_6H_3[4]\,ONa$<br>$O$<br>$OC - C_6H_4$<br>*Or*<br> $O:[4]\,C_6H_3<\begin{matrix}[2]\,O\,[2]\\ [1]\,C\,[1]\end{matrix}>C_6H_3[4]\,ONa$<br>$C_6H_4\cdot CO_2Na$ |
| 511 | **Chrysoline.**<br>[*Mo.*] | Sodium salt of benzyl-fluoresceïne. | | |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Etherification of Rhodamine B by means of ethyl chloride (Monnet) or with ethyl alcohol and hydrochloric or sulphuric acid (Schmid.) | 1891. | P. Monnet.<br>Eng. Pat. 4677$^{92}$.<br>Am. Pat. 499927$^{92}$.<br>Fr. Pat. 216407$^{91}$.<br>J. Soc. Chem. Ind. 1892, 516, 677.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 7298$^{92}$.<br>Ger. Pats. 66238, 71490, & 73451.<br>A. Bernthsen.<br>J. Soc. Chem. Ind. 1893, 513. | **Appearance of dyestuff**: brownish red bronzy powder.—**In water**: violet red solution, fluorescent when dilute.—**On addition of hydrochloric acid**: yellow solution, becoming red again on dilution.—**On addition of caustic soda**: no change in the cold; on warming saponified with separation of tetraethylrhodamine base.—**In conc. sulphuric acid**: greenish yellow solution; red on dilution.—**Dyes**: silk, wool, and mordanted cotton bluish red. |
| Action of aniline (or *p*-toluidine) upon fluoresceïn chloride and sulphonation of the product. | 1888.<br>1888. | J. Schmid.<br>Boedeker.<br>Bad. Anil. & Soda Fabrik.<br>Ger. Pat. 46807$^{88}$.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 9600$^{88}$.<br>Ger. Pat. 49057$^{88}$. | **Appearance of dyestuff**: maroon powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: purple precipitate.—**On addition of caustic soda**: cherry red solution.—**In conc. sulphuric acid**: reddish orange solution; reddish violet precipitate on dilution with water.—**Dyes**: wool and silk reddish violet in level shades, fairly fast to washing, alkalies, dilute acids, and light. |
| Action of *o*-toluidine upon fluoresceïn chloride and sulphonation of the product. | 1888. | Boedeker.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 9600$^{88}$.<br>Ger. Pats. 46807 & 49057. | **Appearance of dyestuff**: violet red powder.—**In water**: easily soluble to violet red solution.—**On addition of hydrochloric acid**: bluish red precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: yellowish red solution; bluish red solution and precipitate on dilution.—**Dyes**: silk and wool level shades of reddish violet, tolerably fast to light, alkalies, etc. |
| Action of mesidine upon fluoresceïn chloride and sulphonation of the product. | | Meister, Lucius, & Brüning.<br>Ger. Pat. 63844$^{91}$. | **Appearance of dyestuff**: light red powder.—**In water**: yellowish red solution.—**On addition of hydrochloric acid**: red flocculent precipitate.—**On addition of caustic soda**: solution yellower.—**In conc. sulphuric acid**: brownish yellow solution; redder solution and then red precipitate when diluted.—**Dyes**: silk and wool a fast and brilliant pink. |
| Action of *p*-phenetidine upon fluoresceïn chloride, and sulphonation of the product. | 1889. | Boedeker.<br>Meister, Lucius, & Brüning.<br>Ger. Pat. 53300$^{89}$. | **Appearance of dyestuff**: dark bluish violet powder.—**In water**: easily soluble to dark blue solution.—**In alcohol**: sparingly soluble.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: violet solution; on heating, redder.—**In conc. sulphuric acid**: dark bordeaux red solution; blue precipitate on dilution.—**Dyes**: wool and silk blue in fast level shades. |
| Heating resorcinol with phthalic anhydride, alone or in presence of zinc chloride or sulphuric acid. | 1871. | Ad. Baeyer.<br>Ber. (1871) **4**, 558, 662; (1875) **8**, 146.<br>Ann. (1876) **183**, 2; (1882) **212**, 347.<br>E. Fischer.<br>Ber. (1874) **7**, 1211.<br>O. Mühlhäuser.<br>J. Soc. Chem. Ind. 1887, 283; 1892, 675.<br>A. Bernthsen.<br>Chem. Zeit. (1892) **16**, 1956.<br>J. Soc. Chem. Ind. 1893, 513.<br>*Other references:*<br>Ber. **21**, 3376; **24**, 1412; **25**, 1385, 2118, 3586; **28**, 28, 44, 312, 396, 428. | **Appearance of dyestuff**: yellowish brown powder.—**In water**: yellow solution, with intense green fluorescence visible in extreme dilution.—**In alcohol**: easily soluble.—**On addition of hydrochloric acid to the aqueous solution**: yellow precipitate.—**On addition of caustic soda to the aqueous solution**: the colour and fluorescence become darker.—**In conc. sulphuric acid**: yellow solution with very slight fluorescence; yellow solution on dilution with water.—**Dyes**: silk and wool yellow. |
| Heating resorcinol with phthalic anhydride and benzyl chloride in presence of sulphuric acid. | 1877. | F. Reverdin.<br>Mon. Scien. (1877) 860.<br>Zeits. f. Chem. Grossgewerbe (1877 **2**, 456, 668; (1878) **3**, 625.<br>Jahresber. (1887) 1233. | **Appearance of dyestuff**: reddish brown powder or lumps, smelling of benzyl chloride.—**In water**: brown solution with green fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution**: colour becomes darker.—**In conc. sulphuric acid**: yellow solution; yellow precipitate on dilution with water.—**Dyes**: silk yellow. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 512 | **Eosine.*** [*B.*]<br>**Eosine, yellowish.** [*A.*] [*B.S.S.*]<br>**Eosine A.** [*B.*]<br>**Eosine G G F.** [*C.*]<br>**Water-soluble Eosine.** [*M.*]<br>**Eosine B.**<br>**Eosine A extra.** [*D.H.*]<br>**Eosine 3 J and 4 J extra.** [*L.*] | Alkali salts of tetra-bromo-fluoresceïne. | $C_{20}H_6O_5Br_4Na_2$ |  $\begin{array}{c} O:[4]\,C_6HBr_2\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6HBr_2[4]\,ONa\\ \vert\\ C_6H_4\cdot CO_2Na\end{array}$ |
| 513 | **Erythrine.**<br>**Spirit Eosine.** [*B.*]<br>**Primerose à l'alcool.** [*D.H.*]<br>**Methyl Eosine.** [*Mo.*] [*I.*] | Potassium salt of tetrabromo-fluoresceïne-methyl ether. | $C_{21}H_9Br_4O_5K$ |  $\begin{array}{c} O:[4]\,C_6HBr_2\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6HBr_2[4]\,OK\\ \vert\\ C_6H_4\cdot CO_2CH_3\end{array}$ |
| 514 | **Spirit Eosine.**<br>**Ethyl Eosine.**<br>**Eosine S.** [*B.*]<br>**Eosine B B.** [*I.*]<br>**Primerose à l'alcool.**<br>**Eosine à l'alcool.**<br>**Rose J B à l'alcool.** | Potassium salt of tetrabromo-fluoresceïne-ethyl ether. | $C_{22}H_{11}Br_4O_5K$ |  $\begin{array}{c} O:[4]\,C_6HBr_2\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6HBr_2[4]\,OK\\ \vert\\ C_6H_4\cdot CO_2C_2H_5\end{array}$ |
| 515 | **Eosine B N.** [*B.*]<br>**Saffrosine.** [*I.*] [*B.S.S.*]<br>**Methyl Eosine** [*A.*]<br>**Eosine B W.**<br>**Scarlet J, JJ, and V.** [*Mo.*]<br>**Eosine Scarlet B.** [*C.*]<br>**Eosine B.** [*L.*] | Potassium or sodium salt of dibromo-dinitro-fluoresceïne. | $C_{20}H_6N_2O_9Br_2K_2$ |  $\begin{array}{c} O:[4]\,C_6HBr(NO_2)\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6HBr(NO_2)\,[4]\,OK\\ \vert\\ C_6H_4\cdot CO_2K\end{array}$ |
| 516 | **Erythrosine G.** [*B.*]<br>**Dianthine G.**<br>**Pyrosine J.** [*Mo.*]<br>**Iodeosine G.**<br>**Jaune d'Orient.** | Sodium or potassium salt of diiodofluoresceïne. | $C_{20}H_8O_5I_2Na_2$ |  $\begin{array}{c} O:[4]\,C_6H_2I\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6H_2I\,[4]\,ONa\\ \vert\\ C_6H_4\cdot CO_2Na\end{array}$ |
| 517 | **Erythrosine.** [*B.*] [*M.*] [*B.S.S.*]<br>**Erythrosine D.** [*C.*]<br>**Erythrosine B.** [*A.*]<br>**Pyrosine B.** [*Mo.*]<br>**Iodeosine B.**<br>**Eosine, bluish.**<br>**Eosine J.** [*B.*] | Sodium or potassium salt of tetraiodo-fluoresceïne. | $C_{20}H_6O_5I_4Na_2$ |  $\begin{array}{c} O:[4]\,C_6HI_2\begin{smallmatrix}<[2]\,O\,[2]>\\ \leqslant[1]\,C\,[1]>\end{smallmatrix}C_6HI_2\,[4]\,ONa\\ \vert\\ C_6H_4\cdot CO_2Na\end{array}$ |

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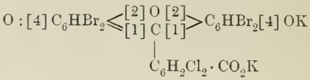
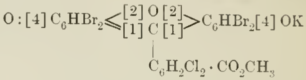
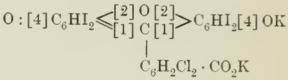
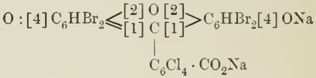
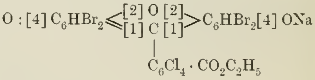
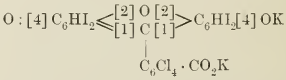
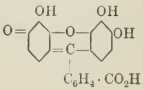
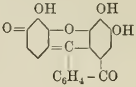
* Varying mixtures of di- and tetra-bromo-fluoresceïne come into

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Bromination of fluoresceïne in aqueous or alcoholic solution. | 1874. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>A. W. Hofmann.<br>Ber. (1875) **8**, 62.<br>Ad. Baeyer.<br>Ber. (1875) **8**, 147.<br>Ann. (1876) **183**, 2.<br>O. Mühlhäuser.<br>Ding. Pol. J. (1887) **263**, 49 ; (1892) **284**, 21 and 46.<br>J. Chem. Ind. 1887, 283 ; 1892, 673.<br>A. Bernthsen.<br>Chem. Zeit. (1892) **16**, 1956.<br>J. Soc. Chem. Ind. 1893, 513. | **Appearance of dyestuff:** small bluish red glistening crystals or brownish red powder.—**In water:** bluish red solution ; the dilute solution has a green fluorescence.—**In alcohol:** easily soluble with bluish red colour and yellowish green fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** yellowish red precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** yellow solution ; yellowish red precipitate on dilution with water.—**Dyes:** wool and silk yellowish red.—Largely employed for making pigments ("vermilionette," etc.), for which purpose it is usually precipitated as an insoluble lead lake upon a basis of red-lead, orange-lead, white-lead, etc. |
| Methylation of Eosine. | 1874. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Ad. Baeyer.<br>Ann. (1876) **183**, 53.<br>A. Bernthsen.<br>Chem. Zeit. (1892) **16**, 1956.<br>J. Soc. Chem. Ind. 1893, 513. | **Appearance of dyestuff:** green glistening powder or flakes.—**In water:** sparingly soluble cold, more readily on boiling, with a cherry red colour.—**In alcohol:** red solution with brownish yellow fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution:** the colour and fluorescence becomes darker.—**In conc. sulphuric acid:** yellow solution ; evolves bromine on heating.—**Dyes:** silk bluish red with reddish fluorescence. |
| Ethylation of Eosine. | 1874. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Ad. Baeyer.<br>Ann. (1876) **183**, 46.<br>O. Mühlhäuser.<br>Ding. Pol. J. (1887) **263**, 49 and 99 ; (1892) **283**, 210.<br>J. Chem. Ind. 1887, 283 ; 1892, 675. | **Appearance of dyestuff:** brown powder mixed with small green crystals.—**In water:** sparingly soluble cold, soluble on boiling to a cherry red solution with slight greenish yellow fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** yellowish brown precipitate.—**On addition of caustic soda to the aqueous solution:** brownish yellow precipitate.—**In conc. sulphuric acid:** yellow solution ; on warming bromine is evolved.—**Dyes:** wool yellowish red with slight fluorescence. |
| (*a*) Nitration of dibromofluoresceïne in aqueous solution.<br>(*b*) Bromination of dinitrofluoresceïne in alcoholic solution. | 1875.<br>1876. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Ad. Baeyer.<br>Ann. (1876) **183**, 61.<br>O. Mühlhäuser.<br>Ding. Pol. J. **263**, 49, 99.<br>J. Soc. Chem. Ind. 1887, 283 ; 1892, 739. | **Appearance of dyestuff:** brown crystalline powder.—**In water:** yellowish red solution.—**On addition of hydrochloric acid to the aqueous solution:** yellowish green flocculent precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** brownish yellow solution, evolves bromine on heating ; brownish yellow precipitate on dilution with water.—**Dyes:** silk and wool bluish red. |
| Iodation of fluoresceïne in aqueous solution. | 1875. | E. Nölting. | **Appearance of dyestuff:** yellowish brown powder.—**In water:** cherry red solution without fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** brownish yellow solution ; evolves iodine vapours on heating ; brownish yellow precipitate on dilution with water.—**Dyes:** wool yellowish red with yellowish red fluorescence. |
| Iodation of fluoresceïne in aqueous or alcoholic solution. | 1876. | Bindschedler & Busch.<br>O. Mühlhäuser.<br>Ding. Pol. J. **263**, 49, 99 ; **283**, 258.<br>J. Chem. Ind. (1887), 283 ; (1892), 677. | **Appearance of dyestuff:** brown powder.—**In water:** cherry red solution without fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** brownish yellow precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** brownish yellow solution ; evolves iodine vapours on heating ; brownish yellow precipitate on dilution with water.—**Dyes:** silk and wool bluish red. Chiefly employed in paper staining. |

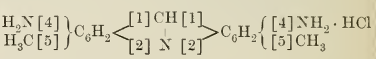
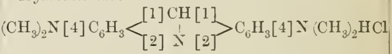
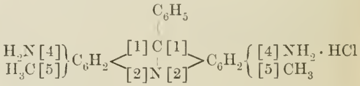
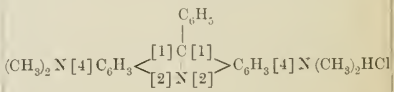
commerce as **Eosine-Orange** [*I.*], **Eosine 3 G.** [*C.*], **Salmon Pink**, etc.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 518 | **Phloxine P.**<br>[*B.*]<br>**Phloxine.**<br>**New Pink.** | Alkaline salts of tetrabromodichlorofluoresceïne. | $C_{20}H_4Cl_2Br_4O_5K_2$ | <br>$O:[4]\,C_6HBr_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6H_2Cl_2\cdot CO_2K\end{array}>C_6HBr_2[4]\,OK$ |
| 519 | **Cyanosine A.**<br>[*Mo.*]<br>**Cyanosine spirit soluble.**<br>[*M.*] [*K.*] [*K.S.*] | Alkaline salt of tetrabromodichlorofluoresceïne-methyl-ether. | $C_{21}H_7Cl_2Br_4O_5K$ | <br>$O:[4]\,C_6HBr_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6H_2Cl_2\cdot CO_2CH_3\end{array}>C_6HBr_2[4]\,OK$ |
| 520 | **Rose Bengal.**<br>[*B.*] [*R.*]<br>**Rose Bengal N.**<br>[*C.*]<br>**Rose Bengal A T.**<br>[*A.*] [*B.*]<br>**Rose Bengal G.**<br>[*M.*] | Alkaline salt of tetraiododichlorofluoresceïne. | $C_{20}H_4Cl_2I_4O_5K_2$ | <br>$O:[4]\,C_6HI_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6H_2Cl_2\cdot CO_2K\end{array}>C_6HI_2[4]\,OK$ |
| 521 | **Phloxine.**<br>[*B.*] [*M.*] [*A.*]<br>**Phloxine T A.**<br>[*Mo.*]<br>**Eosine 10 B.**<br>[*C.*] | Sodium salt of tetrabromotetrachlorofluoresceïne. | $C_{20}H_2Cl_4Br_4O_5Na_2$ | <br>$O:[4]\,C_6HBr_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6Cl_4\cdot CO_2Na\end{array}>C_6HBr_2[4]\,ONa$ |
| 522 | **Cyanosine B.**<br>[*I.*] | Sodium salt of tetrabromotetrachlorofluoresceïne-ethyl-ether. | $C_{22}H_7Cl_4Br_4O_5Na$ | <br>$O:[4]\,C_6HBr_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6Cl_4\cdot CO_2C_2H_5\end{array}>C_6HBr_2[4]\,ONa$ |
| 523 | **Rose Bengal 3 B.**<br>[*M.*] [*D.H.*]<br>**Rose Bengal.**<br>[*B.*] [*C.*] [*K.S.*] | Potassium salt of tetraiodotetrachlorofluoresceïne. | $C_{20}H_2Cl_4I_4O_5K_2$ | <br>$O:[4]\,C_6HI_2<\begin{array}{c}[2]\,O\,[2]\\ [1]\,C\,[1]\\ \vert\\ C_6Cl_4\cdot CO_2K\end{array}>C_6HI_2[4]\,OK$ |
| 524 | **Cyclamine.**<br>[*Mo.*] | | | |
| 525 | **Galleïne.**<br>[*B.*] [*By.*] [*M.*]<br>**Alizarine Violet.**<br>**Anthracene Violet.** | Pyrogallol-phthaleïn. | $C_{20}H_{12}O_7$ |  |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of bromine on dichlorofluoresceïne from dichlorophthalic acid and resorcinol. | 1875. | E. Nölting.<br>John Castelhaz.<br>Eng. Pat. $447^{79}$. | **Appearance of dyestuff**: brownish yellow powder.—**In water**: cherry red solution with greenish yellow fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: brownish yellow precipitate on warming.—**On addition of caustic soda to the aqueous solution**: colour becomes a bluer red.—**In conc sulphuric acid**: brownish yellow solution, no change on heating; brown precipitate on dilution with water.—**Dyes**: wool bluish red without fluorescence. |
| Methylation of phloxine. | 1876. | E. Nölting. | **Appearance of dyestuff**: brownish red powder.—**In water**: insoluble cold, slightly on boiling.—**In alcohol**: bluish red solution with reddish yellow fluorescence.—**On addition of hydrochloric acid to the alcoholic solution**: the fluorescence disappears.—**On addition of caustic soda to the alcoholic solution**: no change.—**In conc. sulphuric acid**: yellow solution; evolves bromine on heating; reddish brown precipitate on dilution with water.—**Employment**: in silk dyeing. |
| Action of iodine upon dichlorofluoresceïne obtained from dichlorophthalic acid and resorcinol. | 1875. | E. Nölting. | **Appearance of dyestuff**: brown powder.—**In water**: cherry red solution without fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: brownish red precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: brownish yellow solution, evolves iodine vapours on heating; brownish red flocculent precipitate on dilution with water.—**Dyes**: wool bluish red without fluorescence. |
| Bromination of tetrachlorofluoresceïne obtained from tetrachlorophthalic acid and resorcinol. | 1882. | R. Gnehm. | **Appearance of dyestuff**: brick red powder.—**In water**: easily soluble with bluish red colour and slight dark green fluorescence.—**In alcohol**: bluish red solution with brick red fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: decolourised with separation of a reddish precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: yellow solution; yellowish red precipitate on dilution with water. |
| Ethylation of tetrabromotetrachloro-fluoresceïne. | 1882. | R. Gnehm. | **Appearance of dyestuff**: red crystalline powder.—**In water**: sparingly soluble with red colour and yellow fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: brownish red flocculent precipitate.—**On addition of caustic soda**: colour becomes rather darker.—**In conc. sulphuric acid**: yellowish brown solution; brownish red precipitate on dilution with water.—**Dyes**: wool bluish red. |
| Action of iodine upon tetrachlorofluoresceïne obtained from tetrachlorophthalic acid and resorcinol. | 1882. | R. Gnehm. | **Appearance of dyestuff**: brownish red powder.—**In water**: bluish red solution without fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: flesh pink flocculent precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: brown solution; flesh pink precipitate on dilution with water.—**Dyes**: wool bluish red. |
| Bromination of the product of the action of sodium sulphide upon dichlorofluorescein. | 1889. | Société Gilliard Monnet & Cartier.<br>Ger. Pat. $52139^{89}$.<br>Chem. Ztg. (1890) Rep. 36.<br>Text. Merc. 1889, 410.<br>J. Soc. Dyers & Colorists, 1889, 170. | **Appearance of dyestuff**: powder.—**In water**: magenta red solution without fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: precipitation of the colour acid.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: orange yellow solution.—**Dyes**: wool and silk bluish red from a neutral bath. |
| Heating gallic acid (or pyrogallol) with phthalic anhydride at 200°. | 1871. | Ad. Baeyer.<br>Ber. (1871) 4, 457, 555, 663.<br>Durand & Huguenin.<br>K. Buchka.<br>Ann. (1881) 209, 249.<br>A. de Montlaur.<br>Mon. Scien. 10, 1338.<br>O. Gürke.<br>Ger. Pat. $30648^{84}$.<br>Orndorff & Brewer.<br>Chem. Centralbl. 1901, 775. | **Appearance of dyestuff**: violet paste, or dark green metallic glistening crystalline powder.—**In water**: sparingly soluble cold, more easily hot with a scarlet red colour.—**In alcohol**: slightly soluble cold, more easily hot with a reddish brown colour.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes a yellowish brown.—**On addition of caustic soda to the aqueous solution**: colour changes to a beautiful blue.—**In conc. sulphuric acid**: reddish yellow solution; unchanged on dilution.—**Dyes**: chrome mordanted wool, silk, or cotton violet. Not fast. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 526 | **Cœruleïne.**<br>[*B.*] [*By.*] [*M.*]<br>**Alizarine Green.**<br>**Anthracene Green.** | | $C_{20}H_{10}O_6$ |  |
| 527 | **Cœruleïne S.**<br>[*B.*] [*By.*] [*M.*]<br>**Alizarine Green.**<br>**Anthracene Green.** | Sodium bisulphite compound of cœruleïne. | $C_{20}H_{10}O_6$<br>$+2NaHSO_3$ | |

## XII. ACRIDINE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 528 | **Acridine Yellow.**<br>[*L.*] | Hydrochloride of diamidodimethyl-acridine. | $C_{15}H_{16}N_3Cl$ |  $\left.\begin{matrix}H_2N[4]\\ H_3C[5]\end{matrix}\right\}C_6H_2<\begin{matrix}[1]CH[1]\\ \mid\\ [2]\;N\;[2]\end{matrix}>C_6H_2\left\{\begin{matrix}[4]NH_2\cdot HCl\\ [5]CH_3\end{matrix}\right.$ |
| 529 | **Acridine Orange, NO.*** [*L.*] | Zinc-double-chloride of tetramethyl-diamidoacridine. | $C_{17}H_{17}N_3ZnCl_3$ | *Hydrochloride:*<br> $(CH_3)_2N[4]C_6H_3<\begin{matrix}[1]CH[1]\\ \mid\\ [2]\;N\;[2]\end{matrix}>C_6H_3[4]N(CH_3)_2HCl$ |
| 530 | **Benzoflavine.**<br>[*O.*] | Hydrochloride of diamido-phenyl-dimethyl-acridine. | $C_{21}H_{19}N_3HCl$ |  $\left.\begin{matrix}H_2N[4]\\ H_3C[5]\end{matrix}\right\}C_6H_2<\begin{matrix}C_6H_5\\ \mid\\ [1]C[1]\\ \mid\\ [2]N[2]\end{matrix}>C_6H_2\left\{\begin{matrix}[4]NH_2\cdot HCl\\ [5]CH_3\end{matrix}\right.$ |
| 531 | **Acridine Orange R extra.** [*L.*] | Salt of tetramethyl-diamido-phenyl-acridine. | $C_{23}H_{23}N_3HCl$ |  $(CH_3)_2N[4]C_6H_3<\begin{matrix}C_6H_5\\ \mid\\ [1]C[1]\\ \mid\\ [2]N[2]\end{matrix}>C_6H_3[4]N(CH_3)_2HCl$ |

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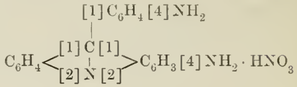
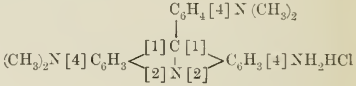
* **Acridine Scarlet R, 2 R, and 3 R** [*L.*] **are**

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating Galleïn with conc. sulphuric acid at 200°. | 1871. | Ad. Baeyer.<br>Ber. (1871) 4, 566.<br>K. Buchka.<br>Ann. (1881) **209**, 272.<br>Orndorff & Brewer.<br>Chem. Centralbl. 1901, 778. | **Appearance of dyestuff**: black paste.—**In water**: insoluble.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the diluted paste**: no change.—**On addition of caustic soda to the diluted paste**: dull green colour.—**In conc. sulphuric acid**: dull yellowish brown solution; on dilution with water becomes reddish brown and then greenish with a green black precipitate.—**Dyes**: chrome mordanted wool, silk, or cotton green Used in cotton printing. |
| Treatment of cœruleïne with sodium bisulphite. | 1879. | Prud'homme.<br>Bull. de Mulh. **49**, 1879.<br>Bad. Anil. & Soda Fabrik.<br>K. Buchka.<br>Ann. (1881) **209**, 272.<br>Eng. Pat. (prov. only) 3850$^{81}$. | **Appearance of dyestuff**: black powder.—**In water**: slightly soluble in the cold, more easily on boiling, with dull greenish brown colour.—**In alcohol**: insoluble in the cold, somewhat soluble on boiling, with a gray blue colour.—**On addition of hydrochloric acid to the aqueous solution**: no change of colour, on warming sulphurous acid is evolved.—**On addition of caustic soda to the aqueous solution**: olive green precipitate.—**In conc. sulphuric acid**: dark brown solution, black precipitate on dilution with water.—**Dyes**: chrome mordanted wool, silk, or cotton a very fast green. Chiefly used in calico printing. |

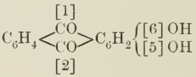
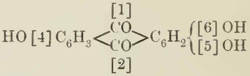
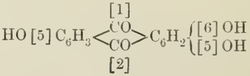
## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of formaldehyde upon *m*-tolylene diamine, conversion of the tetra-amido-ditolyl-methane obtained into diamido-hydroacridine by splitting off ammonia, and oxidation with ferric chloride. | 1889. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. 17971$^{89}$.<br>Ger. Pat. 52324$^{89}$.<br>Fr. Pat. 201798. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution with green fluorescence.—**In alcohol**: yellow solution, with strong green fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: yellow precipitate.—**On addition of caustic soda to the aqueous solution**: yellow precipitate.—**In conc. sulphuric acid**: light yellow solution; yellow precipitate on dilution with water.—**Dyes**: silk greenish yellow with green fluorescence, cotton mordanted with tannin yellow. |
| Condensation of formaldehyde with *m*-amido-dimethyl-aniline, heating the tetramethyl-tetra-amido-di-phenyl-methane with acids, and oxidation of the tetramethyl-diamido-hydroacridine obtained. | 1889. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. 8243$^{90}$.<br>Am. Pat. 503305.<br>Fr. Pat. 205459.<br>Ger. Pat. 59179$^{89}$.<br>*Employment:*<br>J. Soc. Chem. Ind. 1892, 30. | **Appearance of dyestuff**: orange powder.—**In water**: orange solution with greenish fluorescence.—**In alcohol**: orange solution with greenish fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: the colour becomes red.—**On addition of caustic soda to the aqueous solution**: yellow precipitate.—**In conc. sulphuric acid**: almost colourless solution with greenish fluorescence; red and finally orange on dilution with water.—**Dyes**: silk orange with a greenish fluorescence, cotton mordanted with tannin orange, also leather. Moderately fast to light, tolerably fast to soap. |
| Condensation of benzaldehyde with *m*-tolylene diamine, splitting off ammonia from the tetramido-phenyl-di-tolyl-methane by heating with acids, and oxidation of the diamido-phenyl-dimethyl-hydro-acridine obtained. | 1887. | C. Rudolph.<br>K. Oehler.<br>Eng. Pat. 9614$^{88}$.<br>Am. Pat. 382832.<br>Ger. Pats. 43714$^{87}$ & 43720$^{87}$. | **Appearance of dyestuff**: brownish orange yellow powder.—**In water**: yellow solution.—**In alcohol**: reddish yellow solution with strong greenish yellow fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: orange precipitate.—**On addition of caustic soda to the aqueous solution**: yellowish white precipitate.—**In conc. sulphuric acid**: greenish yellow solution, with very strong green fluorescence; on dilution with water the solution at first remains yellow and then gives an orange precipitate.—**Dyes**: silk, wool, and mordanted cotton yellow. |
| Condensation of benzaldehyde with *m*-amido-dimethyl-aniline, splitting off ammonia from the product by heating with acids, and oxidation of the leuco base obtained. | 1889. | Bender.<br>A. Leonhardt & Co.<br>Ger. Pat. 68908$^{90}$. | **Appearance of dyestuff**: orange red powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid**: red solution.—**On addition of caustic soda**: yellow precipitate.—**In conc. sulphuric acid**: yellow solution with green fluorescence; red on dilution.—**Dyes**: tanned cotton orange red. |

mixtures of Acridine Orange with Pyronine.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 532 | **Phosphine.** [*B.S.S.*] [*B.*] [*C.*] [*M.*] [*H.*] [*O.*] [*K.*]<br>**Leather Yellow.** [*M.*] [*D.*] [*L.*] [*D.H.*]<br>**Xanthine.**<br>**Philadelphia Yellow G.** [*A.*] | Nitrate of chrysaniline (unsym. diamido-phenyl-acridine, and homologues. | $C_{19}H_{16}N_4O_3$ |  $C_6H_4\lt\begin{array}{c}[1]\,C_6H_4\,[4]\,NH_2\\ \vert \\ [1]\,C\,[1]\\ \vert \\ [2]\,N\,[2]\end{array}\gt C_6H_3\,[4]\,NH_2\cdot HNO_3$ |
| 533 | **Rheonine.** [*B*]. | Hydrochloride of tetramethyl-triamido-phenyl-acridine. | | *Probably:*  $(CH_3)_2N\,[4]\,C_6H_3\lt\begin{array}{c}C_6H_4\,[4]\,N\,(CH_3)_2\\ \vert \\ [1]\,C\,[1]\\ \vert \\ [2]\,N\,[2]\end{array}\gt C_6H_3\,[4]\,NH_2HCl$ |

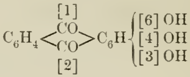
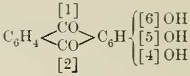
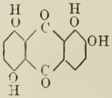
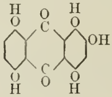
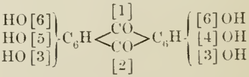
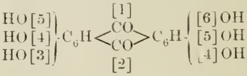
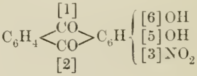
## XIII. ANTHRACENE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 534 | **Alizarine V 1.** [*B.*]<br>**Alizarine No. I.** [*M.*]<br>**Alizarine I e.** [*By.*]<br>**Alizarine V.** [*I.*]<br>**Alizarine P.** [*Br. A.*] | α β-Dioxyanthraquinone. | $C_{14}H_8O_4$ |  $C_6H_4\lt\begin{array}{c}[1]\\ CO\\ CO\\ [2]\end{array}\gt C_6H_2\left\{\begin{array}{l}[6]\,OH\\ [5]\,OH\end{array}\right.$ |
| 535 | **Alizarine R G. and G 1.** [*B.*]<br>**Alizarine S D G.** [*M.*]<br>**Alizarine X.** [*By.*]<br>**Alizarine Y C A.** [*Br. A.*] | Flavopurpurin. Oxyanthraflavic acid. | $C_{14}H_8O_5$ |  $HO\,[4]\,C_6H_3\lt\begin{array}{c}[1]\\ CO\\ CO\\ [2]\end{array}\gt C_6H_2\left\{\begin{array}{l}[6]\,OH\\ [5]\,OH\end{array}\right.$ |
| 536 | **Alizarine S X. and G D.** [*B.*]<br>**Alizarine R X.** [*M.*]<br>**Alizarine S X. extra.** [*By.*]<br>**Alizarine S C.** [*Br. A.*] | Isopurpurin. Anthrapurpurin. Oxyisoanthraflavic acid. | $C_{14}H_8O_5$ |  $HO\,[5]\,C_6H_3\lt\begin{array}{c}[1]\\ CO\\ CO\\ [2]\end{array}\gt C_6H_2\left\{\begin{array}{l}[6]\,OH\\ [5]\,OH\end{array}\right.$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| By-product in the manufacture of magenta. | 1862. | E. C. Nicholson.<br>Simpson, Maule, & Nicholson.<br>A. W. Hofmann.<br>Wagner's Jahresber. 1862, 346.<br>Ber. (1869) **2**, 379.<br>O. Fischer & G. Körner.<br>Ber. (1884) **17**, 203.<br>R. Anschütz.<br>Ber. (1884) **17**, 433. | **Appearance of dyestuff**: orange yellow powder.—**In water**: orange yellow solution.—**In alcohol**: soluble.—**On addition of hydrochloric acid to the aqueous solution**: the colour becomes brighter.—**On addition of caustic soda to the aqueous solution**: light yellow precipitate.—**In conc. sulphuric acid**: reddish yellow solution with green fluorescence; reddish yellow solution on dilution with water.—**Employment**: for dyeing leather a reddish yellow. |
| Heating *m*-amidophenylauramine hydrochloride at 200°. | 1894. | C. L. Müller.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $1352^{95}$.<br>Am. Pat. $546177^{95}$.<br>Ger. Pat. $82989^{94}$.<br>Fr. Pat. $244660^{95}$. | **Appearance of dyestuff**: brown powder.—**In water or alcohol**: brownish yellow solution with green fluorescence.—**On addition of hydrochloric acid**: brownish red solution with orange red fluorescence.—**On addition of caustic soda**: light brown precipitate. — **In conc. sulphuric acid**: brown solution with green fluorescence; brownish red with orange red fluorescence on dilution.—**Dyes**: tannined cotton and leather brownish yellow. |

## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Fusion of anthraquinone-monosulphonic acid with caustic alkalies and potassium chlorate. | 1826.<br>1868.<br>1869. | Robiquet & Colin.<br>(from Madder).<br>C. Graebe & C. Liebermann.<br>(from dibromanthraquinone)<br>Ber. (1869) **2**, 14 & 232.<br>Ann. Suppl. **7**, 257.<br>Ann. **160**, 121.<br>Eng. Pat. $3850^{68}$.<br>Am. Pat. 95465.<br>H. Caro, C. Graebe & C. Liebermann.<br>(from anthraquinone-sulphonic acid.)<br>Eng. Pat. $1936^{69}$.<br>Am. Pat. 153536.<br>W. H. Perkin.<br>Eng. Pat. $1948^{69}$.<br>Ber. (1876) **9**, 281.<br>J. Levinstein.<br>J. Soc. Chem. Ind. 1883, 213. | **Appearance of dyestuff**: ochre yellow paste.—**In water**: insoluble.—**In alcohol**: insoluble cold, soluble on boiling with a yellowish red colour.—**On addition of hydrochloric acid to the diluted paste**: no change.—**On addition of caustic soda to the diluted paste**: violet solution.—**In conc. sulphuric acid**: deep yellowish red solution; orange yellow precipitate on dilution with water.—**Dyes**: cotton mordanted with alumina scarlet red, with tin bluish red, with iron violet, and with chromium puce brown. Employed for dyeing "*Turkey Red*" upon cotton mordanted with "sulphated oil" and alumina. Wool is mordanted with cream of tartar and alum, or with cream of tartar and potassium bichromate. |
| Fusion of anthraquinone-α-disulphonic acid with caustic soda and potassium chlorate. | 1876. | E. Schunck & H. Römer.<br>Ber. **9**, 679; **10**, 1821.<br>H. Caro.<br>Ber. **9**, 682. | **Appearance of dyestuff**: brownish yellow paste.—**In water**: insoluble cold, very sparingly hot. — **In aqueous caustic soda**: violet solution. — **In aqueous ammonia**: brown solution. — **In conc. sulphuric acid**: reddish brown solution; orange yellow precipitate on dilution with water.—**Dyes**: cotton mordanted with alumina red. |
| Fusion of anthraquinone-β-disulphonic acid with caustic soda and potassium chlorate. | 1873. | W. H. Perkin.<br>Jahresber. 1873, 450.<br>G. Auerbach.<br>Jahresber. 1874, 488.<br>Ber. (1876) **9**, 682. | **Appearance of dyestuff**: brownish yellow paste.—**In water**: insoluble cold, very sparingly boiling.—**On addition of caustic soda**: bluish violet solution.—**In aqueous ammonia**: reddish violet solution.—**In conc. sulphuric acid**: cherry red solution; orange yellow precipitate on dilution with water.—**Dyes**: cotton mordanted with alumina red. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 537 | **Purpurine.**<br>[*B.*] [*By.*]<br>**Alizarine No. 6.**<br>[*M.*] | Trioxyanthraquinone. | $C_{14}H_8O_5$ |  $C_6H_4<\overset{[1]}{\underset{[2]}{\begin{matrix}CO\\CO\end{matrix}}}>C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[4]}\,OH\\ {[3]}\,OH\end{matrix}\right.$ |
| 538 | **Anthracene Brown.**<br>[*B.*] [*By.*] [*Br. A.*]<br>**Anthragallol.**<br>**Alizarine Brown.**<br>[*M.*] | Trioxyanthraquinone. | $C_{14}H_8O_5$ |  $C_6H_4<\overset{[1]}{\underset{[2]}{\begin{matrix}CO\\CO\end{matrix}}}>C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[4]}\,OH\end{matrix}\right.$ |
| 539 | **Alizarine Bordeaux B & B D.**<br>[*By.*]<br>**Alizarine Cyanine 3 R.** | Tetraoxyanthraquinone. | $C_{14}H_8O_6$ |  |
| 540 | **Alizarine Cyanine R.** [*By.*] | Chiefly a pentaoxyanthraquinone. | $C_{14}H_8O_7$ |  |
| 541 | **Alizarine Cyanine G.*** [*By.*] | Imide of the tri- or tetra-oxy-anthradiquinone. | | |
| 542 | **Anthracene Blue W R.†** [*B.*] | Hexaoxyanthraquinone. | $C_{14}H_8O_8$ |  $\left.\begin{matrix}HO\,{[6]}\\ HO\,{[5]}\\ HO\,{[3]}\end{matrix}\right\}C_6H<\overset{[1]}{\underset{[2]}{\begin{matrix}CO\\CO\end{matrix}}}>C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[4]}\,OH\\ {[3]}\,OH\end{matrix}\right.$ |
| 543 | **Rufigallol.**<br>[*B.*] | Hexaoxyanthraquinone. | $C_{14}H_8O_8$ |  $\left.\begin{matrix}HO\,{[5]}\\ HO\,{[4]}\\ HO\,{[3]}\end{matrix}\right\}C_6H<\overset{[1]}{\underset{[2]}{\begin{matrix}CO\\CO\end{matrix}}}>C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[4]}\,OH\end{matrix}\right.$ |
| 544 | **Alizarine Brown.**<br>[*B.*]<br>**Alpha-nitro-alizarine.** [*M.*] | α-Nitroalizarine. | $C_{14}H_7NO_6$ |  $C_6H_4<\overset{[1]}{\underset{[2]}{\begin{matrix}CO\\CO\end{matrix}}}>C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[3]}\,NO_2\end{matrix}\right.$ |

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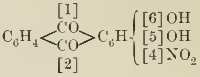
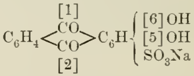
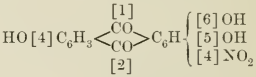
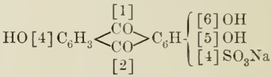
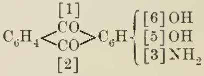
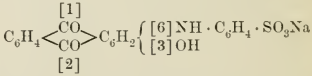
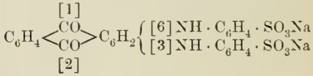
* **Alizarine Cyanine 3 G** [*By.*] **is a sulphonic acid of a polyamido-oxy-**

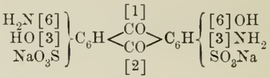
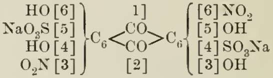
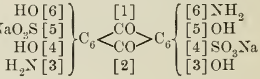
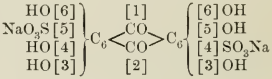
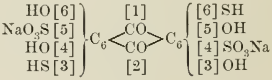
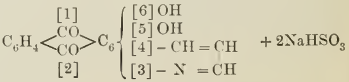
† **Brilliant Alizarine Cyanine G &**

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Oxidation of alizarine with manganese dioxide and sulphuric acid. | 1826.<br>1874. | Robiquet & Colin.<br>(from madder)<br>Bull. de Mulhouse (1826) **1**, 146.<br>F. de Lalande.<br>(by oxidation of alizarine)<br>Ber. (1874) **7**, 1545.<br>H. Caro.<br>(from α-nitroalizarine and sulphuric acid)<br>Ann. (1880) **201**, 353. | **Appearance of dyestuff**: reddish brown paste.—**In water**: insoluble cold, slightly on boiling.—**In aqueous caustic soda or ammonia**: magenta red solution.—**In conc. sulphuric acid**: reddish yellow solution; reddish brown precipitate on dilution with water.—**Dyes**: cotton mordanted with alumina red, with chromium reddish brown. |
| (*a*) Heating gallic acid with benzoic acid and sulphuric acid.<br>(*b*) Heating gallic acid with phthalic anhydride and zinc chloride. | 1877. | C. Seuberlich.<br>Ber. (1877) **10**, 38.<br>G. Auerbach.<br>Chem. Ztg. 1882, 910.<br>R. Bourcart.<br>J. Soc. Chem. Ind. (1884) **3**, 141.<br>Bad. Anil. & Soda Fabrik. | **Appearance of dyestuff**: dark brown paste.—**In water**: insoluble.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the diluted paste**: no change.—**On addition of caustic soda to the diluted paste**: greenish blue solution.—**In conc. sulphuric acid**: brownish red solution; brown precipitate on dilution with water.—**Dyes**: cotton mordanted with chromium a very fast brown. Employed in calico printing. |
| Oxidation of alizarine with fuming sulphuric acid (high percentage of anhydride) and saponification of the sulphuric-ether of the tetraoxyanthraquinone which is first formed. | 1890. | R. E. Schmidt.<br>Jour. Pr. Chem. **43**, 237;<br>J. Soc. Chem. Ind. 1891, 536.<br>Fr. Bayer & Co.<br>Eng. Pats. $8725^{90}$; $12715^{90}$; $17712^{90}$; $18729^{90}$; $4871^{91}$.<br>Ber. **23**, 3739.<br>Ann. **240**, 301. | **Appearance of dyestuff**: brownish red paste.—**In water**: insoluble. **In aqueous caustic soda**: reddish violet solution.—**In conc. sulphuric acid**: bluish violet solution; brownish red precipitate on dilution with water.—**Dyes**: wool mordanted with alumina bordeaux, with chromium dark violet blue. |
| Oxidation of alizarine-bordeaux in sulphuric acid solution with manganese dioxide, and heating the intermediate sulphuric ether with dilute acid. | 1890. | R. E. Schmidt.<br>Jour. Pr. Chem. **43**, 242;<br>J. Soc. Chem. Ind. 1891, 536.<br>Fr. Bayer & Co.<br>Eng. Pats. $12715^{90}$; $17712^{90}$; $18729^{90}$; $4871^{91}$.<br>Am. Pat. 446829.<br>Ger. Pat. $62018^{90}$. | **Appearance of dyestuff**: dark brown paste.—**In water**: insoluble.—**In glacial acetic acid**: yellowish red solution with green fluorescence.—**In conc. sulphuric acid**: blue solution with red fluorescence.—**In aqueous caustic soda**: blue solution.—**Dyes**: wool mordanted with alumina violet, with chromium blue. Fast to light, milling, acids, and alkalies. |
| Treatment of alizarine-cyanine R or its sulphuric ether with air and ammonia. | 1890. | R. E. Schmidt.<br>Jour. Pr. Chem. **43**, 245;<br>J. Soc. Chem. Ind. 1891, 536.<br>Fr. Bayer & Co.<br>Eng. Pats. $17712^{90}$, $4871^{91}$, $1657^{92}$.<br>Ger. Pat. 62505. | **Appearance of dyestuff**: black paste.—**In water**: insoluble.—**In alcohol**: blue violet solution.—**In aqueous caustic soda or ammonia**: greenish blue solution.—**In conc. sulphuric acid**: red solution.—**Dyes**: wool mordanted with alumina blue, with chromium bluish green; the colours are fast to milling, light, acids, and alkalies. |
| Action of sulphuric anhydride of 40% upon 1:5-dinitroanthraquinone, and treatment of the product with ordinary sulphuric acid. | 1891. | R. Bohn.<br>J. Lifschütz.<br>Ber. **17**, 893.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $19589^{91}$ & $13029^{92}$.<br>Am. Pat. $500917^{93}$.<br>Ger. Pat. $67102^{91}$. | **Appearance of dyestuff**: blackish brown powder.—**In water**: insoluble.—**In alcohol**: red solution with yellow fluorescence.—**In caustic soda**: blue solution.—**In conc. sulphuric acid**: violet blue solution with brownish red fluorescence.—**Dyes**: wool mordanted with alumina violet, with chrome blue. |
| Action of sulphuric acid upon gallic acid. | 1835. | Robiquet.<br>Ann. (1836) **19**, 20 | **Appearance of dyestuff**: brownish red powder.—**In water**: insoluble.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: blue solution, which quickly changes in the air.—**In conc. sulphuric acid**: red solution.—**Dyes**: chrome mordanted wool brown. |
| Nitration of alizarine dissolved in sulphuric acid containing arsenic acid, or in fuming sulphuric acid of 20% anhydride. | 1876. | W. H. Perkin.<br>J. Chem. Soc. 1876, **2**, 578.<br>R. Brasch.<br>Ber. **24**, 1610.<br>Schunck & Römer.<br>Ber. **12**, 587.<br>Meister, Lucius, & Brüning.<br>Ger. Pats. 66811 & 74431.<br>Fr. Bayer & Co.<br>Ger. Pat. 74598. | **Appearance of dyestuff**: brownish yellow powder.—**In water**: sparingly soluble with bluish red colour.—**In alcohol**: yellowish red solution.—**On addition of hydrochloric acid**: greenish yellow precipitate.—**On addition of caustic soda**: dark violet red solution.—**In conc. sulphuric acid**: orange red solution; yellow precipitate on dilution. |

anthraquinone, and dyes very level and light-fast shades upon wool.
**3 G** [*By.*] are analogous products.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 545 | **Alizarine Orange.**<br>**Alizarine Orange A.** [*B.*] [*M.*]<br>**Alizarine O R and O G.** [*By.*]<br>**Alizarine Orange N.** [*M.*]<br>**Alizarine Orange A O.** [*Br. A.*] | $\beta$-Nitroalizarin. | $C_{14}H_7NO_6$ |  $C_6H_4\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[4]}\,NO_2\end{matrix}\right.$ |
| 546 | **Alizarine Red S.** [*B.*] [*Br. A.*]<br>**Alizarine W S.** [*M.*]<br>**Alizarine Powder W.** [*By.*]<br>**Alizarine Carmine.** [*Br. A.*] | Sodium salt of alizarine-mono-sulphonic acid. | $C_{14}H_7O_7SNa$ |  $C_6H_4\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ SO_3Na\end{matrix}\right.$ |
| 547 | **Alizarine Orange G.** [*M.*] | Nitroflavopurpurin. | $C_{14}H_7NO_7$ |  $HO\,[4]\,C_6H_3\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[4]}\,NO_2\end{matrix}\right.$ |
| 548 | **Alizarine Red 3 W S.** [*M.*] | Sodium salt of flavopurpurin-sulphonic acid. | $C_{14}H_7O_8SNa$ |  $HO\,[4]\,C_6H_3\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[4]}\,SO_3Na\end{matrix}\right.$ |
| 549 | **Alizarine Garnet R.** [*M.*]<br>**Alizarine Cardinal.** [*By.*] | $\alpha$-Amidoalizarin. | $C_{14}H_9NO_4$ |  $C_6H_4\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H\left\{\begin{matrix}{[6]}\,OH\\ {[5]}\,OH\\ {[3]}\,NH_2\end{matrix}\right.$ |
| 550 | **Alizarine Maroon.** [*B.*] | Amidoalizarins mixed with amidopurpurins. | | |
| 551 | **Quinizarine Blue.** [*By.*] | Sodium salt of anilido-oxy-anthraquinone-sulphonic acid. | | *Probably:*<br> $C_6H_4\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H_2\left\{\begin{matrix}{[6]}\,NH\cdot C_6H_4\cdot SO_3Na\\ {[3]}\,OH\end{matrix}\right.$ |
| 552 | **Alizarine Cyanine Greens.** [*By.*]<br>**Quinizarine Greens.**<br>**Alizarine Viridine.** [*By.*] | Sodium salts of dialphylido-anthraquinone-sulphonic acids. | | *For instance:*<br> $C_6H_4\overset{[1]}{\underset{[2]}{<\begin{smallmatrix}CO\\ CO\end{smallmatrix}>}}C_6H_2\left\{\begin{matrix}{[6]}\,NH\cdot C_6H_4\cdot SO_3Na\\ {[3]}\,NH\cdot C_6H_4\cdot SO_3Na\end{matrix}\right.$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Nitration of alizarine dissolved in sulphuric acid containing boric acid. | 1874. | STROBEL.<br>H. CARO.<br>Eng. Pat. $1229^{76}$.<br>Am. Pat. $186032^{77}$.<br>Ber. (1877) **10**, 1760.<br>A. ROSENSTIEHL.<br>Comp. rend. **82**, 1455 ; **83**, 73.<br>Ann. Chim. et. Phys. [5] **12**, 519.<br>SCHUNCK & RÖMER.<br>Ber. (1879) **12**, 583 & 1008.<br>R. BRASCH.<br>Ber. **24**, 1610.<br>FR. BAYER & CO.<br>Ger. Pat. 74562. | **Appearance of dyestuff :** brownish yellow paste.—**In water :** insoluble.—**In aqueous sodium carbonate :** magenta red solution.—**With zinc dust and caustic soda :** the red solution becomes yellowish brown ; on exposure of the reduced solution to air it turns blue.—**In conc. sulphuric acid :** yellowish brown solution , light yellow precipitate on dilution with water.—**Dyes :** cotton mordanted with alumina orange, with iron reddish violet, and with chromium reddish brown. Also employed for wool. Very fast to light. |
| Action of conc. sulphuric acid upon alizarine. | 1871.<br>1876.<br>1878. | C. GRAEBE &<br>C. LIEBERMANN.<br>Ann. (1871) **160**, 144.<br>E. ULLRICH.<br>H. v. PERGER.<br>Jour. Pr. Chem. [2] **18**, 174.<br>PRZIBRAM & CO.<br>Ger. Pat. 3565.<br>Eng. Pats. $1117^{78}$ & $8725^{90}$.<br>C. GRAEBE.<br>Ber. (1879) **12**, 571.<br>R. E. SCHMIDT.<br>Jour. Pr. Chem. **43**, 232. | **Appearance of dyestuff :** orange yellow powder.—**In water :** easily soluble with yellowish red colour.—**In alcohol :** yellow solution.—**On addition of hydrochloric acid to the aqueous solution :** colour becomes light yellow.—**On addition of caustic soda to the aqueous solution :** colour becomes violet.—**In conc. sulphuric acid :** yellowish red solution ; bright yellow on dilution with water.—**Dyes :** wool mordanted with alumina scarlet red, with chromium bordeaux red. |
| Action of nitric acid upon flavopurpurin. | 1889. | MEISTER, LUCIUS, &<br>BRÜNING. | **Appearance of dyestuff :** brownish orange paste.—**In water :** insoluble.—**In alcohol :** easily soluble with orange yellow colour.—**In aqueous caustic soda :** blood red solution.—**In conc. sulphuric acid :** orange red solution ; light orange yellow precipitate on dilution.—**Dyes :** alumina mordanted wool or cotton a fast orange. |
| Sulphonation of flavopurpurin. | 1886. | MEISTER, LUCIUS, &<br>BRÜNING. | **Appearance of dyestuff :** yellowish brown powder.—**In water :** yellowish brown solution.—**On addition of hydrochloric acid :** light yellow.—**On addition of caustic soda :** violet red solution.—**In conc. sulphuric acid :** orange red solution ; light yellow on dilution. |
| Reduction of α-nitroalizarin. | 1877. | W. H. PERKIN.<br>R. BRASCH.<br>Ber. 24, 1610. | **Appearance of dyestuff :** carmine red or reddish brown paste.—**In water :** insoluble.—**In alcohol :** readily soluble with carmine red colour.—**On addition of hydrochloric acid :** brown.—**On addition of caustic soda to the paste :** carmine red solution.—**In conc. sulphuric acid :** brown solution ; red precipitate on dilution.—**Dyes :** cotton mordanted with alumina a very bluish red. Also used for wool dyeing and calico printing. |
| Reduction of the nitration-product of coml. alizarin in sulphuric acid solution. | 1885. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $1229^{76}$. | **Appearance of dyestuff :** dark violet paste.—**In water :** insoluble.—**On addition of hydrochloric acid to the diluted paste :** no change.—**On addition of caustic soda to the diluted paste :** violet solution.—**In conc. sulphuric acid :** red solution.—**Dyes :** cotton mordanted with alumina garnet red, with chrome mordant maroon. |
| Action of aniline (1 mol.) upon chrysazine, and sulphonation of the product. | 1894. | R. E. SCHMIDT.<br>FR. BAYER & CO.<br>Eng. Pat. $23927^{94}$.<br>Ger. Pat. 86150. | **Dyes :** wool from an acid bath in very bright reddish blue shades, chromed wool a very green blue of great fastness to milling. |
| Action of amines (aniline, paratoluidine, etc.) upon quinizarine, leuco-quinizarine, or dichloranthraquinone, and subsequent sulphonation. | 1894. | R. E. SCHMIDT.<br>FR. BAYER & CO.<br>Eng. Pat. $23927^{94}$.<br>Ger. Pats. 86150, 91149, 91150, 94396, 95625, & 125698.<br>Fr. Pat. 243315.<br>Am. Pats. 599426 & 599427.<br>BUNTROCK.<br>Z. Farb. Chem. 1902, 128. | **Dyes :** chromed wool pure green shades fast to milling, and remarkably fast to light. Also dyes wool from an acid bath, the shade being unchanged by subsequent chroming. The colour is equally fast when unchromed. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 553 | **Alizarine Saphirol B.*** [*By.*] | Sodium salt of diamido-anthrarufin-disulphonic acid. | $C_{14}H_8N_2O_{10}S_2Na_2$ |  $\left.\begin{array}{r}H_2N\,[6]\\HO\,[3]\\NaO_3S\end{array}\right\}C_6H<\begin{array}{c}[1]\\CO\\CO\\[2]\end{array}>C_6H\left\{\begin{array}{l}[6]\,OH\\[3]\,NH_2\\SO_3Na\end{array}\right.$ |
| 554 | **Dinitro-anthra-chrysone-di-sulphonic acid.** [*M.*] | Sodium salt of dinitrotetraoxy-anthraquinone-di-sulphonic acid. | $C_{14}H_4N_2O_{16}S_2Na_2$ |  $\left.\begin{array}{r}HO\,[6]\\NaO_3S\,[5]\\HO\,[4]\\O_2N\,[3]\end{array}\right\}C_6<\begin{array}{c}1]\\CO\\CO\\[2]\end{array}>C_6\left\{\begin{array}{l}[6]\,NO_2\\[5]\,OH\\[4]\,SO_3Na\\[3]\,OH\end{array}\right.$ |
| 555 | **Diamido-anthra-chrysone-di-sulphonic acid.** [*M.*] | Sodium salt of diamidotetraoxy-anthraquinone-di-sulphonic acid. | $C_{14}H_8N_2O_{12}S_2Na_2$ |  $\left.\begin{array}{r}HO\,[6]\\NaO_3S\,[5]\\HO\,[4]\\H_2N\,[3]\end{array}\right\}C_6<\begin{array}{c}[1]\\CO\\CO\\[2]\end{array}>C_6\left\{\begin{array}{l}[6]\,NH_2\\[5]\,OH\\[4]\,SO_3Na\\[3]\,OH\end{array}\right.$ |
| 556 | **Acid Alizarine Blue BB & GR.** [*M.*] | Sodium salt of hexaoxyanthra-quinone-disulphonic acid. | $C_{14}H_6O_{14}S_2Na_2$ |  $\left.\begin{array}{r}HO\,[6]\\NaO_3S\,[5]\\HO\,[4]\\HO\,[3]\end{array}\right\}C_6<\begin{array}{c}[1]\\CO\\CO\\[2]\end{array}>C_6\left\{\begin{array}{l}[6]\,OH\\[5]\,OH\\[4]\,SO_3Na\\[3]\,OH\end{array}\right.$ |
| 557 | **Acid Alizarine Green B & G.** [*M.*] | Sodium salt of disulphydro-tetraoxy-anthraquinone-di-sulphonic acid. | $C_{14}H_6O_{12}S_4Na_2$ |  $\left.\begin{array}{r}HO\,[6]\\NaO_3S\,[5]\\HO\,[4]\\HS\,[3]\end{array}\right\}C_6<\begin{array}{c}[1]\\CO\\CO\\[2]\end{array}>C_6\left\{\begin{array}{l}[6]\,SH\\[5]\,OH\\[4]\,SO_3Na\\[3]\,OH\end{array}\right.$ |
| 558 | **Anthracene Blues WG & WB.** [*B.*] | | | |
| 559 | **Anthracene Blue new WG.** [*B.*] | | | |
| 560 | **Anthracene Blue WGG and WGG extra.** [*B.*] | Sodium salt of diamidodioxy-anthraquinone-sulphonic acid. | | |
| 561 | **Alizarine Green S.** [*M.*] | Bisulphite compound of dioxyanthra-quinone-α-quinoline. | $C_{17}H_9NO_4 + 2NaHSO_3$ |  $C_6H_4<\begin{array}{c}[1]\\CO\\CO\\[2]\end{array}>C_6\left\{\begin{array}{l}[6]\,OH\\[5]\,OH\\[4]-CH=CH\\[3]-N\ \ =CH\end{array}\right.+2NaHSO_3$ |

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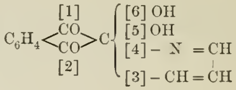
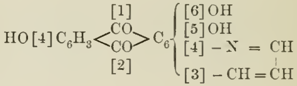
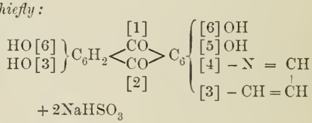
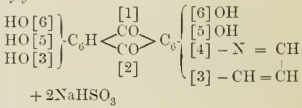
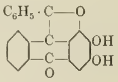
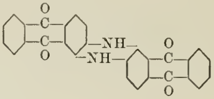
* **Alizarine Saphirol SE [*By.*] is the**

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| By successive sulphonation, nitration, and reduction of anthrarufin. | 1897. | R. Schmidt.<br>Fr. Bayer & Co.<br>Eng. Pat. $12011^{97}$.<br>Ger. Pats. 96364, 100136, 100137, 105501, 108362, 103395.<br>Fr. Pat. 266999.<br>Z. Farb. Chem. 1902, 350. | **Dyes**: wool from an acid bath in clear bright blue shades which are extremely level and remarkably fast to light. |
| Sulphonation and nitration of anthrachrysone. | 1892. | Laubmann.<br>Meister, Lucius, & Brüning.<br>Ger. Pats. 70803 & $70806^{92}$. | **Appearance of dyestuff**: greenish yellow powder.—**In water**: yellow solution.—**In alcohol**: easily soluble.—**On addition of hydrochloric acid**: little change.—**On addition of caustic soda**: reddish orange coloration.—**In conc. sulphuric acid**: brownish yellow solution; yellow solution on dilution.—**Dyes**: wool brown, fast to light and milling. |
| Reduction of dinitro-anthrachrysone-disulphonic acid (No. 554). | 1893. | Laubmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $13395^{93}$.<br>Ger. Pat. $73684^{93}$. | **Appearance of dyestuff**: brownish black powder.—**In water**: sparingly soluble with violet red colour.—**In alcohol**: insoluble.—**On addition of hydrochloric acid**: red coloration.—**On addition of caustic soda**: bluish violet solution and precipitate.—**In conc. sulphuric acid**: brownish red solution; red on dilution.—**Dyes**: wool from an acid bath violet, upon an alumina mordant violet blue, upon a chrome mordant blue. |
| Boiling diamido-anthrachrysone-disulphonic acid (No. 555) with alkali. | 1893. | Laubmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $17543^{93}$.<br>Ger. Pat. $75490^{93}$.<br>Fr. Pat. 232906. | **Appearance of dyestuff**: dark or light red crystalline powder.—**In water**: red solution.—**On addition of hydrochloric acid**: reddish violet precipitate.—**On addition of caustic soda**: violet blue solution.—**In conc. sulphuric acid**: bluish red solution.—**Dyes**: wool from an acid bath red which by subsequent chroming is converted into a pure blue, very fast to light, milling, alkalies, and acids. |
| Reduction of dinitro-anthrachrysone-disulphonic acid (No. 554) with sodium sulphide in alkaline solution. | 1893. | Laubmann.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $13395^{93}$.<br>Ger. Pat. $73684^{93}$.<br>Fr. Pat. 231479. | **Appearance of dyestuff**: reddish black or greenish black crystalline powder.—**In water**: bluish green solution. **On addition of hydrochloric acid**: reddish blue.—**On addition of caustic soda**: violet solution and precipitate.—**In conc. sulphuric acid**: blue or red solution with strong fluorescence; violet red on dilution.—**Dyes**: wool from an acid bath greenish blue, which by subsequent chroming is converted into a pure green, very fast to light, milling, alkalies, and acids. |
| Successive action of fuming sulphuric acid and of ordinary sulphuric acid upon 1 : 5-dinitro-anthraquinone with or without the presence of a reducing agent (*e.g.* sulphur). | 1891. | R. Bohn.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $19588^{91}$; $19599^{91}$; & $16495^{97}$.<br>Am. Pats. $502603^{93}$ & $617686^{97}$.<br>Ger. Pats. 67102; 76262; 87729; 89144; 79768; & 109613.<br>Fr. Pat. 269849. | **Appearance of dyestuff**: bluish black pastes.—**In water**: WG is soluble on boiling with violet blue colour; WB is insoluble.—**In caustic soda**: greenish blue solution.—**In conc. sulphuric acid**: reddish brown solution.—**Dyes**: WG, alumina-mordanted wool pure blue, chromed wool bluish green; WB, alumina-mordanted wool greenish blue. |
| Long heating of Anthracene Blue with caustic soda and ammonia in a closed vessel. | 1899. | O. Bally. | **Appearance of dyestuff**: bluish black paste.—**In water**: nearly insoluble.—**In alcohol**: violet solution.—**In caustic soda**: pure blue solution, precipitated by hydrochloric acid.—**In conc. sulphuric acid**: yellowish red solution.—**Dyes**: chromed wool greenish blue of great fastness to milling. |
| Heating dinitroanthraquinone with fuming sulphuric acid, sulphur, and boric acid. | 1897. | M. H. Isler.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $16495^{97}$.<br>Am. Pat. $617686^{99}$.<br>Ger. Pat. $109613^{97}$.<br>Fr. Pat. $269849^{97}$. | **Appearance of dyestuff**: blue black powder or paste.—**In water**: soluble hot with a blue colour.—**In hydrochloric acid**: soluble hot with a blue colour.—**In caustic soda**: blue solution.—**In conc. sulphuric acid**: brownish yellow solution.—**Dyes**: wool from an acid bath bluish violet, chromed wool bluish green. |
| Heating α-amidoalizarin (No. 549) with glycerine, nitrobenzene, and sulphuric acid, the product being converted into the bisulphite compound. | 1892. | R. Brasch.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $14717^{92}$.<br>Ger. Pat. $67470^{92}$.<br>Fr. Pat. 223766. | **Appearance of dyestuff**: bluish red crystalline paste or powder.—**In water**: easily soluble with reddish violet colour.—**In alcohol**: insoluble.—**In caustic soda**: carmine red solution.—**In conc. sulphuric acid**: cherry red solution with evolution of sulphurous acid; bluish green precipitate on dilution.—**Dyes**: chrome mordanted cotton or wool bluish green. Best fixed upon a nickel magnesia mordant. Chiefly employed in printing. |

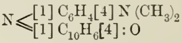
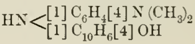
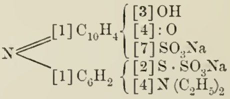
corresponding monosulphonic acid.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 562 | **Alizarine Blue.**<br>[*B.*] [*M.*]<br>**Alizarine Blue R and G W.** [*By.*]<br>**Alizarine Blue ABI & BSS.**<br>[*Br. A.*] | Dioxyanthraquinone-$\beta$-quinoline.<br>(BSS is the sodium salt.) | $C_{17}H_9NO_4$ |  $C_6H_4\left<\begin{matrix}\overset{[1]}{CO}\\ \underset{[2]}{CO}\end{matrix}\right>C\begin{cases}[6]\,OH\\ [5]\,OH\\ [4]-N=CH\\ [3]-CH=CH\end{cases}$ |
| 563 | **Alizarine Blue S.** [*B.*] [*By.*]<br>**Alizarine Blue ABS.** [*Br. A.*]<br>**Anthracene Blue S.** | Sodium bisulphite compound of dioxyanthraquinone-$\beta$-quinoline. | $C_{17}H_{11}NO_{10}S_2Na_2$ | |
| 564 | **Alizarine Black P.** [*M.*] | Flavopurpurinquinoline. | $C_{17}H_9NO_5$ |  $HO\,[4]\,C_6H_3\left<\begin{matrix}\overset{[1]}{CO}\\ \underset{[2]}{CO}\end{matrix}\right>C_6\begin{cases}[6]\,OH\\ [5]\,OH\\ [4]-N=CH\\ [3]-CH=CH\end{cases}$ |
| 565 | **Alizarine Black S.** [*M.*] | Bisulphite compound of Alizarine Black P. | $C_{17}H_9NO_5 + 2NaHSO_3$ | |
| 566 | **Alizarine Green S.** [*B.*] | Mixture of the bisulphite compounds of tri- and tetra-oxyanthraquinonequinoline and their sulphonic acids. | *Chiefly:*<br>$C_{17}H_9NO_6 + 2NaHSO_3$ | *Chiefly:*<br> $\left.\begin{matrix}HO\,[6]\\ HO\,[3]\end{matrix}\right\}C_6H_2\left<\begin{matrix}\overset{[1]}{CO}\\ \underset{[2]}{CO}\end{matrix}\right>C_6\begin{cases}[6]\,OH\\ [5]\,OH\\ [4]-N=CH\\ [3]-CH=CH\end{cases} + 2NaHSO_3$ |
| 567 | **Alizarine Indigo Blue S.** [*B.*] | Mixture of the bisulphite compounds of tetra- and penta-oxyanthraquinonequinoline and their sulphonic acids. | *Chiefly:*<br>$C_{17}H_9NO_7 + 2NaHSO_3$ | *Chiefly:*<br> $\left.\begin{matrix}HO\,[6]\\ HO\,[5]\\ HO\,[3]\end{matrix}\right\}C_6H\left<\begin{matrix}\overset{[1]}{CO}\\ \underset{[2]}{CO}\end{matrix}\right>C_6\begin{cases}[6]\,OH\\ [5]\,OH\\ [4]-N=CH\\ [3]-CH=CH\end{cases} + 2NaHSO_3$ |
| 568 | **Benzoin Yellow.**<br>[*B.*] | | $C_{21}H_{12}O_2$ |  |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Action of glycerine and sulphuric acid upon β-nitro-alizarin.<br>(*b*) Action of glycerine, nitrobenzene, and sulphuric acid upon β-amidoalizarin. | 1877. | PRUD'HOMME.<br>H. BRUNCK.<br>Ber. (1878) **11**, 522.<br>C. GRAEBE.<br>Ber. (1878) **11**, 1646.<br>Ber. (1879) **12**, 1416.<br>ALB. SCHEURER.<br>Bull. de Mulhouse 1884, 327.<br>Ann. **201**, 333.<br>Ber. **18**, 170.<br>CARO.<br>Am. Pat. 186032. | **Appearance of dyestuff**: small dark blue glistening crystals.—**In water**: insoluble.—**In alcohol**: slightly soluble on boiling with a blue colour.—**On addition of hydrochloric acid to the hot alcoholic solution**: colour becomes yellowish red.—**On addition of caustic soda to the hot alcoholic solution**: colour becomes a beautiful green.—**In conc. sulphuric acid**: carmine red solution; yellowish red on dilution with water.—**Dyes**: fabrics mordanted with chromium very fast blue shades. |
| Action of sodium bisulphite upon alizarine blue (No. 562). | 1881. | H. BRUNCK.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $3601^{81}$ & $627^{82}$.<br>Am. Pats. 258530; 258531; 274081.<br>Ger. Pats. $17695^{81}$ & $23008^{82}$.<br>Fr. Pat. $144386^{81}$.<br>H. BRUNCK & C. GRAEBE.<br>Ber. (1882) **15**, 1783.<br>Ann. (1880) **201**, 333.<br>I. LEVINSTEIN.<br>J. Soc. Chem. Ind. 1883, 223. | **Appearance of dyestuff**: chocolate brown powder.—**In water**: easily soluble, with yellowish brown colour.—**In alcohol**: insoluble.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes more reddish yellow.—**On addition of caustic soda to the aqueous solution**: colour becomes bluish violet.—**In conc. sulphuric acid**: dark yellow solution; brown precipitate on dilution.—**Dyes**: chrome mordanted fabrics blue. Used in printing in conjunction with chromium acetate. |
| Heating β-nitro-flavopurpurin with glycerine and sulphuric acid or β-amidoflavopurpurin with glycerine, nitrobenzene, and sulphuric acid. | 1892. | MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $5780^{90}$.<br>Ger. Pat. 54624.<br>Fr. Pat. 205076. | **Appearance of dyestuff**: greenish black paste.—**In water**: insoluble.—**In alcohol**: sparingly soluble.—**In hydrochloric acid**: paste changes to brown.—**In caustic soda**: deep dull green solution.—**In conc. sulphuric acid**: dull reddish brown solution; on dilution light brown solution and then brown precipitate.—**Dyes**: chromed wool violet-gray to black of good fastness. Also used in calico printing. |
| Digesting Alizarine Black P paste (No. 564) with sodium bisulphite. | | | **Appearance of dyestuff**: dark brown solution.—**In water**: soluble.—**On addition of hydrochloric acid**: black precipitate.—**On addition of caustic soda**: blackish violet solution.—**In conc. sulphuric acid**: brown solution with evolution of sulphurous acid; brown precipitate on dilution.—**Dyes**: chromed wool gray to black. Chiefly used in calico printing. |
| Action of sulphuric acid upon the product of the oxidation of Alizarine Blue with sulphuric anhydride, and conversion into the bisulphite compound. | 1888. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $14353^{88}$.<br>Am. Pats. 399479; 399480; 399481; 401633; 401635.<br>Ger. Pat. $46654^{88}$.<br>Fr. Pat. $192582^{88}$.<br>J. Soc. Chem. Ind. 1889, 770; 1890, 53; 1891, 1003.<br>J. Soc. Dyers & Colorists 1889, 106; 1893, 68.<br>Ber. **23**, 3739.<br>Chem. Ztg. 1891, 150.<br>Jour. pr. Chem. **44**, 103.<br>Ann. **276**, 21. | **Appearance of dyestuff**: brownish black solution.—**In water**: soluble cold, on boiling alizarine green separates out.—**On addition of caustic soda**: violet solution.—**In conc. sulphuric acid**: dark blue solution; dark blue precipitate on dilution.—**Dyes**: chrome mordanted wool fast bluish green. Used for cotton printing. |
| Action of sulphuric acid upon alizarine green at 200° and subsequent treatment of the product with sodium hydric sulphite. | 1888. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $15121^{88}$.<br>Am. Pat. $399482^{89}$.<br>Ger. Pat. $47252^{88}$.<br>Fr. Pat. 192582 (supp.).<br>J. Soc. Dyers & Colorists 1889, 106; 1893, 68.<br>Ber. **23**, 3739; **24**, 2297.<br>Jour. pr. Chem. **44**, 103.<br>Ann. **276**, 21. | **Appearance of dyestuff**: brownish black paste.—**In cold water**: red solution; on boiling the solution by itself or with hydrochloric acid, alizarine-indigo blue separates out.—**On addition of caustic soda**: blue solution.—**In conc. sulphuric acid**: blue solution; on dilution reddish violet precipitate and solution.—**Dyes**: chrome mordanted wool indigo blue. |
| Condensation of benzoin with gallic acid in presence of cold sulphuric acid. | 1897. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Am. Pat. 623069.<br>Ger. Pat. 95739.<br>Fr. Pat. 268637.<br>Chem. Zeit. 1898, 542. | **Appearance of dyestuff**: yellow paste.—**In water**: insoluble.—**In caustic soda**: cherry red solution.—**In conc. sulphuric acid**: yellow solution with strong green fluorescence.—**Dyes**: chromed wool yellow very fast to milling but not to light. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 569 | **Indanthrene X.*** [*B.*] | Anthraquinoneazine. | $C_{28}H_{14}N_2O_4$ |  (?) |
| 570 | **Flavanthrene.** [*B.*] | | $C_{28}H_{14}N_2O_2$ | |

## XIV. INDOPHENOLS, INDAMINES,

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 571 | **Indophenol.** [*D.H.*] | Oxidation product of dimethyl-*p*-amidophenyl-*p*-oxy-*a*-naphthylamine. | $C_{18}H_{16}N_2O$ |  $N\lessgtr\begin{array}{l}[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_6[4]:O\end{array}$ |
| 572 | **Indophenol White.** [*D.H.*] [*C.*]<br>**Leucindophenol.** | Tin compound of dimethyl-*p*-amidophenyl-*p*-oxy-*a*-naphthylamine. | $C_{18}H_{18}N_2O$ |  $HN<\begin{array}{l}[1]\,C_6H_4[4]\,N\,(CH_3)_2\\ [1]\,C_{10}H_6[4]\,OH\end{array}$ |
| 573 | **Indochromogen S.** [*K.S.*] | Sodium salt of sulpho-oxy-indophenol-thiosulphonic acid. | $C_{20}H_{17}N_2O_8S_3Na_2$ |  $N\begin{array}{l}=[1]\,C_{10}H_4\left\{\begin{array}{l}[3]\,OH\\ [4]:O\\ [7]\,SO_3Na\end{array}\right.\\ -[1]\,C_6H_2\left\{\begin{array}{l}[2]\,S\cdot SO_3Na\\ [4]\,N\,(C_2H_5)_2\end{array}\right.\end{array}$ |
| 574 | **Ursol D.**<br>**Ursol P.**<br>**Ursol DD.**<br>[*A.*] | Hydrochlorides of *p*-phenylene diamine, *p*-amidophenol, and diamidodiphenylamine, respectively. | | |
| 575 | **Durophenine Brown.** [*Cl. Co.*] | | | |

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* **Indanthrene S.** [*B.*] is the leuco compound,

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| By fusing $\beta$-amidoanthraquinone with caustic potash at 250°. | 1901. | R. Bohn.<br>Bad. Anilin & Soda Fabrik.<br>Eng. Pats. 3239$^{01}$ & 12185$^{01}$.<br>Am. Pat. 682523$^{01}$.<br>Ger. Pats. 129845$^{01}$ & 129848$^{01}$.<br>Fr. Pats. 309503 & additions; 313772 & addition.<br>J. Soc. Dyers, 1902, 187.<br>Z. Farb. Chem. 1902, 130, 137, 223, & 342. | **Appearance of dyestuff**: the pure dyestuff forms beautiful coppery blue crystals.—**In water**: insoluble.—**In hydrochloric acid**: insoluble.—**In caustic soda**: insoluble, but dissolving on addition of a reducing agent.—**In conc. sulphuric acid**: yellowish brown solution.—**Dyes**: cotton and other vegetable fibres from a reduced vat (like indigo) in bright blue shades which are very level and of remarkable fastness to light, washing, alkalies, and acids, but not to chlorine. Its fastness to light considerably exceeds that of indigo. Employed in printing as the leuco compound. |
| Oxidation of $\beta$-amidoanthraquinone. | 1901. | R. Bohn.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. 24354$^{01}$.<br>Ger. Pat. appls. 29973, 30019, 30505, & 30506. | **Appearance of dyestuff**: yellowish brown needles or paste.—**In water**: insoluble.—**In caustic soda or hydrochloric acid**: insoluble.—**In conc. sulphuric acid**: olive coloured solution with red fluorescence.—**Reducing agents**: convert it in alkaline solution into a soluble blue leuco compound which crystallises in coppery needles. The latter dyes cotton and other vegetable fibres blue which on air oxidation becomes yellow. The yellow is extremely fast to light and washing, and by admixture with Indanthrene produces very fast greens. |

## AND ALLIED COMPOUNDS.

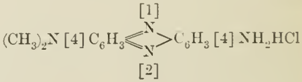
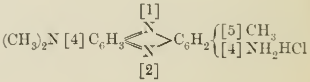
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Action of nitroso-dimethylaniline upon $\alpha$-naphthol.<br>(*b*) Oxidation of amido-dimethylaniline and $\alpha$-naphthol. | 1881. | H. Köchlin & O. N. Witt.<br>Ger. Pat. 15915$^{81}$.<br>Bull. de Mulhouse (1882) **52**, 532.<br>J. Soc. Chem. Ind. (1882) **1**, 255.<br>Färberztg. **1**, 2.<br>Ber. **16**, 2851; **18**, 2913.<br>L. Cassella & Co.<br>Eng. Pats. 1373$^{81}$ & 5249$^{81}$.<br>Am. Pat. 261518.<br>Ger. Pats. 18903$^{81}$; 19231$^{81}$; 20850$^{81}$. | **Appearance of dyestuff**: dark brown powder.—**In water**: quite insoluble.—**In alcohol**: blue solution.—**On addition of hydrochloric acid to the alcoholic solution**: colour becomes reddish brown.—**On addition of caustic soda to the alcoholic solution**: no change.—**In conc. sulphuric acid**: yellowish brown solution; brown precipitate on dilution with water.—**On addition of stannous chloride to the alcoholic solution**: reduced to indophenol white, but the colour quickly returns on making slightly alkaline.—**Employment**: see indophenol white. |
| Reduction of indophenol with stannous acetate. | 1881. | H. Köchlin & O. N. Witt.<br>Bull. de Mulhouse (1882) **52**, 532.<br>J. Chem. Ind. (1882) **1**, 255. | **Appearance of dyestuff**: yellowish white paste.—**In water**: soluble on boiling.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of ammonia or caustic soda to the paste**: blue flocculent precipitate of indophenol on shaking with air.—**Employment**: for tissue-printing, or in vat-dyeing in conjunction with indigo. |
| Action of $\beta$-naphthoquinone-disulphonic acid upon *p*-amido-diethylaniline-thiosulphonic acid in cold slightly alkaline solution. | 1893. | A. Böniger.<br>Sandoz & Co., Basle.<br>Eng. Pat. 3886$^{94}$.<br>Fr. Pat. 234838.<br>Ger. Pat. 109273$^{93}$. | **Appearance of dyestuff**: blue powder.—**In water**: reddish violet solution.—**On addition of hydrochloric acid**: yellowish brown solution.—**On addition of caustic soda**: dull violet solution; on boiling the solution becomes blue with formation of the thiazine "Indochromine T."—**In conc. sulphuric acid**: greenish yellow solution; yellowish brown on dilution.—**Employment**: printed on oiled calico in conjunction with a chrome mordant, and steamed, it gives a bright greenish blue fast to light and readily discharged by ferricyanides. |
| The colours are produced by oxidation of the diamine or amidophenol upon the fibre by means of hydrogen peroxide, bichromate, or quinone. | 1888. | E. Erdmann.<br>Eng. Pat. 2525$^{89}$.<br>Ger. Pats. 47349, 51073, & 80814.<br>Fr. Pats. 195492 & 205259.<br>Zeits. f. angew. Chem. 1895, 424.<br>Färberztg. 1897, 197, 266. | **Employment**: for dyeing fur, feathers, and hair, brown to black shades. |
| By boiling nitrosophenol with dilute sulphuric acid. | 1898. | A. G. Green & A. Meyenberg.<br>The Clayton Aniline Co.<br>Ger. Pat. 106036. | **Appearance of dyestuff**: black powder.—**In water**: insoluble; dissolves in aqueous alkalies or sodium sulphide.—**On addition of hydrochloric acid to alkaline solution**: blackish brown precipitate.—**In conc. sulphuric acid**: violet black solution; on dilution dark brown precipitate.—**Dyes**: cotton dark violet brown from a sodium sulphide solution. |

and is principally used for printing.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 576 | **New Gray.** [*By.*]<br>**Nigrisine.** [*P.*]<br>**Methylene Gray.** [*M.*]<br>**New Methylene Gray.** [*M.*]<br>**Malta Gray.** [*P.*]<br>**Direct Gray.** | | | |
| 577 | **Aniline Black** (on fibre).<br>**Aniline Black in Paste.** | Salts of nigraniline. | *Nigraniline:* $(C_6H_5N)_x$ | |
| 578 | **Clayton Fast Blacks.** [*Cl. Co.*]<br>**Clayton Fast Grays.** [*Cl. Co.*] | Probably sulphides or thiosulphonic acids of Aniline Black and analogues. | | |

## XV. AZINES & AZONIUM

### (Eurodines, Safranines,

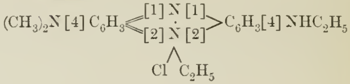
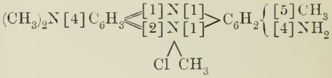
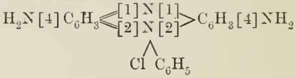
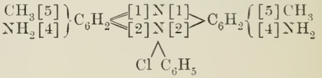
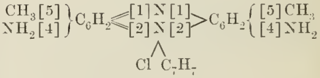
| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 579 | **Neutral Violet.** [*C.*] [*D.H.*] | Hydrochloride of dimethyldiamidophenazine. | $C_{14}H_{15}N_4Cl$ |  $(CH_3)_2N\ [4]\ C_6H_3 \ll \overset{\overset{[1]}{N}}{\underset{\underset{[2]}{N}}{}} > C_6H_3\ [4]\ NH_2HCl$ |
| 580 | **Neutral Red.** [*C.*] [*D.H.*]<br>**Toluylene Red.** | Hydrochloride of dimethyldiamidotoluphenazine. | $C_{15}H_{17}N_4Cl$ |  $(CH_3)_2N\ [4]\ C_6H_3 \ll \overset{\overset{[1]}{N}}{\underset{\underset{[2]}{N}}{}} > C_6H_2 \begin{cases}[5]\ CH_3 \\ [4]\ NH_2HCl\end{cases}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| (*a*) Boiling nitrosodimethylaniline hydrochloride with water or alcohol.<br>(*b*) Oxidation of dimethyl-*p*-phenylene diamine. | 1885.<br>1888. | E. ULLRICH.<br>W. LÖW & C. DUISBERG.<br>FR. BAYER & CO.<br>ED. EHRMANN.<br>SOC. ANON. DES MAT. COLORANTES ET DES PROD. CHIMIQUES.<br>Eng. Pat. $5032^{89}$.<br>Am. Pat. 420311.<br>Ger. Pat. $49446^{89}$.<br>Lehne's Färberztg. **1**, 130.<br>Deutsche Färberztg. **26**, 331.<br>DAWSON.<br>Eng. Pat. $16448^{89}$. | **Appearance of dyestuff**: grayish black powder.—**In water**: reddish gray solution.—**In alcohol**: reddish gray solution.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes grayish blue.—**On addition of caustic soda to the aqueous solution**: grayish black precipitate of base, soluble in ether with cherry red colour; the ethereal solution gives a beautiful bluish green colour when shaken with water.—**In conc. sulphuric acid**: greenish solution; reddish gray on dilution with water.—**Dyes**: unmordanted cotton and cotton mordanted with tannin silver gray or blackish gray. |
| Oxidation of aniline with chlorates, in presence of salts of copper or vanadium; or with bichromates or ferricyanides. | 1834.<br>1840. | RUNGE.<br>FRITZSCHE.<br>Jour. Pk. Chem. **20**, 454; **28**, 202.<br>J. LIGHTFOOT.<br>Eng. Pat. of 28th Jan. 1863.<br>NÖLTING.<br>Histoire scientifique et industrielle du noir d'aniline.<br>Lehne's Färberztg. **1**, 242, 258, 274, 292, 332, 333, 354.<br>NIETZKI.<br>Ber. **11**, 1093.<br>LIECHTI & SUIDA.<br>Ding. Pol. J. **254**, 265.<br>J. Soc. Chem. Ind. (1885) **4**, 206.<br>See also Eng. Pats. $17082^{92}$ & $7638^{92}$; Am. Pats. 529498 & 529499. | **Appearance of dyestuff**: greenish black powder.—**In water or alcohol**: insoluble.—**The base nigraniline** is a violet black powder, soluble in phenol with a bluish green colour, in aniline with a violet colour which soon becomes brown.—**In conc. sulphuric acid**: violet solution; dark green precipitate of the sulphate on dilution with water.—**Employment**: in dyeing and printing black by direct formation on the fibre by oxidation of aniline. |
| (1) Conjoint oxidation of a di- or tetra-thiosulphonic acid of *p*-phenylene diamine (or of *p*-amidophenol) with an amine, phenol, amidophenol, or diamine.<br>(2) Conjoint oxidation of a *p*-diamine (or *p*-amidophenol) and 1 or more mols. of a primary amine (*e.g.* aniline) in presence of sodium thiosulphate. | 1898. | A. G. GREEN & A. MEYENBERG.<br>THE CLAYTON ANILINE CO.<br>Eng. Pats. $21832^{98}$, $22460^{98}$, $22847^{98}$, $5039^{99}$, $18658^{99}$, & $4792^{00}$.<br>Am. Pats. 641587, 641588, 641589, 641953, & 641954.<br>Fr. Pat. $288465^{99}$.<br>Ger. Pat. appls. $C7842^{98}$, $C7869^{98}$, $C7904^{98}$, $C7905^{98}$, $C8280^{99}$, & $C8528^{99}$.<br>Belg. Pat. $143793^{99}$.<br>Lefêvre's Revue Générale, 1899, 358; 1900, 2 & 6.<br>J. Soc. Dyers, 1901, 89. | **Appearance of dyestuff**: black powders.—**In water**: insoluble.—**In aqueous sodium sulphide or sodium sulphite**: dissolves.—**In conc. sulphuric acid**: blue black solution; black precipitate on dilution.—**Employment**: dyes cotton from a bath containing sodium sulphide or caustic soda and glucose. After fixation with bichromate and copper sulphate the colour is very fast to light, soap, alkalies, and acids. Applied with caustic soda upon glucose-prepared calico it gives very fast black prints (see Eng. Pat. $17193^{00}$; Z. Farb. Chem. 1902, 119). |

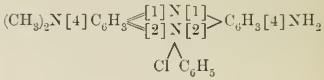
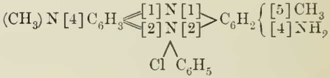
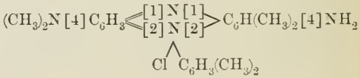
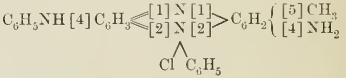
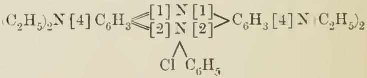
## COLOURING MATTERS.

### Indulines, Rosindulines.)

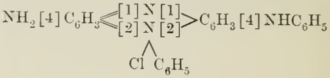
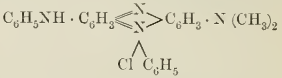
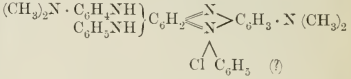
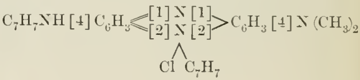
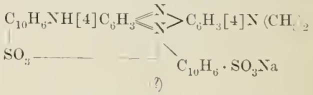
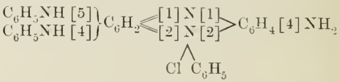
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of hydrochloride of nitrosodimethylaniline upon *m*-phenylene diamine. | 1879. | O. N. WITT.<br>Eng. Pat. $4846^{80}$.<br>Am. Pat. 248246.<br>Ger. Pat. $15272^{80}$. | **Appearance of dyestuff**: greenish black powder, which is very irritating to the mucous membrane.—**In water**: easily soluble with violet red colour.—**On addition of hydrochloric acid to the aqueous solution**: scarcely any change with a small quantity, blue coloration with a large excess.—**On addition of caustic soda to the aqueous solution**: brown precipitate.—**In conc. sulphuric acid**: green solution, becomes first blue and then violet on dilution with water.—**Dyes**: cotton mordanted with tannin and tartar emetic reddish violet. |
| Action of hydrochloride of nitrosodimethylaniline upon *m*-tolylene diamine. | 1879. | O. N. WITT.<br>Eng. Pat. $4846^{80}$.<br>Am. Pat. 249136.<br>Ger. Pat. $15272^{80}$.<br>Ber. (1879) **12**, 933.<br>BERNTHSEN & SCHWEITZER.<br>Ber. (1886) **19**, 2604.<br>Ann. (1886) **236**, 332. | **Appearance of dyestuff**: dark green powder.—**In water**: carmine red solution.—**In alcohol**: magenta red solution with slight brownish red fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes bluer, pure blue with a large excess.—**On addition of caustic soda to the aqueous solution**: yellowish brown precipitate.—**In conc. sulphuric acid**: green solution; blue and then magenta red on dilution with water.—**Dyes**: cotton mordanted with tannin and tartar emetic bluish red. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 581 | **Fast Neutral Violet B.** [*C.*] | Dimethyldiethyldiamido-phenazonium chloride. | $C_{18}H_{23}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3 \lessgtr \begin{array}{c}[1]\,N\,[1]\\ [2]\,\dot{N}\,[2]\\ \wedge\\ Cl\ \ C_2H_5\end{array} > C_6H_3[4]\,NHC_2H_5$ |
| 582 | **Azine Scarlet G.** [*M.*] | Dimethyldiamido-methyl-toluphenazonium chloride. | $C_{16}H_{19}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3 \lessgtr \begin{array}{c}[1]\,N\,[1]\\ [2]\,N\,[1]\\ \wedge\\ Cl\ \ CH_3\end{array} > C_6H_2\left\{\begin{array}{l}[5]\,CH_3\\ [4]\,NH_2\end{array}\right.$ |
| 583 | **Phenosafranine. Safranine B extra.** [*B.*] | Diamidophenyl-phenazonium chloride. | $C_{18}H_{15}N_4Cl$ |  $H_2N\,[4]\,C_6H_3 \lessgtr \begin{array}{c}[1]\,N\,[1]\\ [2]\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array} > C_6H_3\,[4]\,NH_2$ |
| 584 | **Safranine.**<br>**Safranine T.** [*B.*]<br>**Safranine extra G.** [*A.*]<br>**Safranine S.** [*C.*]<br>**Safranine FF extra.** [*By.*]<br>**Safranine conc.** [*M.*]<br>**Safranine AG, AGT, & OOF.** [*K.*]<br>**Safranine GOO.** [*I.*] | Mixture of diamido-phenyl- and tolyl-tolazonium chlorides. | $C_{21}H_{21}N_4Cl$<br>and<br>$C_{20}H_{19}N_4Cl$ |  $\left.\begin{array}{r}CH_3\,[5]\\ NH_2\,[4]\end{array}\right\}C_6H_2 \lessgtr \begin{array}{c}[1]\,N\,[1]\\ [2]\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array} > C_6H_2\left\{\begin{array}{l}[5]\,CH_3\\ [4]\,NH_2\end{array}\right.$<br>*and*<br> $\left.\begin{array}{r}CH_3\,[5]\\ NH_2\,[4]\end{array}\right\}C_6H_2 \lessgtr \begin{array}{c}[1]\,N\,[1]\\ [2]\,N\,[2]\\ \wedge\\ Cl\ \ C_7H_7\end{array} > C_6H_2\left\{\begin{array}{l}[5]\,CH_3\\ [4]\,NH_2\end{array}\right.$ |

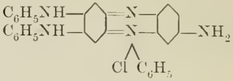
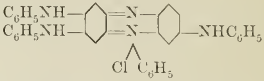
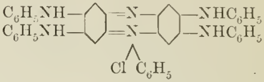
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of nitrosodimethylaniline hydrochloride upon diethyl-*m*-phenylene diamine. | 1880. | L. Cassella & Co.<br>Eng. Pat. $4846^{80}$. | **Appearance of dyestuff**: bronzy powder.—**In water or alcohol**: reddish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: no change; a large excess changes the colour to bluish violet and finally to reddish blue.—**On addition of caustic soda to the aqueous solution**: no change of colour, partial precipitation by an excess.—**In conc. sulphuric acid**: purple gray solution; becoming pure blue, bluish violet, and finally reddish violet, on dilution with water.—**After reduction with zinc dust**: the original colour quickly returns on exposure to air—**Dyes**: tannin-mordanted cotton a fast violet. |
| Action of nitrosodimethylaniline upon *m*-amido-dimethyl-*p*-toluidine. | 1891. | Meister, Lucius, & Brüning.<br>Ger. Pat. $69188^{91}$. | **Appearance of dyestuff**: brown powder.—**In water**: red solution.—**In alcohol**: fluorescent solution.—**On addition of hydrochloric acid**: red solution, with excess blue.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: bluish green, becoming violet and red on dilution.—**Dyes**: like safranine but rather yellower and brighter. |
| 1. Oxidation of 1 mol. *p*-phenylene diamine and 2 mols. aniline.<br>2. Oxidation of 1 mol. di-*p*-amido-diphenylamine and 1 mol. aniline. | 1878. | O. N. Witt.<br>Ber. (1879) 12, 939; (1886) 19, 3121.<br>Williams, Thomas, and Dower.<br>Catalogue of the Paris Exhibition of 1878.<br>R. Nietzki.<br>Ber. (1883) 16, 466.<br>Chem. Ind. 6, 167.<br>R. Bindschedler.<br>Ber. (1880) 13, 207; (1883) 16, 865.<br>A. Bernthsen.<br>Ber. (1886), 19, 2690.<br>R. Nietzki & R. Otto.<br>Ber. (1888) 21, 1590.<br>Fischer and Hepp.<br>Ber. 26, 1655.<br>*Other references:*<br>see safranine. | **Appearance of dyestuff**: green glistening crystals.—**In water**: red solution.—**On addition of hydrochloric acid**: colour becomes a bluer red, violet with large amount, with very large quantity blue.—**On addition of caustic soda**: reddish brown precipitate soluble in much water.—**In conc. sulphuric acid**: green solution; becomes blue, violet, and finally red on dilution with water.—**Dyes**: cotton mordanted with tannin and tartar emetic red. |
| Oxidation of equi-molecular proportions of *p*-tolylene diamine, aniline, and *o*-toluidine, or of *p*-tolylene diamine (1 mol.) and *o*-toluidine (2 mols.) | 1859. | Greville Williams.<br>Eng. Pat. $1000^{59}$.<br>Price.<br>Eng. Pat. $1238^{59}$.<br>A. W. Hofmann & A. Geyger.<br>Ber. (1872) 5, 526.<br>R. Bindschedler.<br>Ber. (1880) 13, 207.<br>R. Nietzki.<br>Ber. (1877) 10, 668; (1883) 16, 465; (1884) 17, 226; (1886) 19, 3017 & 3165; (1888) 21, 1590, 1736; (1895) 28, 1354; (1896) 29, 1442.<br>R. Bindschedler.<br>Ber. (1883) 16, 864, 872.<br>O. N. Witt.<br>Ber. (1879) 12, 939; (1886) 19, 3121; (1888) 21, 719.<br>A. Bernthsen and H. Schweitzer.<br>Ann. (1886) 236, 332; Ber. (1886) 19, 2604 & 2690; Ber. (1887) 20, 179.<br>M. Andresen.<br>Ber. (1886) 19, 2212.<br>O. Mühlhäuser.<br>Mon. Scien., Jan. 1887.<br>Kehrmann.<br>Ber. 24, 584, 2167; 27, 3349; 28, 1709; 29, 2316; Ann. 290, 247.<br>Fischer & Hepp.<br>Ber. 26, 1195, 1655; 28, 2283; 29, 361, & 1870.<br>Ris.<br>Ber. 27, 3318.<br>*Other references:*<br>J. Soc. Chem. Ind. 1883, 270, 271; 1887, 285, 435; 1888, 31, 317, 497. | **Appearance of dyestuff**: reddish brown powder.—**In water**: red solution.—**In alcohol**: red solution with yellowish red fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes bluish violet.—**On addition of caustic soda to the aqueous solution**: brownish red precipitate.—**In conc. sulphuric acid**: green solution; becoming blue and finally red on dilution with water.—**Dyes**: cotton mordanted with tannin and tartar emetic red; employed in calico printing for varying the shade of alizarine red. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 585 | **Methylene Violet 2 RA & 3 RA.** [*M.*]<br>**Fuchsia.** [*I.*]<br>**Safranine MN.** [*B.*]<br>**Clemantine.** [*G.*]<br>**Giroflé.** [*D.H.*] | Dimethyldiamido-phenyl-phenazonium chloride. | $C_{20}H_{19}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3{<}\begin{array}{c}[1]\,N\,[1]\\ {[2]}\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array}{>}C_6H_3\,[4]\,NH_2$ |
| 586 | **Nigramine.** [*N.I.*] |  |  |  |
| 587 | **Wool Gray B, G, & R.** [*M.*] |  |  |  |
| 588 | **Indamine 3 R.** [*N.I.*]<br>**Indamine 6 R.** [*N.I.*]<br>**Rubramine.** [*N.I.*] |  |  |  |
| 589 | **Rhoduline Reds G & B.** [*By.*]<br>**Rhoduline Violets.** [*By.*]<br>**Brilliant Rhoduline Red.** [*By.*] | Alkylated safranines. |  | *For example:*<br> $(CH_3)\,N\,[4]\,C_6H_3{<}\begin{array}{c}[1]\,N\,[1]\\ {[2]}\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array}{>}C_6H_2\left\{\begin{array}{l}[5]\,CH_3\\ {[4]}\,NH_2\end{array}\right.$ |
| 590 | **Tannin Heliotrope.** [*C.*]<br>**Heliotrope B & 2 B.** [*K.*] | Dimethyldiamido-xylyl-xylophen-azonium chloride. | $C_{24}H_{27}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3{<}\begin{array}{c}[1]\,N\,[1]\\ {[2]}\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_3(CH_3)_2\end{array}{>}C_6H(CH_3)_2\,[4]\,NH_2$ |
| 591 | **Rosolane B, R, & OT.** [*M.*] | Phenyldiamido-phenyl-toluphen-azonium chloride. |  |  $C_6H_5NH\,[4]\,C_6H_3{<}\begin{array}{c}[1]\,N\,[1]\\ {[2]}\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array}{>}C_6H_2\left\{\begin{array}{l}[5]\,CH_3\\ {[4]}\,NH_2\end{array}\right.$ (?) |
| 592 | **Amethyst Violet.** [*K.*]<br>**Iris Violet.** [*B.*] | Tetraethyldiamido-phenyl-phenazonium chloride. | $C_{26}H_{31}N_4Cl$ |  $(C_2H_5)_2N\,[4]\,C_6H_3{<}\begin{array}{c}[1]\,N\,[1]\\ {[2]}\,N\,[2]\\ \wedge\\ Cl\ \ C_6H_5\end{array}{>}C_6H_3\,[4]\,N\,(C_2H_5)_2$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Oxidation of a mixture of dimethyl-*p*-phenylene diamine and aniline (or toluidine). | 1887. | Ullrich.<br>Bindschedler.<br>Ber. **13**, 208 ; **16**, 869.<br>Körner & Schraube.<br>Chem. Ztg. 1893, 305. | **Appearance of dyestuff:** brown powder.—**In water:** easily soluble with violet red colour.—**With hydrochloric acid and with caustic soda:** behaviour like safranine.—**In conc. sulphuric acid:** green; on dilution becomes blue and then violet red.—**Employment:** in printing, giving a fairly fast reddish violet. |
| Action of nitrosodimethylaniline hydrochloride upon aniline hydrochloride. | 1889. | Istel.<br>Ger. Pats. 55532 & 58345. | **Appearance of dyestuff:** black powder.—**In water:** bluish violet solution.—**On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** violet precipitate.—**In conc. sulphuric acid:** gray green solution; bluish violet on dilution.—**Dyes:** tannined cotton bluish gray. |
| Action of aniline (or *p*-toluidine) upon the condensation-product from nitrosodimethylaniline and $\beta$-naphthol-sulphonic acid S. | 1890. | Meister, Lucius, & Brüning.<br>Eng. Pat. $4577^{90}$.<br>Ger. Pat. 56992.<br>Fr. Pat. 204545. | **Appearance of dyestuff:** black powder.—**In water:** easily soluble.—**On addition of hydrochloric acid:** precipitate.—**On addition of caustic soda:** brown solution.—**In conc. sulphuric acid:** the R dissolves blue, the B and G yellowish brown.—**Dyes:** wool level shades of gray; suitable for mixtures. |
| Action of nitrosodimethylaniline hydrochloride upon *o*-toluidine or upon a mixture of *o*-toluidine and *p*-toluidine. | 1889. | Istel.<br>Eng. Pat. $17204^{90}$.<br>Ger. Pats. 55532 & 58345.<br>Fr. Pat. 214373. | **Appearance of dyestuff:** greenish or gray black powders.—**In water:** magenta red to reddish violet solution.—**In alcohol:** magenta red to violet red solution.—**On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** violet or red soluble precipitate.—**In conc. sulphuric acid:** green solution, becoming first blue and then red on dilution.—**Dyes:** tannined cotton reddish violet to bluish violet. |
| Action of nitroso-alkylanilines or toluidines upon monoalphyl-*m*-tolylene diamines. | 1890. | Reyher & Heymann. | **Appearance of dyestuff:** the G & B are brown powders, the Brilliant Rhoduline violet brown, and the Rhoduline Violet a glistening dark green.—**In water:** red solutions.—**In alcohol:** red to brown fluorescent solutions.—**On addition of hydrochloric acid:** dark precipitates and violet to blue solutions; with Rhoduline Violet there is no precipitation.—**On addition of caustic soda:** complete precipitation.—**In conc. sulphuric acid:** green solution, on dilution becoming blue, violet, and red.—**Dyes:** like safranine, but brighter shades. |
| Action of nitrosodimethylaniline upon crude xylidine hydrochloride. | | | **Appearance of dyestuff:** brown paste or grayish green powder.—**In water or alcohol:** magenta red solution.—**On addition of hydrochloric acid:** red solution, with excess blue.—**On addition of caustic soda:** soluble red precipitate.—**In conc. sulphuric acid:** green solution, becoming blue and then red on dilution.—**Dyes:** tannined cotton reddish violet; employed in calico printing. |
| Conjoint oxidation of *p*-amidodiphenylamine, aniline, and *o*-toluidine. | 1888. | Cobenzl.<br>Ger. Pat. $49853^{88}$. | **Appearance of dyestuff:** olive green powder.—**In water:** sparingly soluble with reddish violet colour.—**On addition of hydrochloric acid:** no change; with large excess blue and green.—**On addition of caustic soda:** precipitation of the base.—**In conc. sulphuric acid:** green, becoming blue and red on dilution.—**Dyes:** silk violet pink. |
| Oxidation of equal mols. of diethyl-*p*-phenylene diamine, diethylaniline, and aliline or *p*-toluidine. | 1883. | R. Nietzki.<br>Ber. (1883) **16**, 464.<br>Chem. Ind. (1883) **6**, 167. | **Appearance of dyestuff:** blackish gray powder.—**In water:** reddish violet solution.—**In alcohol:** magenta red colour with bluish red fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** colour becomes blue.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** bright green solution; on dilution with water the colour becomes blue and then bluish violet.—**Dyes:** silk violet with a red fluorescence. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 593 | **Mauve.**<br>**Chrome Violet.**<br>**Mauveine.**<br>*Obsolete names:*<br>**Mauve Dye.**<br>**Aniline-purple.**<br>**Indisine.**<br>**Anileïne.**<br>**Violeïne.** | Salts of phenyl- and tolyl-safranines. | *Chiefly:*<br>$C_{27}H_{25}N_4Cl$<br>or<br>$(C_{27}H_{25}N_4)_2SO_4$ | *Lowest homologue:*<br><br>$NH_2\,[4]\,C_6H_3 \ll \begin{matrix}[1]\,N\,[1]\\ [2]\,\underset{Cl\quad C_6H_5}{\underset{\wedge}{N}}\,[2]\end{matrix} > C_6H_3\,[4]\,NHC_6H_5$ |
| 594 | **Indazine M.**<br>[*C.*] | Mixture of dimethyl-phenyl-safranine chloride and its dimethyl-amido-anilido derivative. | $C_{26}H_{23}N_4Cl$<br>and<br>$C_{34}H_{33}N_6Cl$ | <br>$C_6H_5NH \cdot C_6H_3 \ll \begin{matrix}N\\ \underset{Cl\quad C_6H_5}{\underset{\wedge}{N}}\end{matrix} > C_6H_3 \cdot N\,(CH_3)_2$<br>and<br><br>$\left.\begin{matrix}(CH_3)_2N \cdot C_6H_4NH\\ C_6H_5NH\end{matrix}\right\} C_6H_2 \ll \begin{matrix}N\\ \underset{Cl\quad C_6H_5}{\underset{\wedge}{N}}\end{matrix} > C_6H_3 \cdot N\,(CH_3)_2$ (?) |
| 595 | **Metaphenylene Blue B.**<br>[*C.*] | Dimethyl-tolyl-diamido-tolyl-phenazonium chloride. | $C_{28}H_{27}N_4Cl$ | <br>$C_7H_7NH\,[4]\,C_6H_3 \ll \begin{matrix}[1]\,N\,[1]\\ [2]\,\underset{Cl\quad C_7H_7}{\underset{\wedge}{N}}\,[2]\end{matrix} > C_6H_3\,[4]\,N\,(CH_3)_2$ |
| 596 | **Naphthazine Blue.** [*D.*] [*M.*] | Sodium salt of the disulphonic acid of dimethyl-β-naphthyl-diamido-β-naphthyl-phenazonium. |  | <br>$\begin{matrix}C_{10}H_6NH\,[4]\,C_6H_3 \ll \begin{matrix}N\\ N\end{matrix} > C_6H_3\,[4]\,N\,(CH_3)_2\\ \vert \qquad\qquad\qquad\qquad \diagdown\\ SO_3 \text{———————} \qquad C_{10}H_6 \cdot SO_3Na\end{matrix}$<br>(?) |
| 597 | **Indamine Blue R & B.** [*M.*] | Amido-dianilido-phenyl-phenazonium chloride. | $C_{30}H_{24}N_5Cl$ | <br>$\left.\begin{matrix}C_6H_5NH\,[5]\\ C_6H_5NH\,[4]\end{matrix}\right\} C_6H_2 \ll \begin{matrix}[1]\,N\,[1]\\ [2]\,\underset{Cl\quad C_6H_5}{\underset{\wedge}{N}}\,[2]\end{matrix} > C_6H_4\,[4]\,NH_2$ |
| 598 | **Paraphenylene Blue R.**<br>[*D.*]<br>**Fast New Blue for cotton.**<br>**Indophenine.**<br>[*By.*] |  |  | Uncertain. |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Oxidation of aniline (containing toluidine) in acid solution. | 1856. | W. H. Perkin.<br>Eng. Pat. 1984$^{56}$.<br>Proc. of Royal Soc. **12**, 713.<br>J. Chem. Soc. **14**, 232; **35**, 717.<br>Jahresber. 1859, 756; 1863, 420.<br>Ann. (1864) **131**, 202.<br>A. Schlumberger.<br>Ding. Pol. J. (1862) **164**, 206.<br>Fischer and Hepp.<br>Ber. **21**, 2620; **26**, 1194. | **Appearance of dyestuff:** reddish violet paste.—**In water:** insoluble cold, sparingly soluble on boiling, with violet red colour.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda to the aqueous solution:** bluish violet precipitate.—**In conc. sulphuric acid:** olive green solution; on dilution with water becoming green, blue, and finally reddish violet.—**Dyes:** silk reddish violet. Is now only employed for whitening skein-silk, and for colouring postage stamps. |
| Action of 3 mols. of hydrochloride of nitrosodimethylaniline upon 1 mol. diphenyl-*m*-phenylene diamine. | 1888. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. 5852$^{88}$.<br>Am. Pat. 395300.<br>Durand, Huguenin, & Co.<br>Ger. Pat. 47549$^{88}$.<br>J. Soc. Dyers & Colorists, 1889, 106.<br>O. Fischer and Hepp.<br>Ann. **262**, 263; **272**, 314; **286**, 203.<br>Ber. **26**, 1195. | **Appearance of dyestuff:** bronzy powder.—**In water:** blue solution.—**In alcohol:** easily soluble.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda to the aqueous solution:** blue precipitate.—**In conc. sulphuric acid:** blackish green solution; blue on dilution with water.—**Dyes:** cotton a dark reddish blue after mordanting with tannin and tartar emetic; the colours are fast to soap, alkalies, and acids. |
| Action of hydrochloride of nitrosodimethylaniline upon di-*o*-tolyl-*m*-phenylene diamine. | 1888. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. 5852$^{88}$.<br>Am. Pat. 395300.<br>Ger. Pat. 47549.<br>Fr. Pat. 190091. | **Appearance of dyestuff:** dark powder.—**In water:** easily soluble with dull bluish violet colour.—**In alcohol:** easily soluble with blue colour.—**On addition of hydrochloric acid to the aqueous solution:** colour rather bluer.—**On addition of caustic soda to the aqueous solution:** violet precipitate.—**In conc. sulphuric acid:** bluish gray solution; dull blue on dilution with water.—**After reduction with zinc dust:** colour partially returns on exposure to air.—**Dyes:** cotton mordanted with tannin indigo blue shades of good fastness to soap, alkalies, and acids, moderately fast to light. |
| Action of nitrosodimethylaniline hydrochloride upon the disulphonic acid of di-*β*-naphthyl-*m*-phenylene diamine. | 1892. | Elsässer.<br>Dahl & Co.<br>Eng. Pat. 233265$^{93}$.<br>Am. Pat. 498382$^{94}$.<br>Ger. Pat. 77227$^{92}$.<br>Fr. Pat. 233265$^{93}$. | **Appearance of dyestuff:** bronzy powder.—**In water:** blue solution.—**On addition of hydrochloric acid:** becomes bluer and precipitates.—**On addition of caustic soda:** rather duller solution.—**In conc. sulphuric acid:** bluish green solution; blue solution and precipitate when diluted.—**Dyes:** wool blue from an acid bath, fast to acids and alkalies, and tolerably fast to light. |
| Heating amidoazobenzene with a large amount of aniline hydrochloride and stopping the melt at an early stage. | 1888. | E. Ullrich.<br>Chem. Ztg. 1890, 375.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. 16325$^{88}$.<br>Am. Pat. 418916.<br>Ger. Pats. 50534 & 50819$^{89}$.<br>Fr. Pat. 197490.<br>Fischer & Hepp.<br>Ann. **262**, 256; Ber. **28**, 2288; **29**, 368; **33**, 1498. | *Indamine Blue R.*<br>**Appearance of dyestuff:** dark blue paste or powder.—**In water:** easily soluble, with bluish violet colour.—**On addition of hydrochloric acid:** solution redder.—**On addition of caustic soda:** dark reddish violet precipitate.—**In conc. sulphuric acid:** blue solution; on dilution redder and blue precipitate.—**Dyes:** tannin-mordanted cotton bluish violet. |
| Action of *p*-phenylene diamine upon hydrochloride of amidoazobenzene. | 1886. | Dahl & Co.<br>Eng. Pat. 10134$^{86}$.<br>Ger. Pats. 36899$^{86}$; 39763$^{86}$; 43088$^{87}$; 44406$^{88}$; 45803$^{88}$.<br>Fr. Bayer & Co.<br>Ger. Pat. 53198.<br>O. Fischer & E. Hepp.<br>Ber. (1890) **23**, 838.<br>*Other references:*<br>Chem. Zeit. **12**, 1748.<br>J. Soc. Chem. Ind. 1888, 561, 1889, 189. | **Appearance of dyestuff:** dark powder.—**In water:** blue solution.—**In alcohol:** blue solution.—**On addition of hydrochloric acid to the aqueous solution:** no change.—**On addition of caustic soda to the aqueous solution:** violet precipitate.—**In conc. sulphuric acid:** blue solution; unchanged by dilution with water.—**Dyes:** cotton mordanted with tannin and tartar emetic blue; the colour becomes darker and faster by subsequent oxidation on the fibre. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 599 | **Induline, spirit soluble.*** [*H.*] [*B.*] [*By.*] [*W.*]<br>**Induline opal.**<br>**Fast Blue R, spirit soluble.** [*A.*] [*W.*]<br>**Induline 3 B, spirit soluble.**<br>**Induline 6 B, spirit soluble.**<br>**Induline 3 B opal & 6 B opal.**<br>**Fast Blue B, spirit soluble.** [*A.*] [*W.*]<br>**Azine Blue, spirit soluble.** [*D.*]<br>**Indigen D & F.** [*By.*]<br>**Printing Blue.** [*A.*] [*C.*] [*M.*]<br>**Acetin Blue.** [*B.*] | Mixtures of dianilido-amido-, trianilido-, and tetraanilido-phenyl-phenazonium chlorides. | $C_{30}H_{24}N_5Cl$<br>$C_{36}H_{28}N_5Cl$ ?<br>$C_{42}H_{33}N_6Cl$ ? | <br><br> |
| 600 | **Nigrosine, spirit soluble.** [*A.*] [*B.*] [*W.*]<br>**Coupier's Blue.**<br>**Sloeline.** [*B.S.S.*]<br>**Spirit Black.**<br>**Oil Black.** | Mixtures of indulines (see above) with allied bases and fluorindines. | | |
| 601 | **Induline, soluble.**<br>**Induline R & B.**<br>**Induline 3 B.**<br>**Induline 6 B.** [*B.*] [*By.*] [*W.*] [*C.R.*]<br>**Fast Blue R & 3 R.**<br>**Fast Blue 2 R, B, & 6 B.** [*C.*] [*W.*] [*B.*] [*A.*] [*T.M.*] [*G.*] [*O.*]<br>**Sloeline R.S. & B.S.** [*B.S.S.*] | Mixtures of the sodium salts of the sulphonic acids of the various spirit-soluble indulines. | | |
| 602 | **Nigrosine soluble.** [*A.*] [*B.*] [*W.*] [*C.R.*] [*K.*] [*G.*] [*D.*]<br>**Gray R & B.** [*I.*]<br>**Bengal Blue.** [*Ib.*] [*K.*] | Sodium salts of sulphonic acids of spirit nigrosines. | | |

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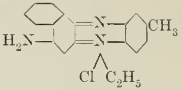
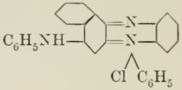
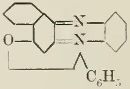
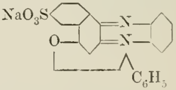
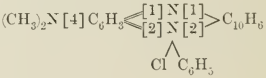
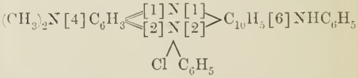
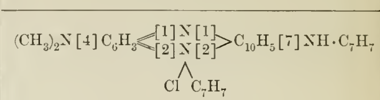
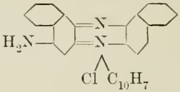
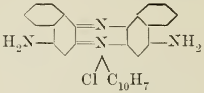
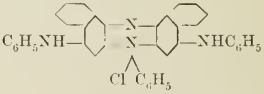
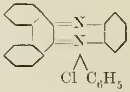
* The general name of **Indulines** was applied by Caro to the products formed by the action of aniline and aniline hydrochloride upon amidoazobenzene or aniline or by oxidation of o-amidodiphenylamine. The simplest technical induline is $C_{30}H_{24}N_5Cl$ (see No. 597), isolated by the method of Eng. Pat. $16325^{88}$. alcoholic solution at 160°.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating amidoazobenzene with aniline and aniline hydrochloride.<br>The red shade indulines are formed by heating the mixture for a short time only and at a low temperature (160°-170°). The bluer shades are obtained by more prolonged heating at a higher temperature.<br>Acetin-blue is a solution of spirit-soluble induline in acetin. | 1863. | H. Caro.<br>Roberts, Dale & Co.<br>Eng. Pat. $3307^{63}$.<br>Martius & Griess.<br>Zeitschr. f. Chem. 1866, 136.<br>Städeler.<br>Ding. Pol. J. (1865), 177, 395.<br>Jour. f. Pk. Chem. (1865) 96, 65.<br>H. Caro.<br>Neues Handwörterbuch d. Chemie. Fehling. Vol. 3, p. 789.<br>Hofmann & Geyger.<br>Ber. (1872) 5, 472.<br>Dechend & Wichelhaus.<br>Ber. (1875) 8, 1609.<br>O. N. Witt & E. Thomas.<br>Eng. Pat. $1487^{81}$.<br>Ger. Pat. 17340 (lapsed).<br>J. Chem. Soc. (1883) 1, 112.<br>Ber. (1883), 16, 1102.<br>O. N. Witt.<br>Ber. (1884) 17, 74 ; (1887) 20, 1538.<br>O. Fischer & E. Hepp.<br>Ann. (1890) 256, 233 ; (1891) 262, 237 ; 266, 256 ; 272, 306 ; 286, 187.<br>Ber. (1887) 20, 2479 ; (1888) 21, 676, 2617 ; (1890) 23, 838 ; 26, 1194, 1655 : 28, 2289 ; 29, 361.<br>J. Soc. Chem. Ind. 1887, 724 ; 1888, 743 ; 1890, 601 ; 1891, 456 ; 1892, 156.<br>Kehrmann.<br>Ber. 24, 2167 ; 28, 1543, 1716.<br>Nietzki.<br>Ber. 28, 1357.<br>*Employment of indulines dissolved in acetins for printing:—*<br>C. Schraube.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $6631^{86}$.<br>Am. Pat. $352361^{86}$.<br>Ger. Pat. $37064^{86}$.<br>Fr. Pat. $74993^{86}$. | **Appearance of dyestuff**: bluish black or brownish black powder.—**In water**: insoluble.—**In alcohol**: bluish violet solution.—**On addition of hydrochloric acid to the alcoholic solution**: colour becomes nearly pure blue.—**On addition of caustic soda to the alcoholic solution**: dull red or reddish violet solution and precipitate.—**In conc. sulphuric acid**: blue solution; violet blue precipitate on dilution with water.—**Employment**: for the preparation of the corresponding water-soluble colours. Also (mixed with chrysoidine, etc.) for the preparation of black spirit-varnishes and polish. And dissolved in acetins, etc., for calico-printing. |
| (*a*) Heating nitrobenzene with aniline, aniline hydrochloride, and iron or copper.<br>(*b*) Heating nitrophenol with aniline and aniline hydrochloride. | 1867. | Coupier.<br>Eng. Pat. $3657^{67}$.<br>*For fluorindines see:*<br>Fischer & Hepp.<br>Ber. 23, 2789 ; 28, 293 ; 29, 367.<br>Kehrmann.<br>Ber. 28, 1543, 1709. | **Reactions**: very similar to the spirit indulines, the solutions being blacker and duller.—**Employment**: for the preparation of corresponding water soluble colours by sulphonation. Also for colouring varnishes, polishes, lacquers, etc. |
| Action of conc. sulphuric acid upon the various spirit-soluble indulines (No. 599). | 1867. | Coupier.<br>Eng. Pat. $3657^{67}$.<br>Fr. Pat. $77854^{67}$. | **Appearance of dyestuff**: bronzy or blue black powder.—**In water**: easily soluble with bluish violet colour.—**In alcohol**: blue solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**On addition of caustic soda**: violet solution.—**In conc. sulphuric acid**: blue solution; violet solution or precipitate on dilution with water.—**Dyes**: wool or silk blue, reddish blue, or bluish violet (according to the brand) from an acid bath. Tolerably fast to light and washing but sensitive to alkalies. Wool is not dyed evenly. Used in silk dyeing and in the manufacture of inks. |
| Action of conc. sulphuric acid upon spirit-soluble nigrosines (No. 600). | 1867. | Coupier.<br>Eng. Pat. $3657^{67}$. | **Appearance of dyestuff**: coal black glistening lumps.—**In water**: blackish blue solution.—**On addition of hydrochloric acid**: blue black precipitate.—**On addition of caustic soda**: solution much redder.—**In conc. sulphuric acid**: indigo blue solution; precipitate on dilution.—**Dyes**: silk and wool blue black from an acid bath. |

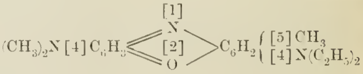
azobenzene. The simplest induline (not prepared technically) is the anilidoaposafranine $C_{24}H_{18}N_4$ of Fischer & Hepp formed by heating aposafranine with The name **Azodiphenyl Blue** was applied by Hofmann and Geyger to an induline produced by heating amidoazobenzene and aniline hydrochloride in

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 603 | **Induline Scarlet.** [*B.*] | Amido-ethyl-tolu-naphthazonium chloride. | $C_{19}H_{18}N_3Cl$ |  |
| 604 | **Azocarmine G.** [*B.*]<br>**Rosazine.** [*P.*] | Sodium salt of phenylrosinduline-disulphonic acid. | $C_{28}H_{17}N_3S_2O_6Na_2$ | *Disulphonic acid of:*  |
| 605 | **Azocarmine B.** [*B.*]<br>**Rosinduline 2 B.** [*K.*] | Acid sodium salt of phenylrosinduline-trisulphonic acid. | $C_{28}H_{17}N_3S_3O_9Na_3$ | |
| 606 | **Rosinduline 2 G.** [*K.*] | Sodium salt of rosindone-B-mono-sulphonic acid. | $C_{22}H_{13}N_2SO_4Na$ | *Sulphonic acid of:*  |
| 607 | **Rosinduline G.** [*K.*] | Sodium salt of rosindone-N-mono-sulphonic acid. | $C_{22}H_{13}N_2SO_4Na$ |  |
| 608 | **Neutral Blue.** [*C.*] | Dimethylamido-phenyl-pheno-naphthazonium chloride. | $C_{24}H_{20}N_3Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3\begin{matrix}<[1]\,N\,[1]>\\ {[2]}\,\underset{Cl\ \ C_6H_5}{\underset{\wedge}{N}}\,[2]\end{matrix}C_{10}H_6$ |
| 609 | **Azine Green G B.** [*L.*] | Dimethylamido-phenylamido-phenyl-phenonaphthazonium chloride. | $C_{30}H_{25}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3\begin{matrix}<[1]\,N\,[1]>\\ {[2]}\,\underset{Cl\ \ C_6H_5}{\underset{\wedge}{N}}\,[2]\end{matrix}C_{10}H_5\,[6]\,NHC_6H_5$ |
| 610 | **Azine Green S.** [*L.*] | Sodium salt of Azine Green sulphonic acid. | | |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Melting azo derivatives of monoethyl-*p*-toluidine with α-naphthylamine hydrochloride. | 1892. | C. Schraube.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $10138^{92}$ & $10138A^{92}$.<br>Am. Pat. $533829^{95}$.<br>Ger. Pat. $77226^{92}$.<br>Fr. Pat. $222863^{92}$. | **Appearance of dyestuff:** red powder.—**In water:** red solution.—**In alcohol:** orange red solution with yellow fluorescence.—**On addition of hydrochloric acid:** no change.—**On addition of caustic soda:** tarry violet precipitate.—**On addition of ammonia:** no change.—**In conc. sulphuric acid:** wine red solution; green and then red on dilution.—**Dyes:** tannined cotton scarlet red. Chiefly used in printing. |
| Action of fuming sulphuric acid upon the rosinduline obtained by heating benzene-azo-α-naphthylamine with aniline and aniline hydrochloride. | 1888. | C. Schraube.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $15259^{88}$; $6875^{90}$; $5540^{92}$.<br>Am. Pats. 428530; 430975; 431404.<br>Ger. Pat. $45370^{88}$.<br>O. Fischer & E. Hepp.<br>Ann. (1890) **256**, 240; (1891) **262**, 237.<br>Ber. **21**, 2617.<br>J. Soc. Chem. Ind. 1888, 743; 1889, 877; 1890, 53; 1891, 456; 1892, 30.<br>Kehrmann & Messinger.<br>Ber. **24**, 584. | **Appearance of dyestuff:** glistening red paste.—**In water:** sparingly soluble with bluish red colour.—**On addition of hydrochloric acid to the aqueous solution:** red precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** green solution; red precipitate on dilution with water.—**Dyes:** very level shades of bluish red upon wool and is employed as a substitute for archil. |
| Further sulphonation of phenylrosinduline or its disulphonic acid (No. 604) with fuming sulphuric acid. | 1888. | Hepp.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $19167^{90}$.<br>Ger. Pat. $58601^{90}$.<br>Kalle & Co.<br>Am. Pat. 466826. | **Appearance of dyestuff:** red brown powder.—**In water:** easily soluble with bluish red colour.—**On addition of hydrochloric acid:** brown precipitate.—**On addition of caustic soda:** no change.—**In conc. sulphuric acid:** green solution.—**Dyes:** wool bluish red. Substitute for archil. |
| Heating phenylrosinduline trisulphonic acid (No. 606) with water at 160°-180°. | 1890. | Hepp.<br>Kalle & Co.<br>Ger. Pat. 67198. | **Appearance of dyestuff:** scarlet red powder.—**In water:** scarlet red solution.—**On addition of hydrochloric acid:** yellow precipitate.—**On addition of caustic soda:** scarlet red precipitate.—**In conc. sulphuric acid:** dull green solution; diluted somewhat and allowed to stand deposits golden yellow crystals.—**Dyes:** silk and wool from an acid bath orange red, fairly fast to washing and of good fastness to acids and alkalies. |
| Heating phenylrosinduline-N-monosulphonic acid with water under pressure. | 1890. | Hepp.<br>Kalle & Co.<br>Ger. Pat. 72343.<br>Fischer & Hepp.<br>Ann. **286**, 216. | **Appearance of dyestuff:** red powder.—**In water:** orange red solution.—**On addition of hydrochloric acid:** yellow precipitate.—**On addition of caustic soda:** scarlet red soluble precipitate.—**In conc. sulphuric acid:** dull green solution; brownish precipitate on dilution.—**Dyes:** wool and silk scarlet. Chiefly used for printing on wool and silk in discharge style. Fairly fast. |
| Action of hydrochloride of nitrosodimethylaniline upon phenyl-β-naphthylamine. | 1882. | O. N. Witt.<br>Ber. (1888) **21**, 723.<br>L. Cassella & Co.<br>Ger. Pat. $19224^{82}$. | **Appearance of dyestuff:** dull brown powder.—**In water:** easily soluble with violet colour.—**In alcohol:** easily soluble with reddish violet colour.—**On addition of hydrochloric acid to the aqueous solution:** no change, rather bluer with a large excess.—**On addition of caustic soda to the aqueous solution:** violet precipitate.—**In conc. sulphuric acid:** brownish violet solution; violet on dilution with water.—**Dyes:** tannined cotton blue, not fast to light or soap. |
| Action of hydrochloride of nitrosodimethylaniline upon (2 : 6)-diphenylnaphthylene diamine. | 1889. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $3098^{90}$.<br>Ger. Pat. $54087^{89}$.<br>The Dyer (1890) **10**, 70.<br>J. Soc. Dyers and Colorists, 1892, 30. | **Appearance of dyestuff:** dark green powder.—**In water:** green solution.—**In alcohol:** green solution.—**On addition of hydrochloric acid to the aqueous solution:** green precipitate.—**On addition of caustic soda to the aqueous solution:** green precipitate.—**In conc. sulphuric acid:** brownish solution; green on dilution with water.—**Dyes:** tannin-mordanted cotton dark green. Tolerably fast to washing and light. |
| Sulphonation of Azine Green (No. 609). | 1890. | F. Bender.<br>A. Leonhardt & Co.<br>Ger. Pat. $58576^{90}$. | **Appearance of dyestuff:** blackish powder.—**In water:** blue green solution.—**In alcohol:** nearly insoluble.—**On addition of hydrochloric acid or caustic soda:** nearly unchanged.—**In conc. sulphuric acid:** bluish violet solution; on dilution brownish and then bluish green.—**Dyes:** wool from an acid bath bluish green fast to light. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 611 | **Basle Blue R.*** [*D.H.*] | Dimethylamido-tolylamido-tolyl-phenonaphthazonium chloride. | $C_{32}H_{29}N_4Cl$ |  $(CH_3)_2N\,[4]\,C_6H_3{<}\begin{matrix}[1]\,N\,[1]\\ {[2]}\,\underset{Cl\quad C_7H_7}{\underset{\wedge}{N}}\,[2]\end{matrix}{>}C_{10}H_5\,[7]\,NH\cdot C_7H_7$ |
| 612 | **Basle Blue S.** [*D.H.*] | Sodium salt of Basle Blue sulphonic acid. | | |
| 613 | **Paraphenylene Violet.** [*D.*] | | | |
| 614 | **Magdala Red.**<br>**Naphthalene Red.**<br>**Naphthalene Rose.**<br>**Naphthylamine Pink.** [*D.H.*]<br>**Sudan Red.** | Mixture of amido-naphthyl-naphthazonium chloride and diamido-naphthyl-naphthazonium chloride. | $C_{30}H_{20}N_3Cl$<br>and<br>$C_{30}H_{21}N_4Cl$ |  <br>and<br> |
| 615 | **Milling Blue.** [*K.*] | Sodium salt of a sulphonic acid of diphenyl-diamido-phenyl-naphthazonium chloride. | | *Sulphonic acid of:*<br> |
| 616 | **Flavinduline.** [*B.*] | Phenyl-phenanthra-phenazonium chloride. | $C_{26}H_{17}N_2Cl$ |  |

## XVI. OXAZINE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 617 | **Capri Blue G O N.** [*L.*] [*By.*] | Zinc double chloride of dimethyldiethyl-diamido-toluphen-oxazonium chloride. | $C_{17}H_{20}N_3OCl$ |  $(CH_3)_2N\,[4]\,C_6H_3{<}\begin{matrix}\overset{[1]}{N}\\ {[2]}\\ O\end{matrix}{>}C_6H_2\left\{\begin{matrix}[5]\,CH_3\\ {[4]}\,N(C_2H_5)_2\end{matrix}\right.$ |

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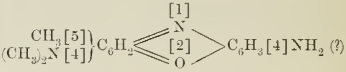
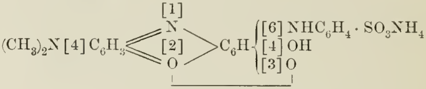
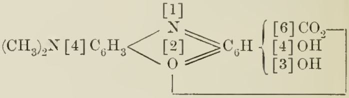
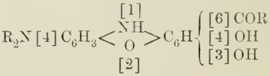
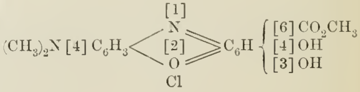
* **Basle Blue BB.** [*D.H.*] is the corresponding compound from

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of hydrochloride of nitrosodimethylaniline upon (2 : 7)-ditolylnaphthylene diamine. | 1886. | J. ANNAHEIM.<br>Ber. (1887) 20, 1371.<br>L. DURAND & HUGUENIN.<br>Eng. Pat. 14283$^{86}$.<br>Am. Pat. 369764.<br>Ger. Pat. 40886$^{86}$.<br>FISCHER & HEPP.<br>Ann. 272, 325. | **Appearance of dyestuff**: brown crystalline powder.—**In water**: bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution**: blue precipitate.—**In conc. sulphuric acid**: greenish brown solution; on dilution with water the colour becomes green, then violet, and finally gives a bluish violet precipitate.—**Dyes**: cotton mordanted with tannin and tartar emetic blue. |
| Sulphonation of Basle Blue (No. 611). | 1890. | DURAND, HUGUENIN, & CO.<br>Ger. Pat. 58363$^{90}$.<br>Fr. Pat. 178364. | **Appearance of dyestuff**: coppery powder.—**In water**: easily soluble.—**In conc. sulphuric acid**: yellow solution.—**Dyes**: wool and silk blue from an acid bath. |
| Heating amidoazonaphthalene or benzeneazo-α-naphthylamine with *p*-phenylene diamine. | 1888. | DAHL & CO.<br>Ger. Pats. 45803, 57346, & 69096. | **Appearance of dyestuff**: dark violet powder.—**In water**: violet solution.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes redder.—**On addition of caustic soda to the aqueous solution**: brownish violet precipitate.—**In conc. sulphuric acid**: green solution.—**Dyes**: tannin-mordanted cotton violet. Fairly fast to light, washing, alkalies, and acids. |
| Heating α-amidoazo-naphthalene with α-naphthylamine. | 1868. | SCHIENDL.<br>A. W. HOFMANN.<br>Ber. (1869) 2, 374, 412.<br>P. JULIUS.<br>Ber. (1886) 19, 1365.<br>Ger. Pat. 40868$^{86}$.<br>Eng. Pats. 225$^{68}$ & 2296$^{68}$.<br>O. MÜHLHÄUSER.<br>Chem. Ztg. 1893, 497. | **Appearance of dyestuff**: dark brown powder.—**In water**: sparingly soluble on boiling.—**In alcohol**: red solution with splendid red fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes rather bluer.—**On addition of caustic soda to the aqueous solution**: reddish violet precipitate.—**In conc. sulphuric acid**: grayish violet solution; violet red precipitate on dilution with water.—**Dyes**: silk from a "killed" soap bath pink with a slight fluorescence. |
| Sulphonation of the naphthazonium chloride obtained by heating benzeneazo-α-naphthylamine with α-naphthylamine hydrochloride and aniline, or benzeneazo-phenyl-α-naphthylamine with phenol at 120° to 150°. | 1890. | HEPP & MUCHALL.<br>KALLE & CO.<br>Ger. Pats. 62179 & 63181. | **Appearance of dyestuff**: bronzy powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: blue precipitate.—**On addition of caustic soda**: blue black solution.—**In conc. sulphuric acid**: blue green solution; blue on dilution.—**Dyes**: chromed wool blue. |
| Action of phenanthraquinone upon *o*-amidodiphenylamine. | 1893. | SCHRAUBE.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 18374$^{93}$.<br>Am. Pat. 543784$^{95}$.<br>Ger. Pat. 79570$^{93}$.<br>Fr. Pat. 222863$^{93}$. | **Appearance of dyestuff**: orange powder.—**In water**: orange yellow solution.—**On addition of hydrochloric acid**: little change.—**On addition of caustic soda**: grayish green precipitate, becoming grayish yellow.—**In conc. sulphuric acid**: bluish red solution; yellow on dilution.—**Dyes**: tannined cotton yellow. Especially suitable for printing in discharge styles. |

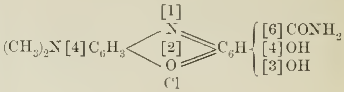
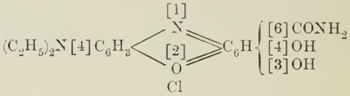
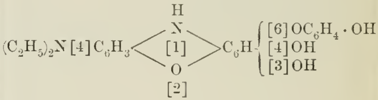
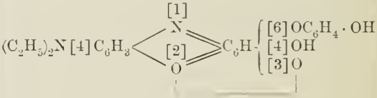
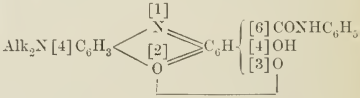
## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of nitrosodimethylaniline with diethyl-*m*-amidocresol. | 1890. | BENDER.<br>A. LEONHARDT & CO.<br>Eng. Pats. 13565$^{90}$ & 18623$^{90}$.<br>Am. Pat. 494838.<br>Fr. Pat. 211035.<br>Ger. Pats. 62367$^{90}$; 63238$^{90}$; 69820$^{90}$; & 71250.<br>MÖHLAU, KLIMMER, & KAHL.<br>Z. Farb. Chem. 1902, 313. | **Appearance of dyestuff**; green glistening crystals.—**In water or alcohol**: blue solution.—**On addition of hydrochloric acid**: red solution.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: green solution in thin layers, red in thick; red solution on dilution.—**Dyes**: tannined cotton greenish blue, fast to light and washing. |

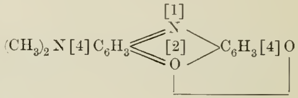
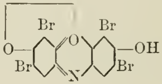
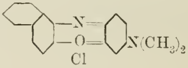
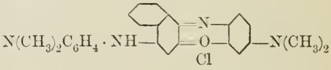
nitrosodiethylaniline, and dyes purer and bluer shades.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 618 | **Cresyl Blue BB & BBS.** [*L.*] | Possibly dimethyl-diamido-toluphen-oxazonium chloride, and homologues. | | *For instance:*<br><br>$\left.\begin{matrix}CH_3\,{[5]}\\(CH_3)_2N\,{[4]}\end{matrix}\right\}C_6H_2\left<\begin{matrix}{[1]}\\N\\{[2]}\\O\end{matrix}\right>C_6H_3\,{[4]}\,NH_2$ (?) |
| 619 | **Delphine Blue.** [*K.S.*] | Ammonium salt of the sulphonic acid of dimethylphenyl-diamido-oxy-phen-oxazone.<br>$C_{20}H_{20}N_4SO_6$ | | <br>$(CH_3)_2N\,{[4]}\,C_6H_3\left<\begin{matrix}{[1]}\\N\\{[2]}\\O\end{matrix}\right>C_6H\left\{\begin{matrix}{[6]}\,NHC_6H_4\cdot SO_3NH_4\\{[4]}\,OH\\{[3]}\,O\end{matrix}\right.$ |
| 620 | **Gallocyanine DH & BS.** [*D.H.*]<br>**Fast Violet.** [*D.H.*]<br>**Gallocyanine RS, BS, & D.** [*C.R.*] | Dimethylamido-dioxy-phenazoxonium carboxylate. (BS is the bisulphite compound.) | $C_{15}H_{12}N_2O_5$ | <br>$(CH_3)_2N\,{[4]}\,C_6H_3\left<\begin{matrix}{[1]}\\N\\{[2]}\\O\end{matrix}\right>C_6H\left\{\begin{matrix}{[6]}\,CO_2-\\{[4]}\,OH\\{[3]}\,OH\end{matrix}\right.$ |
| 621 | **Chromocyanine V & B.**<br>**Blue PRC.**<br>**Brilliant Gallocyanine.** [*D.H.*] | Sulphonic acids of leuco-gallocyanines. | | |
| 622 | **Indalizarine R & J.** [*D.H.*] | | | |
| 623 | **Indalizarine Green.** [*D.H.*] | Nitro-gallocyanine-sulphonic acids. | | |
| 624 | **Gallocyanine S.** [*D.H.*] | Gallocyanine-sulphonic acid. | | |
| 625 | **Blue 1900.**<br>**Deep Blue extra R.**<br>**Violet Moderne.** [*D.H.*] | Leuco-gallocyanines. | | <br>$R_2N\,{[4]}\,C_6H_3\left<\begin{matrix}{[1]}\\NH\\O\\{[2]}\end{matrix}\right>C_6H\left\{\begin{matrix}{[6]}\,COR\\{[4]}\,OH\\{[3]}\,OH\end{matrix}\right.$ |
| 626 | **Prune, pure.** [*K.S.*]<br>**Parme R.** [*K.S.*] | Methyl ether of gallocyanine. | $C_{16}H_{15}N_2O_5Cl$ | <br>$(CH_3)_2N\,{[4]}\,C_6H_3\left<\begin{matrix}{[1]}\\N\\{[2]}\\O\\Cl\end{matrix}\right>C_6H\left\{\begin{matrix}{[6]}\,CO_2CH_3\\{[4]}\,OH\\{[3]}\,OH\end{matrix}\right.$ |

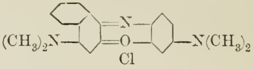
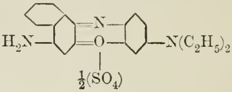
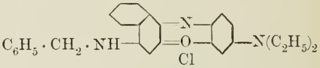
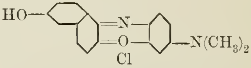
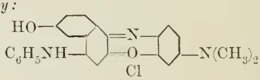
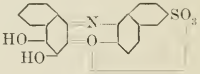
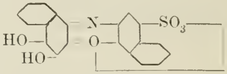
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Condensation of nitroso-dialkyl-*m*-amido-*p*-cresol with meta-diamines or para-diamines. | 1892. | BENDER.<br>A. LEONHARDT & Co.<br>Eng. Pats. $1390^{92}$ & $21154^{92}$.<br>Ger. Pats. $74918^{92}$ ; $75234^{92}$ ; & $75243^{93}$.<br>Fr. Pat. 224047. | *Mark BBS.*<br>**Appearance of dyestuff :** green powder.—**In water :** blue solution.—**On addition of hydrochloric acid :** dark brown solution.—**On addition of caustic soda :** brown precipitate.—**In conc. sulphuric acid :** green and violet red dichroic solution ; brown on dilution.—**Dyes :** tannined cotton blue fast to light and washing. |
| Heating gallocyanine hydrochloride with aniline, and sulphonation of the product. | 1889. | HAGENBUCH.<br>SANDOZ & Co.<br>Ger. Pat. 55942. | **Appearance of dyestuff :** olive-brown powder or dark paste.—**In water :** blue violet solution.—**On addition of hydrochloric acid :** redder solution and dark flocculent precipitate.—**In conc. sulphuric acid :** reddish violet solution ; dark blue precipitate on dilution.—**Dyes :** chromed wool indigo blue shades fast to light and milling. Employed in **calico printing** with a chrome mordant. |
| Action of nitroso-dimethylaniline hydrochloride upon gallic acid in alcoholic solution. | 1881. | H. KÖCHLIN.<br>Ger. Pat. $19580^{81}$.<br>Eng. Pat. $4899^{81}$.<br>Am. Pats. 253721 & 257498.<br>Mon. Scien. (1883) [3] **13**, 292<br>Bull. de Mulhouse (1883) **53**, 206.<br>R. NIETZKI & R. OTTO.<br>Ber. **21**, 1736 ; **25**, 2994.<br>J. Soc. Chem. Ind. 1888, 559 ; 1893, 137.<br>Z. Farb. Chem. 1902, 244. | **Appearance of dyestuff :** usually a greenish gray paste ; when dry a bronzy powder.—**In water :** insoluble.—**In alcohol :** bluish violet solution.—**On addition of hydrochloric acid to the paste :** pale magenta red solution.—**On addition of caustic soda to the paste :** reddish violet solution.—**In conc. sulphuric acid :** cornflower blue solution : magenta red on dilution with water.—**Employment :** dyes chrome mordanted wool bluish violet, and is employed in printing upon chrome mordanted wool and cotton. Fast to light, soap, and acids, less fast to alkalies. |
| Action of sulphites upon various gallocyanines. | 1898. | DE LA HARPE & VAUCHER.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $6055^{98}$.<br>Am. Pats. 613578 & 638576.<br>Fr. Pat. $275798^{98}$.<br>Ger. Pats. 104625 & 105736. | **Appearance of dyestuff :** greenish gray paste.—**On addition of caustic soda :** brown solution, becoming blue by oxidation.—**In conc. sulphuric acid :** pale brownish red dichroic solution, becoming blue on addition of an oxidising agent.—**Dyes :** violet to greenish blue shades upon a chrome mordant. Employed also in calico printing. Colours fast and readily dischargeable. |
| Action of sulphites upon gallocyanine-sulphonic acids. | 1900. | DE LA HARPE, VAUCHER, & LORÉTAN.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $6055^{98}$.<br>Am. Pats. 613578 & 638576.<br>Fr. Pat. $275798^{98}$.<br>Ger. Pats. 104625 & 105736. | **Appearance of dyestuff :** paste.—**In water :** olive solution.—**In caustic soda :** brown solution, becoming blue by air oxidation.—**In conc. sulphuric acid :** pale bordeaux red dichroic solution.—**Dyes :** fast blue shades upon a chrome mordant. Used in printing. |
| Action of nitric acid upon Indalizarine. | | DE LA HARPE & LORÉTAN.<br>DURAND, HUGUENIN, & Co. | **On addition of hydrochloric acid :** precipitate.—**In conc. sulphuric acid :** dark reddish violet solution.—**Dyes :** chromed wool fast green. |
| Action of dialkylamidoazobenzene upon derivatives of gallic acid. | 1894. | J. BIERER.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. $10333^{94}$ & $14137^{94}$.<br>Am. Pats. 534809 & 543375.<br>Fr. Pat. $227509^{93}$.<br>Ger. Pat. $80434^{94}$. | **In water :** blue solution.—**In conc. sulphuric acid :** blue solution.—**Dyes :** chromed wool blue. |
| Reduction of various gallocyanines. | 1898. | DE LA HARPE & VAUCHER.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. $21415^{98}$.<br>Am. Pat. 629666.<br>Fr. Pat. 280176.<br>Ger. Pat. $108550^{98}$. | **In water :** pale-green blue solution.—**On addition of hydrochloric acid :** violet.—**On addition of caustic soda :** solution rapidly becomes bluish violet by air oxidation.—**In conc. sulphuric acid :** pale red dichroic solution ; becomes blue on adding an oxidising agent.—**Employment :** gives in dyeing and printing blue to violet shades upon a chrome mordant which are readily dischargeable. |
| Action of nitroso-dimethylaniline hydrochloride upon the methyl ether of gallic acid. | 1886. | A. KERN.<br>Eng. Pat. $5953^{87}$.<br>Am. Pat. 396574.<br>Ger. Pat. $45786^{87}$.<br>R. NIETZKI & R. OTTO.<br>Ber. **21**, 1742 ; **25**, 2994.<br>MÖHLAU & KLIMMER.<br>Z. Farb. Chem. 1902, 68. | **Appearance of dyestuff :** brown glistening crystals, or dark brown powder.—**In water :** easily soluble.—**In alcohol :** bluish violet solution.—**On addition of hydrochloric acid to the aqueous solution :** colour becomes magenta red.—**On addition of caustic soda to the aqueous solution :** brown precipitate which dissolves in excess to a violet solution.—**In conc. sulphuric acid :** cornflower blue solution ; magenta red on dilution with water.—**Dyes :** tannin mordanted cotton, or chrome mordanted wool or cotton, bluish violet. Chiefly used in calico-printing. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 627 | **Gallamine Blue.**<br>[*G.*] [*By.*] | Amide of gallocyanine. | $C_{15}H_{14}N_3O_4Cl$ |  |
| 628 | **Coreine 2 R.** [*D.H.*]<br>**Celestine Blue B.** [*By.*] | Amide of diethyl-gallocyanine. | $C_{17}H_{18}N_3O_4Cl$ |  |
| 629 | **Phenocyanine VS.**<br>[*D.H.*] | Diethylamido-dioxy-phenoxazine-oxy-phenyl ether. | $C_{22}H_{22}N_2O_5$ |  |
| 630 | **Phenocyanine TV.**<br>[*D.H.*] | Sulphonic acid of diethylamido-oxy-phenoxazone-oxy-phenyl ether. | | |
| 631 | **Phenocyanine TC.**<br>[*D.H.*] | Diethylamido-oxy-phenoxazone-oxy-phenyl ether. | $C_{22}H_{20}O_5N_2$ |  |
| 632 | **Gallazine A.**<br>[*D.H.*] | | | |
| 633 | **Gallanilic Violets R & B.** [*D.H.*]<br>**Gallanilic Violet BS.** [*D.H.*] | Anilides of dimethyl- and diethyl-gallo-cyanines.<br>(The mark BS is the bisulphite compound.) | |  |
| 634 | **Gallanilic Blue**<br>[*D.H.*]<br>**Gallanilic Indigo P and PS.**<br>[*D.H.*] | | | |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of nitroso-dimethylaniline hydrochloride upon gallamic acid, and conversion into the bisulphite compound. | 1889. | J. R. GEIGY.<br>Eng. Pat. 2941$^{89}$.<br>Am. Pat. 410733.<br>Ger. Pat. 48996$^{89}$.<br>J. Soc. Dyers & Colorists, 1889, 170. | **Appearance of dyestuff:** light gray paste.—**In water:** sparingly soluble with pale bluish colour.—**On addition of hydrochloric acid:** dissolves more readily, solution wine red.—**On addition of caustic soda:** deep bluish violet solution.—**In conc. sulphuric acid:** violet gray solution; wine red on dilution with water.—**Dyes:** chrome mordanted wool blue. Also used in calico-printing. |
| Action of nitroso-diethylaniline or diethylamido-azobenzene upon the amide of gallic acid. | 1893. | BIERER.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. 14137$^{93}$ & 10333$^{94}$.<br>Am. Pat. 534809.<br>Ger. Pat. 76937$^{93}$.<br>Fr. Pat. 227509. | **Appearance of dyestuff:** greenish black powder (Celestine Blue) or thin brown paste (Coreine).—**In water:** reddish violet solution; on great dilution blue.—**In alcohol:** blue solution.—**On addition of hydrochloric acid:** magenta red solution.—**On addition of caustic soda:** blue violet solution.—**In conc. sulphuric acid:** cornflower blue solution; magenta red on dilution.—**Dyes:** chromed wool bluish violet; tolerably fast to light, milling, acids, and alkalies. |
| Action of resorcin upon the gallocyanine from diethylaniline and gallic acid. | 1893. | DE LA HARPE.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. 24802$^{93}$ & 15064$^{94}$.<br>Am. Pat. 555331.<br>Fr. Pat. 231216$^{94}$.<br>Ger. Pats. 77542 & 79839.<br>MÖHLAU & KLIMMER.<br>Z. Farb. Chem. 1902, 65. | **Appearance of dyestuff:** greenish yellow paste or greenish solution.—**In water:** easily soluble.—**In aqueous alkalies:** brown solution, rapidly becoming blue in the air.—**In conc. sulphuric acid:** pale brown solution, which slowly becomes blue by oxidation.—**Employment:** in printing on cotton with a chrome mordant it gives a fine fast blue. |
| Sulphonation of Phenocyanine TC (No. 631) by heating with sulphites. | 1893. | DE LA HARPE.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. 24802$^{93}$; 15064$^{94}$; & 16301$^{94}$.<br>Am. Pat. 585934.<br>Ger. Pats. 77452$^{93}$ & 84775$^{95}$.<br>Fr. Pat. 231216$^{94}$. | **Appearance of dyestuff:** powder or paste.—**In water:** blue solution.—**On addition of hydrochloric acid:** precipitate.—**In conc. sulphuric acid:** blue solution.—**Dyes:** chromed wool and silk a fast blue, and also chrome mordanted cotton. Employed in printing, and in cotton and wool dyeing. |
| Oxidation of Phenocyanine VS (No. 629) by air. | 1893. | DE LA HARPE.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. 24802$^{93}$ & 15064$^{94}$.<br>Am. Pat. 585934.<br>Ger. Pat. 77452$^{93}$.<br>Fr. Pat. 231216$^{94}$. | **In water:** sparingly soluble.—**On addition of caustic soda:** blue solution.—**In conc. sulphuric acid:** blue solution.—**Dyes:** chrome mordanted cotton fast blue. |
| Condensation of gallocyanine with $\beta$-naphthol-sulphonic acid S. | 1893. | DE LA HARPE.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pats. 24802$^{93}$ & 15064$^{94}$.<br>Am. Pat. 531148.<br>Ger. Pats. 77452$^{93}$ & 79839$^{94}$.<br>Fr. Pat. 231216$^{94}$. | **Appearance of dyestuff:** black paste.—**In water:** soluble.—**In aqueous alkalies:** violet solution.—**On addition of hydrochloric acid:** precipitate and red solution.—**In conc. sulphuric acid:** blue solution; violet solution and violet precipitate on dilution.—**Dyes:** chromed wool indigo blue, fairly fast to light, milling, washing, alkalies, and acids. Also employed in printing. |
| Action of nitroso-dimethyl- or diethyl-aniline upon the anilide of gallic acid. | 1889. | J. MOHLER.<br>SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BASLE.<br>Eng. Pats. 11848$^{89}$ & 15360$^{89}$.<br>Am. Pats. 420164; 440359; & 451502.<br>Ger. Pat. 50998$^{89}$.<br>NIETZKI AND BOSSI.<br>Ber. 25, 2995. | *Mark BS.*<br>**Appearance of dyestuff:** black fluid paste.—**In water or alcohol:** very sparingly soluble, with a blue colour.—**On addition of caustic soda to the aqueous or alcoholic solution:** bright bluish violet colour.—**In conc. sulphuric acid:** grayish red solution; dull claret on dilution with water.—**Dyes:** metallic mordanted wool or silk, shades of violet redder than gallocyanine; direct from an acid bath bluer shades. |
| Action of aniline upon Gallanilic Violets R & B (No. 633). The brand PS is the sulphonic acid of the product.) | 1889 & 1890. | J. MOHLER & C. MAYER.<br>DURAND, HUGUENIN, & Co.<br>Eng. Pat. 583$^{91}$.<br>Am. Pats. 444538 & 451502.<br>Fr. Pat. 199850.<br>Ger. Pat. 56991. | **Appearance of dyestuff:** blue paste with coppery reflection.—**In water:** P is insoluble, PS gives an indigo blue solution.—**On addition of hydrochloric acid to the aqueous solution of the PS:** dark brown precipitate.—**On addition of caustic soda:** the PS gives a bluish violet solution.—**In conc. sulphuric acid:** the PS gives a brownish violet solution; on dilution a brown precipitate.—**Employment:** the P gives an indigo blue upon a chrome mordant, the PS dyes silk and wool either from an acid bath or upon a chrome mordant. |

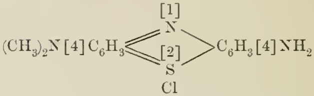
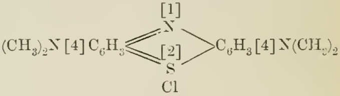
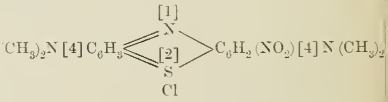
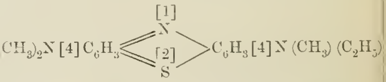
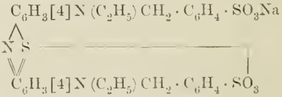
| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 635 | **Gallanilic Green.**<br>[*D.H.*]<br>**Fast Green G.**<br>[*D.H.*] | | | |
| 636 | **Coreine AR & AB.**<br>[*D.H.*] | | | |
| 637 | **Resorcin Blue.**<br>[*M.*]<br>**Nitroso Blue.**<br>[*M.*]<br>(On the fibre.) | Tannin compound of dimethylamido-phenoxazone. | |  |
| 638 | **Fluorescent Blue.**<br>[*I.*]<br>**Resorcin Blue.**<br>[*K.S.*]<br>**Iris Blue.**<br>[*B.*] | Ammonium salt of tetrabromoresorufin. | $C_{12}H_6Br_4N_2O_3$ |  |
| 639 | **Meldola's Blue.**<br>**New Blue.**<br>[*G.*] [*C.*] [*By.*] [*C.R.*]<br>**Naphthylene Blue R in crystals.** [*By.*]<br>**Fast Blue R, 2 R, & 3 R for cotton, in crystals.** [*A.*] [*M.*<br>**Cotton Blue R.**<br>[*B.*] [*P.*]<br>**Fast Navy Blue R.** [*O.*]<br>**Fast Navy Blue RM & MM.** [*K.*]<br>**Naphthol Blue R & D.** | Zinc double chloride of dimethylamido-naphtho-phen-oxazonium chloride. | $C_{18}H_{15}N_2OCl$ |  |
| 640 | **New Blue B or G.**<br>[*C.*] [*I.*] [*T.M.*]<br>**Fast Blue 2 B for Cotton.**<br>[*A.*] [*P.*] [*K.S.*]<br>**Fast Cotton Blue B.** [*M.*]<br>**Fast Navy Blue G** [*O.*], **BM & GM** [*K.*]<br>**Metamine Blue B & G.** [*L.*]<br>**Naphthol Blue B.** | Dimethylamido-dimethylamido-anilido-naphtho-phenazoxonium chloride. | $C_{26}H_{25}N_4OCl$ |  |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Nitration of Gallanilic Indigo PS (No. 634). | 1895. | BRACK.<br>DURAND, HUGUENIN, & Co.<br>Fr. Pat. 251086.<br>Ger. Pat. $86415^{95}$. | **Appearance of dyestuff:** dark brown paste or bronzy powder.—**In water:** easily soluble with bluish green colour.—**On addition of hydrochloric acid:** dark blue precipitate.—**On addition of caustic soda:** violet solution; with excess a bluish green precipitate.—**In conc. sulphuric acid:** crimson red solution; brown precipitate on dilution.—**Dyes:** chromed wool green. |
| Heating Coreine 2 R (No. 628) with aniline, and sulphonation. | 1894. | DURAND, HUGUENIN, & Co.<br>Eng. Pats. $10333^{94}$ & $3854^{95}$.<br>Am. Pats. 534809 & 543375.<br>Fr. Pats. 242956 & 227509.<br>Ger. Pats. $80434^{94}$ & $87935^{95}$. | **Appearance of dyestuff:** black paste.—**In water:** blue solution.—**On addition of hydrochloric acid:** AB gives a brown precipitate, AR a reddish violet precipitate.—**In conc. sulphuric acid:** reddish violet solution; carmine red on dilution.—**Employment:** dyes chromed wool blue tolerably fast to light, washing, milling, acids, and alkalies; chiefly used for printing. |
| Action of nitroso-dimethylaniline upon resorcin in presence of tannin (on the fibre). | 1898. | ULLRICH.<br>MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pat. $6050^{98}$.<br>Am. Pats. 676570 & 710940.<br>Ger. Pats. $103921^{98}$ & $108779^{98}$.<br>Fr. Pat. 276555 & addition. | **Employment:** produced on the fibre it gives indigo blue shades. |
| Bromination of resorufin, obtained by heating nitroso-resorcinol with resorcinol in presence of conc. sulphuric acid. | 1880. | P. WESELSKY & R. BENEDIKT.<br>Mon. f. Chem. **5**, 605; Ber. **18**, ref. 76; Ann. **162**, 273.<br>BINDSCHEDLER & BUSCH.<br>Ger. Pat. $14622^{80}$ (expired).<br>Eng. Pat. $939^{81}$.<br>H. BRUNNER & CH. KRÄMER.<br>Ber. **17**, 1847, 1867, 1875.<br>R. NIETZKI, A. DIETZE, & H. MÄCKLER.<br>Ber. **22**, 3030.<br>J. Soc. Chem. Ind. 1890, 489. | **Appearance of dyestuff:** brownish red solution filled with small green crystals.—**In boiling water:** reddish violet solution with green fluorescence.—**On addition of hydrochloric acid to the aqueous solution:** yellowish brown precipitate.—**On addition of caustic soda to the aqueous solution:** no change.—**In conc. sulphuric acid:** the dry dyestuff gives a blue solution, which on dilution with water first becomes violet and then deposits a reddish brown precipitate.—**By zinc dust and caustic soda:** decolorised; the decolorised solution becomes blue on exposure to air.—**Dyes:** silk and wool blue with a brownish fluorescence. |
| Action of nitroso-dimethylaniline hydrochloride upon $\beta$-naphthol. | 1879. | R. MELDOLA.<br>Ber. (1879) **12**, 2065.<br>A. BERNTHSEN.<br>Verh. Heidl. (1886) **3**, 5, Heft.<br>F. REVERDIN & E. NÖLTING.<br>Sur la constitution de la naphtaline et de ses dérivés, page 72.<br>R. NIETZKI & R. OTTO.<br>Ber. (1888) **21**, 1745.<br>O. N. WITT.<br>Ber. (1890) **23**, 2247.<br>R. NIETZKI & A. BOSSI.<br>Ber. **25**, 2994. | **Appearance of dyestuff:** dark violet bronzy powder, or crystals; the powder is excessively irritating to the mucous membrane.—**In water:** easily soluble with bluish violet colour.—**In alcohol:** blue solution.—**On addition of hydrochloric acid to the aqueous solution:** the violet solution becomes blue.—**On addition of caustic soda to the aqueous solution:** brown precipitate.—**In conc. sulphuric acid:** blackish green solution; blue on dilution with water.—**Dyes:** cotton mordanted with tannin and tartar emetic indigo blue. Tolerably fast to light, air, acids, and soap, but not to alkalies. Used as a substitute for indigo and for topping vat blues. |
| Condensation of Meldola's Blue (No. 639) with dimethyl-$p$-phenylene diamine. | 1889. | M. HOFFMANN & A. WEINBERG.<br>L. CASSELLA & Co.<br>Ger. Pat. 56722.<br>O. N. WITT.<br>Ger. Pat. 61662.<br>Ber. **23**, 2247. | **Appearance of dyestuff:** dark violet powder.—**In water:** easily soluble with blue colour.—**In alcohol:** blue solution.—**On addition of hydrochloric acid:** dull violet solution.—**On addition of caustic soda:** brown precipitate.—**In conc. sulphuric acid:** dirty green solution; on dilution dull violet and then blue.—**Dyes:** cotton mordanted with tannin and antimony blue. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 641 | **New Methylene Blue G G.**<br>[*C.*] | Tetramethyldiamido-naphtho-phenazoxonium chloride. | $C_{20}H_{20}N_3OCl$ |  |
| 642 | **Nile Blue A.**<br>[*B.*] [*By.*] | Diethyldiamido-naphtho-phenazoxonium sulphate. | $(C_{20}H_{20}N_3O)_2SO_4$ |  |
| 643 | **Nile Blue 2 B.**<br>[*B.*] | Diethylbenzyl-diamido-naphtho-phenazoxonium chloride. | $C_{27}H_{26}N_3OCl$ |  |
| 644 | **Muscarine.**<br>[*D.H.*]<br>**Campanuline.**<br>[*A.*] | Dimethylamido-oxy-naphtho-phenazoxonium chloride. | $C_{18}H_{15}N_2O_2Cl$ |  |
| 645 | **Fast Green M.**<br>[*D.H.*] | Probably dimethyl-phenyl-diamido-oxy-naphtho-phenazoxonium chloride. | | *Probably:*  |
| 646 | **Alizarine Green G.**<br>[*D.*] | Dioxynaphth-azoxonium sulphonate. | $C_{20}H_{11}NO_6S$ |  |
| 647 | **Alizarine Green B.**<br>[*D.*] | Dioxynaphth-azoxonium sulphonate. | $C_{20}H_{11}NO_6S$ |  |
| 648 | **Fast Black.**<br>[*L.*]<br>**Fast Blue Black.**<br>[*L.*] | | | Uncertain. |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of dimethylamine upon Meldola's Blue (No. 639), and subsequent oxidation | 1890. | M. Hoffmann & A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $6946^{90}$.<br>Ger. Pat. $54658^{90}$.<br>C. C. Schlarb.<br>Chem. Zeit. (1891) **15**, 1281, 1387.<br>J. Soc. Chem. Ind. (1892) 25.<br>Soc. Dyers & Colorists 1893, 15. | **Appearance of dyestuff**: greenish gray powder.—**In water**: blue solution.—**In alcohol**: greenish blue solution.—**On addition of hydrochloric acid to the aqueous solution**: no change, brown with excess.—**On addition of caustic soda to the aqueous solution**: bluish black precipitate.—**In conc. sulphuric acid**: reddish brown solution; dull green and finally pure blue on dilution with water.—**Dyes**: cotton mordanted with tannin a very greenish blue, fast to light and washing; silk from a "killed" soap bath a beautiful blue fairly fast to light. |
| Action of nitroso-diethyl-*m*-amido-phenol hydrochloride upon α-naphthylamine. | 1888. | Th. Reissig.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $4476^{88}$ & $11046^{91}$.<br>Am. Pat. $431541^{90}$.<br>Ger. Pats. $45268^{88}$ & $74391^{91}$.<br>Fr. Pat. $189359^{88}$.<br>Fr. Bayer & Co.<br>Ger. Pat. $49844^{89}$.<br>Fr. Pat. 198598.<br>Möhlau & Uhlmann.<br>Ann. **289**, 111. | **Appearance of dyestuff** (sulphate): bronzy crystalline powder.—**In water**: sparingly soluble cold, easily hot with a blue colour.—**In alcohol**: blue solution.—**On addition of hydrochloric acid to the warm aqueous solution**: precipitates the hydrochloride in small needles, which appear violet by transmitted, green by reflected light.—**On addition of caustic soda to the aqueous solution**: red precipitate, soluble in ether to a brownish orange solution with dark green fluorescence.—**In conc. sulphuric acid**: yellow solution, green and then blue on dilution with water.—**Dyes**: cotton mordanted with tannin and tartar emetic blue. |
| Action of nitroso-diethyl-*m*-amido-phenol hydrochloride upon benzyl-α-naphthylamine. | 1891. | P. Julius.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $10619^{91}$.<br>Ger. Pat. $60922^{91}$<br>addn. to 45268.<br>Fr. Pat. $189359^{91}$. | **Appearance of dyestuff**: green powder with metallic lustre.—**In water**: sparingly soluble cold, more readily hot to a blue solution.—**In alcohol**: greenish blue solution.—**On addition of hydrochloric acid to the warm aqueous solution**: separation of a green iridescent crystalline precipitate.—**On addition of caustic soda to the aqueous solution**: red precipitate, soluble in ether with an orange yellow colour and green fluorescence.—**In conc. sulphuric acid**: reddish yellow solution; green and then blue on dilution.—**Dyes**: tannin mordanted cotton greenish blue. |
| Action of nitroso-dimethyl-aniline hydrochloride upon (2 : 7)-dioxynaphthalene. | 1885. | J. Annaheim.<br>Durand & Huguenin.<br>Am. Pat. 413562.<br>Fr. Pat. 178364.<br>Nietzki & Bossi.<br>Ber. **25**, 3002. | **Appearance of dyestuff**: brown violet powder.—**In water**: sparingly soluble cold, easily hot, with a bluish violet colour.—**On addition of hydrochloric acid to the aqueous solution**: bluish violet precipitate.—**On addition of caustic soda to the aqueous solution**: colour becomes yellowish brown.—**After reduction with zinc dust**: colour returns on exposure to air.—**In conc. sulphuric acid**: bluish green solution; on dilution with water the solution becomes blue, then violet, and finally gives a violet precipitate.—**Dyes**: cotton mordanted with tannin and tartar emetic blue. Moderately fast. Employed for calico-printing. |
| Action of aniline upon Muscarine (No. 644). | 1894. | J. Bierer.<br>Durand, Huguenin, & Co.<br>Eng. Pat. $14983^{94}$.<br>Fr. Pat. 235561.<br>Ger. Pat. 79122. | **Appearance of dyestuff**: coppery brown powder.—**In water or alcohol**: insoluble.—**In acetic acid**: greenish blue solution.—**In conc. hydrochloric acid**: yellowish brown solution.—**On addition of caustic soda**: precipitate.—**In conc. sulphuric acid**: brownish violet solution; orange on dilution.—**Employment**: printed on cotton in conjunction with tannin it gives a fine green fast to light. |
| Condensation of β-naphthoquinone sulphonic acid with 1 : 2 : 6-amido-β-naphthol-sulphonic acid. | 1895. | Elsaesser.<br>Dahl & Co.<br>Eng. Pat. $5153^{95}$.<br>Ger. Pats. 82097 & 82740.<br>Fr. Pat. 246450.<br>Ber. **25**, 1400; **26**, 1279. | **Appearance of dyestuff**: brownish black powder.—**In water**: sparingly soluble cold, gray green solution hot.—**On addition of hydrochloric acid**: bordeaux red solution and precipitate.—**On addition of caustic soda**: brownish violet precipitate.—**In conc. sulphuric acid**: bluish green solution; on dilution blue, then violet, and finally red precipitate.—**Dyes**: a tolerably fast green upon a chrome mordant. |
| Condensation of β-naphthoquinone-sulphonic acid with 2 : 1 : 4-amido-α-naphthol-sulphonic acid. | 1895. | Elsaesser.<br>Dahl & Co.<br>Eng. Pat. $5153^{95}$.<br>Ger. Pat. 92740.<br>Fr. Pat. 246450. | **Appearance of dyestuff**: dark green powder.—**In water**: green solution.—**On addition of hydrochloric acid**: red crystalline precipitate; partially dissolves on boiling.—**On addition of caustic soda**: green flocculent precipitate.—**In conc. sulphuric acid**: dull bluish violet solution; on dilution yellowish green solution and then a red precipitate.—**Dyes**: green upon chrome mordants. |
| Action of nitroso-dimethyl-aniline hydrochloride upon *m*-oxydiphenylamine. | 1889. | F. Bender.<br>A. Leonhardt & Co.<br>Eng. Pat. $8264^{89}$.<br>Ger. Pat. $50612^{89}$.<br>Fr. Pat. 198511. | **Appearance of dyestuff**: black paste or powder.—**In water**: violet black solution.—**In alcohol**: blue black solution.—**On addition of hydrochloric acid to the aqueous solution**: blue black precipitate.—**On addition of caustic soda to the aqueous solution**: violet black precipitate.—**In conc. sulphuric acid**: nearly black solution; violet black on dilution with water.—**Dyes**: tannin mordanted cotton blue black, fast to light, soap, alkalies, and acids. |

## XVII. THIAZINE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 649 | **Gentianine.** [*G.*] | Zinc-double-chloride of dimethyl-diamido-phenazthionium chloride. | $C_{14}H_{14}N_3SCl$ |  |
| 650 | **Methylene Blue B & B G.*** [*B.*] [*C.R.*]<br>**Methylene Blue B B in powder extra D.** [*M.*] [*A.*]<br>**Methylene Blue B B in powder extra.** [*B.*] [*M.*] [*A.*]<br>**Methylene Blue A extra.** [*Mo.*] | Chloride (*methylene blue* B G, B B *in powder extra* D, *and printing blue*) or Zinc-double-chloride (*methylene blue* B, B B *in powder extra, dyeing blue*) of tetramethyl-diamido-phenazthionium. | *Chloride:*<br>$C_{16}H_{18}N_3SCl$<br>*Zinc-double-chloride:*<br>$(C_{16}H_{18}N_3SCl)_2 + ZnCl_2 + H_2O$ |  |
| 651 | **Methylene Green G conc. extra yellow shade.** [*M.*] | Nitromethylene Blue. | |  |
| 652 | **Thionine Blue G & O extra.** [*M.*] | Zinc-double-chloride of trimethylethyl-diamido-phenazthionium chloride. | $(C_{17}H_{20}N_3SCl)_2ZnCl_2$ |  |
| 653 | **Thiocarmine R.** [*C.*] | Sodium salt of diethyldibenzyl-diamido-phenazthionium-disulphonic acid. | $C_{30}H_{28}N_3S_3O_6Na$ |  |

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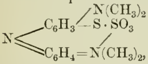
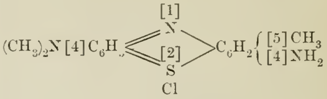
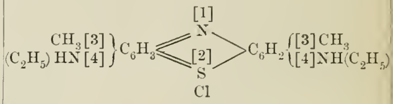
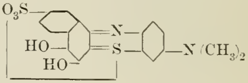
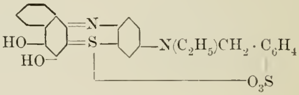
* Marine Blue and New Methylene Blue NX [C.]

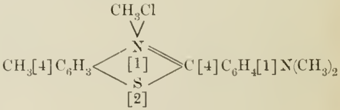
## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Conjoint oxidation of *p*-phenylene diamine and dimethyl-*p*-phenylene diamine in presence of hydric sulphide. | 1886. | Ed. Creppin.<br>J. R. Geigy & Co.<br>Am. Pat. $368716^{87}$.<br>Fr. Pat. 180487. | **Appearance of dyestuff**: reddish brown powder.—**In water**: readily soluble with blue violet colour.—**On addition of hydrochloric acid**: solution greener.—**On addition of caustic soda**: solution becomes more violet and then precipitates.—**In conc. sulphuric acid**: yellowish green solution; blue and bluish violet on dilution.—**Dyes**: mordanted cotton bluish violet. |
| Preparation of the thiosulphonic acid $C_6H_3\left\{\begin{array}{l}[1]\,N(CH_3)_2\\ [3]\,S\cdot SO_3H\\ [4]\,NH_2\end{array}\right.$ by the action of thiosulphuric acid upon the oxidation-product $C_6H_4\left\{\begin{array}{l}[1]:N(CH_3)_2Cl\\ [4]:NH\end{array}\right.$ of dimethyl-*p*-phenylene diamine, or by oxidation of dimethyl-*p*-phenylene diamine in presence of sodium thiosulphate; followed by conjoint oxidation of the thiosulphonic acid and dimethylaniline, by bichromate, to the insoluble compound  which by boiling with aqueous zinc-chloride is converted into leuco-methylene blue, and thence by further oxidation into methylene blue. | 1876.<br>1882.<br>1885.<br>1887. | H. Caro.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pat. $3751^{77}$.<br>Am. Pat. $204796^{78}$.<br>Ger. Pat. $1886^{77}$.<br>O. Mühlhäuser.<br>Ding. Pol. J. (1886), **262**, 371.<br>J. Chem. Ind. **6**, 136<br>E. Hepp.<br>K. Oehler.<br>Eng. Pat. $4048^{82}$.<br>Am. Pat. 270311.<br>Ger. Pat. $24125^{82}$.<br>E. Ullrich.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $43^{86}$.<br>Am. Pats. 362592, 366639, 366640, & 384480.<br>Ger. Pats. $38573^{85}$, $39757^{86}$.<br>Fr. Pats. 173137 & 181827.<br>A. Bernthsen.<br>Ber. **16**, 1025; **17**, 611, 2854, 2860.<br>Ann. **230**, 137; **251**, 1.<br>J. Soc. Chem. Ind. (1885), **4**, 276; (1887) **6**, 136; (1889), **8**, 452.<br>Bad. Anil. & Soda Fabrik.<br>Eng. Pats. $10314^{88}$ & $8221^{93}$.<br>Ger. Pats. $45839^{87}$, $46805^{87}$, & $47374^{88}$.<br>Koch.<br>Ber. **12**, 592. | **Appearance of dyestuff**: dark blue or reddish brown bronzy powder.—**In water**: easily soluble with a blue colour.—**In alcohol**: less easily soluble.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: colour becomes more violet, a large excess gives a dull violet precipitate.—**In conc. sulphuric acid**: yellowish green solution; blue on dilution with water.—**Reducing agents**: convert it into leuco-methylene blue, which is reoxidised to methylene blue by air.—**Dyes**: cotton mordanted with tannin blue, tolerably fast to light and washing. Employed as chloride (free from zinc) for calico printing and for medicinal purposes. |
| Nitration of Methylene Blue (No. 650). | 1886. | Ullrich.<br>Meister, Lucius, & Brüning.<br>Eng. Pat. $8992^{86}$.<br>Ger. Pat. $38979^{86}$.<br>Fr. Pat. 177331. | **Appearance of dyestuff**: dark brown powder.—**In water**: easily soluble with greenish blue colour.—**In alcohol**: sparingly soluble.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: violet solution and precipitate.—**In conc. sulphuric acid**: dark green solution; blue on dilution.—**Employment**: dyed or printed on cotton it gives a bluish green of greater fastness to light and washing than Methylene Blue. |
| Oxidation of dimethyl-*p*-phenylene-diamine-thiosulphonic acid (see No. 650) with ethylmethylaniline, and boiling the intermediate green indamine with zinc chloride. | 1885. | Ullrich.<br>Meister, Lucius, & Brüning. | **Appearance of dyestuff**: reddish brown powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: no change.—**On addition of caustic soda**: violet solution, violet precipitate with large excess.—**In conc. sulphuric acid**: yellowish green solution; blue solution on dilution.—**Dyes**: tannined cotton blue. |
| Sulphobenzylethyl-*p*-phenylene-diamine-thiosulphonic acid, obtained by oxidation of benzylethyl-*p*-phenylene-diamine-sulphonic acid in presence of sodium thiosulphate, is oxidised together with benzylethylaniline-sulphonic acid, and the sulpho-indamine-thiosulphonate thus obtained is heated to boiling. | 1890. | A. Weinberg.<br>L. Cassella & Co.<br>Eng. Pat. $4596^{90}$.<br>Am. Pat. 434493.<br>*Employment:*<br>J. Soc. Chem. Ind. 1892, 30. | **Appearance of dyestuff**: indigo blue powder or paste.—**In water**: very soluble with a pure blue colour.—**In alcohol** (95%): sparingly soluble.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda**: no change in the cold, violet on heating.—**In conc. sulphuric acid**: grass green solution; bright blue on dilution with water.—**After reduction with zinc dust**: colour returns on exposure to air.—**Dyes**: wool and silk blue of indigo carmine shade from an acid bath. The shades are level and tolerably fast to milling, acids, and alkalies, but not very fast to light. |

are mixtures of Methylene Blue 2 B and Methyl Violet.

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 654 | **Toluidine Blue O.**<br>[*B.*] [*M.*] [*A.*] | Zinc-double-chloride of dimethyldiamidotoluphenazthionium chloride. | $(C_{15}H_{16}N_3SCl)_2ZnCl_2$ |  |
| 655 | **New Methylene Blue N.**<br>[*C.*] | Diethyldiamidotoluphenazthionium chloride. | $C_{18}H_{22}N_3SCl$ |  |
| 656 | **Brilliant Alizarine Blue G & R.**<br>[*By.*]<br>**Indochromine T.**<br>[*K.S.*] | | | <br>*Or,*<br> |
| 657 | **Urania Blue.**<br>[*D.*] | | | |

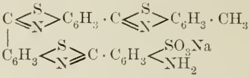
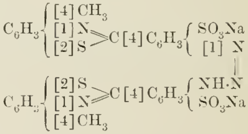
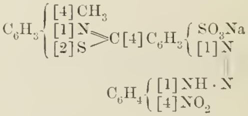
## XVIII. THIAZOL or THIOBENZENYL

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 658 | **Thioflavine T.**<br>[*C.*] | Dimethyl-dehydrothiotoluidine-methylochloride. | $C_{17}H_{19}N_2SCl$ |  |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Oxidation of the dimethyl-*p*-phenylene-diamine-thiosulphonic acid (see No. 650) together with *o*-toluidine to the insoluble green indamine, boiling the latter with aqueous zinc chloride, and oxidation of the leuco-compound obtained. | 1888. | BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 10314$^{88}$.<br>Ger. Pat. 47374$^{88}$.<br>Am. Pat. 416055$^{89}$.<br>MEISTER, LUCIUS, & BRÜNING.<br>Ger. Pat. 47345$^{88}$. | **Appearance of dyestuff**: dark green powder.—**In water**: easily soluble with bluish violet colour.—**In alcohol**: blue solution.—**On addition of hydrochloric acid to the aqueous solution**: blue solution.—**On addition of caustic soda to the aqueous solution**: dull violet precipitate.—**In conc. sulphuric acid**: yellowish green solution; blue on dilution with water.—**Dyes**: mordanted cotton blue. |
| Ethyl-*p*-tolylene-diamine-thiosulphonic acid, obtained by oxidation of *p*-amido-ethyl-*o*-toluidine in presence of sodium thiosulphate, is oxidised together with ethyl-*o*-toluidine, and the green indamine obtained is heated. | 1891. | A. WEINBERG.<br>L. CASSELLA & Co.<br>Eng. Pat. 8407$^{91}$.<br>Am. Pat. 469329$^{92}$. | **Appearance of dyestuff**: metallic glistening crystalline powder.—**In water**: easily soluble, violet blue when cold, pure blue when hot.—**In alcohol**: tolerably soluble with a greenish blue colour.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: immediate chocolate brown precipitate.—**In conc. sulphuric acid**: yellowish green solution; pure blue on dilution with water.—**After reduction with zinc dust**: colour returns on exposure to air.—**Dyes**: tannin mordanted cotton blue of fuller and redder shade than Methylene Blue B B. |
| Condensation of β-naphthoquinone-disulphonic acid with dimethyl-*p*-phenylene-diamine-thiosulphonic acid, or of β-naphthoquinone with sulphobenzylethyl-*p*-phenylene-diamine-thiosulphonic acid. | 1892. | B. HEYMANN.<br>FR. BAYER & Co.<br>Ger. Pat. 83046$^{92}$. | *Brand G.*<br>**Appearance of dyestuff**: greenish brown bronzy paste.—**In water**: soluble hot.—**On addition of caustic soda**: violet blue solution; gives with hydrochloric acid a violet precipitate.—**In conc. sulphuric acid**: green solution; violet precipitate on dilution.—**Dyes**: chromed wool, cotton, and silk a very fast blue. Suitable for calico printing. |
| Conjoint oxidation of di-β-naphthyl-*m*-phenylene-diamine-disulphonic acid and dimethyl-*p*-phenylene-diamine-thiosulphonic acid. | 1896. | ELSAESSER.<br>DAHL & Co.<br>Ger. Pat. 90275.<br>Fr. Pat. 244671$^{96}$. | **Appearance of dyestuff**: blue violet bronzy powder.—**In water**: blue solution.—**On addition of hydrochloric acid**: dark blue soluble precipitate.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: brownish green solution; blue on dilution.—**Dyes**: wool and silk blue from an acid bath. |

## COLOURING MATTERS.

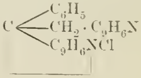
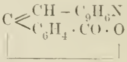
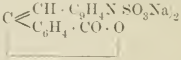
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Methylation of dehydrothiotoluidine by heating under pressure with methyl alcohol and hydrochloric acid. | 1888.<br>1888. | J. ROSENHECK.<br>A. G. GREEN and T. A. LAWSON.<br>J. Chem. Soc. (1889) **55**, 230.<br>L. CASSELLA & Co.<br>Eng. Pats. 6319$^{88}$ & 14884$^{88}$.<br>Am. Pat. 412978.<br>Ger. Pat. 51738.<br>J. Soc. Chem. Ind. 1890, 54.<br>J. Soc. Dyers & Colorists 1889, 106. | **Appearance of dyestuff**: yellow crystalline powder.—**In water**: easily soluble with a yellow colour.—**In alcohol**: easily soluble with yellow colour and green fluorescence.—**On addition of hydrochloric acid to the aqueous solution**: no change.—**On addition of caustic soda to the aqueous solution**: no change.—**Conc. sulphuric acid**: colourless solution; yellow on dilution.—**Dyes**: tannin-mordanted cotton pure greenish yellow, silk yellow with a green fluorescence. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 659 | **Primuline.**<br>[*B.S.S.*] [*By.*]<br>[*Cl. Co.*] [*K.*]<br>**Polychromine.**<br>[*G.*]<br>**Thiochromogen.**<br>[*D.*]<br>**Aureoline.**<br>[*R.H.*]<br>**Sulphine.**<br>[*B.*] | Sodium salt of the mono-sulphonic acids of the dehydrothionated condensation-products of dehydrothiotoluidine (mixed with some sodium dehydrothiotoluidine-sulphonate). | *Chief constituent :*<br>$C_{28}H_{17}N_4O_3S_4Na$ | *Chief constituent :*<br> |
| 660 | **Clayton Yellow.**<br>[*Cl. Co.*]<br>**Turmerine.**<br>[*B.S.S.*]<br>**Thiazol Yellow.**<br>[*By.*]<br>**Mimosa.** [*G.*] | Sodium salt of the diazo-amido compound of dehydrothiotoluidine-sulphonic acid, or of the mixed diazo-amido compound of dehydrothiotoluidine-sulphonic acid and primuline. | $C_{28}H_{19}N_5S_4O_6Na_2$ (from dehydrothiotoluidine-sulphonic acid alone). | <br>(from dehydrothiotoluidine-sulphonic acid alone). |
| 661 | **Nitrophenine.**<br>[*Cl. Co.*] | Sodium salt of diazo-dehydrothiotoluidine-sulphonic acid-*p*-nitranilide. | $C_{20}H_{14}N_5O_5SNa$ |  |
| 662 | **Thioflavine S.**<br>[*C.*]<br>**Chromine G.**<br>[*K.*] | Sodium salt of methylated primuline. | | |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| By heating paratoluidine (2 mols.) with sulphur (4-5 atoms) at 200°-280°, and sulphonation of the product ("primuline base") with fuming sulphuric acid. | 1887. | A. G. Green.<br>The Dyer (1887) **7**, 101; (1888) **8**, 54.<br>J. Soc. Chem. Ind. (1888) **7**, 179.<br>J. Soc. of Dyers & Colorists (1888) **4**, 39.<br>J. Chem. Soc. (1889) **55**, 227.<br>Ber. **22**, 968.<br>Brooke, Simpson, & Spiller.<br>Fr. Bayer & Co.<br>Eng. Pat. $6319^{88}$.<br>Ger. Pat. $50525^{88}$.<br>Dahl & Co.<br>Ger. Pat. 47102.<br>A. Kertész.<br>Chem. Zeit. **12**, 923.<br>J. Soc. Chem. Ind. (1888) **7**, 561.<br>P. Jacobsen.<br>Ber. **22**, 330.<br>L. Gattermann.<br>Ber. **22**, 422; J. Soc. Chem. Ind. (1889) **8**, 275.<br>R. Anschutz & G. Schultz.<br>Ber. **22**, 580.<br>W. Pfitzinger and L. Gattermann.<br>Ber. **22**, 1063; J. Soc. Chem. Ind. (1889) **8**, 608.<br>A. G. Green, C. F. Cross, and E. J. Bevan.<br>(*Photographic application.*)<br>J. Soc. Chem. Ind. (1890) **9**, 1001; Ber. **23**, 3131.<br>Eng. Pat. $7453^{90}$.<br>Ger. Pat. $56606^{90}$. | **Appearance of dyestuff**: dull yellow powder.—**In water**: easily soluble with pale yellow colour.—**On addition of hydrochloric acid to the aqueous solution**: orange yellow precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: pale yellow solution with greenish fluorescence; orange yellow precipitate on dilution with water.—**Dyes**: unmordanted cotton primrose yellow direct from an alkaline or neutral bath. It is employed for the production of very fast shades of red, orange, and yellow ("Ingrain colours"), by diazotisation upon the fibre by means of nitrous acid, and subsequent treatment with a phenol or amine, thus:—<br>**Ingrain-red**: β-naphthol.<br>**Ingrain-maroon**: β-naphthol-di-sulphonic acid R.<br>**Ingrain-orange**: resorcinol.<br>**Ingrain-yellow**: phenol.<br>**Ingrain-brown**: *m*-phenylene diamine.<br>**Ingrain-crimson**: α-naphthol-sulphonic acid NW.<br>**Photographic application ("Diazotype Process" of Green, Cross, and Bevan)**: coloured designs, pictures, etc., are produced upon textile fabrics, paper, etc., by exposing the material, dyed with Primuline and diazotised, to the action of light beneath a positive design. The diazo-primuline is rapidly destroyed in the exposed portions, and upon subsequent treatment with a phenol or amine the protected portions alone are developed and a design in colour thus obtained. |
| (1) Combination of diazotised dehydrothiotoluidine-sulphonic acid (or primuline) with dehydrothiotoluidine-sulphonic acid or primuline.<br>(2) Action of aqueous ammonia upon diazotised dehydrothiotoluidine-sulphonic acid. | 1887.<br>1888.<br>1889. | A. G. Green & F. Evershed.<br>W. Pfitzinger.<br>Ph. Brunner & J. Hall.<br>The Clayton Aniline Co.<br>Eng. Pat. $14207^{89}$.<br>F. Bayer & Co.<br>Eng. Pat. $18354^{89}$.<br>Am. Pat. 428629.<br>Ger. Pat. $53935^{89}$.<br>Ch. Ris.<br>J. R. Geigy & Co.<br>Eng. Pat. $1771^{90}$.<br>Am. Pat. $440281^{91}$.<br>Ger. Pats. $53666^{90}$ & $56593^{90}$. | **Appearance of dyestuff**: yellow powder.—**In water**: yellow solution.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: reddish yellow precipitate.—**On addition of caustic soda**: orange red coloration and precipitate.—**In conc. sulphuric acid**: brownish yellow solution; on dilution the colour becomes paler.—**Dyes**: unmordanted cotton direct from a salt bath bright greenish yellow, not fast to alkalies, acids, or light. Valuable on account of its pure yellow shade for admixture with other direct cotton colours. |
| Combination of diazotised *p*-nitraniline with the sodium salt of dehydrothiotoluidine-sulphonic acid. | 1893. | C. Dreyfus.<br>The Clayton Aniline Co.<br>Eng. Pat. $24870^{93}$. | **Appearance of dyestuff**: brown powder.—**In water**: reddish yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: yellow precipitate.—**On addition of caustic soda to the aqueous solution**: dark violet solution or precipitate.—**In conc. sulphuric acid**: golden yellow solution; yellow precipitate on dilution.—**Dyes**: unmordanted cotton direct greenish yellow, not fast to alkalies. |
| Sulphonation of the methyl derivative of primuline base, or methylation of primuline. | 1888. | J. Rosenheck.<br>L. Cassella & Co.<br>Eng. Pats. $6319^{88}$ & $14884^{88}$.<br>Am. Pat. 412979.<br>Ger. Pats. 51738 & 55333.<br>J. Soc. Dyers & Colorists, 1889, 106.<br>J. Soc. Chem. Ind. 1890, 54.<br>Kalle & Co.<br>Ger. Pat. 61204. | **Appearance of dyestuff**: yellow powder.—**In water**: easily soluble with a yellow colour.—**In alcohol**: less soluble than in water; the solution fluoresces green.—**On addition of hydrochloric acid to the aqueous solution**: orange yellow precipitate.—**On addition of caustic soda to the aqueous solution**: no change.—**In conc. sulphuric acid**: brownish yellow solution; orange precipitate on dilution with water.—**Dyes**: unmordanted cotton, silk, and half-silk greenish yellow from an alkaline bath. Tolerably fast to washing and alkalies, but not to light, acids, or chlorine. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 663 | **Chloramine Yellow.** [*By.*]<br>**Chlorophenine Y.** [*Cl. Co.*]<br>**Oxyphenine.** [*Cl. Co.*]<br>**Diamine Fast Yellows B, C, & FF.** [*C.*]<br>**Columbia Yellow.** [*A.*] | Oxidation-products of dehydrothiotoluidine-sulphonic acid or of the latter and primuline together. | | |

## XIX. QUINOLINE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 664 | **Cyanine.**<br>**Quinoline Blue.** [*G.*] | | $C_{29}H_{35}N_2I$ | |
| 665 | **Quinoline Red.** [*A.*] | | $C_{26}H_{19}N_2Cl$ |  $C\begin{cases} C_6H_5 \\ CH_2 \cdot C_9H_6N \\ C_9H_6NCl \end{cases}$ |
| 666 | **Quinoline Yellow, spirit soluble.** [*A.*] [*B.*] [*By.*]<br>**Quinophthalone.** | Quinophthalone. | $C_{18}H_{11}NO_2$ |  $C\begin{cases} CH - C_9H_6N \\ C_6H_4 \cdot CO \cdot O \end{cases}$ |
| 667 | **Quinoline Yellow.** [*A.*] [*B.*] [*By.*]<br>**Quinoline Yellow, water-soluble.** | Sodium salt of the sulphonic acid (chiefly di-sulphonic acid) of quinophthalone. | $C_{18}H_9NO_8S_2Na_2$ |  $C\begin{cases} CH \cdot C_9H_4N\ SO_3Na)_2 \\ C_6H_4 \cdot CO \cdot O \end{cases}$ |

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of hypochlorites upon sodium dehydrothiotoluidine sulphonate or upon the latter together with primuline. | 1887.<br>1890. | A. G. Green.<br>(Oxidation of primuline with hypochlorites on the fibre.)<br>Guinon, Picard, & Jay.<br>(Oxidation of coml. primuline in substance.)<br>Fr. Pat. $209519^{90}$.<br>Fr. Bayer & Co.<br>Eng. Pat. $19061^{91}$.<br>Ger. Pat. $65402^{91}$.<br>Fr. Pat. 216954.<br>Clayton Aniline Co.<br>Eng. Pat. $5761^{92}$.<br>J. Soc. Dyers, 1892, 179.<br>L. Cassella & Co.<br>Eng. Pat. $22914^{94}$.<br>Fr. Pat. 243291. | **Appearance of dyestuff**: brownish yellow to bright orange powder.—**In water**: yellow solution.—**In alcohol**: insoluble.—**On addition of hydrochloric acid**: orange yellow precipitate.—**On addition of caustic soda**: no change of colour.—**In conc. sulphuric acid**: red solution; brownish yellow precipitate on dilution with water.—**Dyes**: unmordanted cotton from neutral bath, wool and silk from acid bath, yellow shades which are very fast to alkalies and acids, and extremely fast to light and chlorine. Not dischargeable by reducing agents. |

## COLOURING MATTERS.

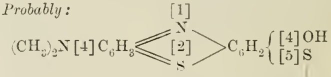
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of amyl iodide upon a mixture of equivalent quantities of quinoline and lepidine ($\gamma$-methyl-quinoline), and treatment of the product with caustic alkalies. | 1856. | Williams.<br>Jour. Pk. Chem. (1861) **83**, 189.<br>Jahresber. 1860, 735.<br>A. W. Hofmann.<br>Zeitschr. f. Chem. **6**, 36.<br>Comp. rend. **55**, 849.<br>Jahresber. 1862, 351.<br>W. Spalteholz.<br>Ber. (1883) **16**, 1847. | **Appearance of dyestuff**: glistening green crystals.—**In water**: insoluble cold, sparingly on warming, with a violet blue colour; the solution smells of quinoline.—**On addition of hydrochloric acid to the aqueous solution**: decolourised.—**On addition of caustic soda to the aqueous solution**: blue bronzy precipitate, becoming brown on warming.—**In conc. sulphuric acid**: colourless solution; evolves iodine on heating; the solution remains colourless on dilution with water.—**Employment**: for isochromatising photographic plates. |
| Action of benzotrichloride upon a mixture of quinaldine (methyl-quinoline) and isoquinoline. | 1882. | E. Jacobsen.<br>Eng. Pat. $814^{82}$.<br>Am. Pat. 257717.<br>Ger. Pats. $19306^{82}$ & $23967^{82}$.<br>A. W. Hofmann.<br>Ber. (1887), **20**, 4.<br>J. Soc. Chem. Ind. 1887, 214.<br>Actiengesellschaft für Anilinfabrikation.<br>Ger. Pat. $40420^{87}$. | **Appearance of dyestuff**: small dark brownish red bronzy needles.—**In water**: insoluble cold, tolerably soluble hot.—**In alcohol**: red solution with yellowish red fluorescence.—**In conc. sulphuric acid**: colourless solution; red on dilution with water.—**Employment**: for isochromatising photographic plates. |
| Heating quinaldine with phthalic anhydride and zinc chloride. | 1882. | E. Jacobsen.<br>Eng. Pat. $1362^{83}$.<br>Am. Pat. 290585.<br>Ger. Pats. $23188^{82}$ & $25144^{83}$.<br>Ber. (1883) **16**, 297, 513, 878, 1082.<br>J. Soc. Chem. Ind. 1883, 274.<br>Ann. **315**, 303. | **Appearance of dyestuff**: yellow powder.—**In water**: insoluble.—**In alcohol**: sparingly soluble with yellow colour.—**In conc. sulphuric acid**: yellowish red solution; yellow flocculent precipitate on dilution with water.—**Employment**: for colouring spirit-varnish, wax, etc. |
| Action of conc. sulphuric acid upon spirit-soluble quinoline-yellow. | 1882. | E. Jacobsen.<br>Eng. Pat. $1362^{83}$.<br>Am. Pat. 290585.<br>Ger. Pats. $23188^{82}$ & $25144^{83}$. | **Appearance of dyestuff**: yellow powder.—**In water**: easily soluble with a yellow colour.—**In alcohol**: yellow solution.—**On addition of hydrochloric acid to the aqueous solution**: colour becomes rather brighter.—**On addition of caustic soda to the aqueous solution**: colour becomes darker.—**In conc. sulphuric acid**: yellowish red solution; yellow on dilution with water.—**Dyes**: silk and wool greenish yellow from an acid bath, very fast to light but not very fast to washing or milling. Not decolourised by reducing agents. |

## XX. SULPHIDE

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 668 | **Cachou de Laval.** [*P.*]<br>**Cachou de Laval S.** [*P.*]<br>**Katigene Black Brown N.** [*By.*] | | $(C_4H_2S_3)_x$ | The constitution of this and other colouring matters of the sulphide class is at present unknown. |
| 669 | **Sulphine Brown.** [*Lepetit Dollfus.*] | | | |
| 670 | **Vidal Black.** [*P.*] [*V.*]<br>**Vidal Black S.** [*P.*] | Possibly the sulphhydro derivative of a polythiazine. | | |
| 671 | **St. Denis Black.** [*P.*] | | | |
| 672 | **Autogene Black.** [*P.*] | | | |
| 673 | **Cotton Black.** [*D.*] | | | |
| 674 | **Thio Cotton Black.** [*D.*] | | | |
| 675 | **Thiocatechine.** [*P.*]<br>**Thiocatechine S.** [*P.*] | | | |
| 676 | **Cotton Brown.** [*D.*] | | | |
| 677 | **Italian Green.** [*Lepetit Dollfus.*]<br>**Verde Italiano.** | | | |

## COLOURING MATTERS.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Heating organic substances such as sawdust, bran, etc., with sodium sulphide. (The brand S is the bisulphite compound.) | 1873. | Croissant & Bretonnière.<br>Soc. Anon. des Mat. Col. de St. Denis.<br>Fr. Pat. 244585$^{95}$.<br>Richardson & Aykroyd.<br>J. Soc. Chem. Ind. 1896, 328.<br>J. Soc. Dyers, 1896, 232. | **Appearance of dyestuff**: black porous hygroscopic lumps, quickly alterable on exposure to air.—**In water**: readily soluble in the cold to a black solution; on long boiling it becomes insoluble.—**Dyes**: unmordanted cotton brown of excellent fastness to washing, acids, and alkalies, fairly fast to light, but destroyed by chlorine. |
| Action of sodium polysulphide upon oils, fats, or fatty acids. | 1898. | Bellerio.<br>Fr. Pat. 290714. | **Appearance of dyestuff**: black coke-like mass.—**In water**: easily soluble to dark green solution.—**On addition of hydrochloric acid**: complete precipitation with evolution of hydric sulphide.—**On addition of caustic soda**: no change.—**In conc. sulphuric acid**: insoluble.—**Dyes**: unmordanted cotton dark brown, changed to reddish brown by oxidising agents. Shades are fast to soap, acids, and light, but not to chlorine. |
| Fusion of *p*-amidophenol (or of *p*-amidophenol and other compounds) with sodium polysulphide. (The brand S is the bisulphite compound.) | 1893. | Raymond Vidal.<br>Monit. Scient. **95**, 26, 207.<br>Eng. Pats. 13093$^{96}$; 16448$^{96}$; 18489$^{96}$.<br>Fr. Pats. 231188; 258978; 264384; 264510; 264511; 264512; 264867; 264900.<br>Ger. Pats. 84632$^{93}$; 91719$^{93}$; 85330$^{93}$. | **Appearance of dyestuff**: black lumps.—**In water**: dark green solution.—**On addition of caustic soda**: no change.—**On addition of hydrochloric acid**: precipitation with evolution of hydric sulphide.—**Dyes**: unmordanted cotton greenish to bluish black. Very fast to washing, light, alkalies, and acids; fastness increased by subsequent oxidation on the fibre. |
| Fusion of *p*-phenylene diamine with sodium polysulphide. | 1894. | Raymond Vidal.<br>Soc. Anon. des Mat. Col. de St. Denis.<br>Eng. Pat. 23578$^{94}$.<br>Fr. Pat. 236406.<br>Ger. Pat. 85330. | **In aqueous alkalies or alkaline suphides**: bottle green solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: solution becomes bluer.—**In conc. sulphuric acid**: yellowish green solution.—**Dyes**: unmordanted cotton grayish blue to black. |
| Condensation of amido- (or diamido-) oxydiphenylamine with the product of the action of sulphur chloride upon phenol, cresol, or amines, and finally fusing with sodium sulphide. | | Soc. Anon. des Mat. Col. de St. Denis.<br>Eng. Pat. 18409.<br>Fr. Pat. 292400.<br>Ger. Pat. 113893.<br>Z. Farb. Chem. 1902, 137. | **In water**: violet black solution.—**On addition of hydrochloric acid**: brown precipitate.—**On addition of caustic soda**: solution bluer.—**In conc. sulphuric acid**: blackish solution.—**Dyes**: unmordanted cotton black without requiring subsequent fixing. |
| Fusion of *o*-*p*-dinitrodiphenylamine-sulphonic acid with sodium polysulphide. | 1898. | Dahl & Co.<br>Ger. Pats. 101862 & 105058. | **Appearance of dyestuff**: black porous lumps.—**In water**: greenish black solution.—**On addition of hydrochloric acid**: brown precipitate.—**In conc. sulphuric acid**: sparingly soluble with brown colour.—**Dyes**: unmordanted cotton fast brownish black. |
| Fusion of a mixture of dinitrophenol and *p*-amidophenol-sulphonic acid with sodium polysulphide. | 1900. | Dahl & Co.<br>Ger. Pat. 116338. | **Appearance of dyestuff**: black porous lumps.—**In water**: bright greenish blue solution.—**In conc. sulphuric acid**: sparingly soluble with dull green colour; in fuming sulphuric acid a violet solution.—**Dyes**: unmordanted cotton deep black. |
| Fusion of *p*-diamines or acetyl-nitramines with sodium polysulphide. (The brand S is the sulphite compound.) | | R. Vidal.<br>Soc. Anon. des Mat. Col. de St. Denis.<br>Fr. Pat. 239714.<br>Ger. Pat. 82748. | **Appearance of dyestuff**: black lumps.—**In water**: brown solution.—**In aqueous alkalies and sulphides**: brown solution.—**In conc. sulphuric acid**: brownish red solution; precipitate on dilution.—**Dyes**: unmordanted brown of excellent fastness to washing, acids, and alkalies, fairly fast to light, but destroyed by chlorine. |
| Fusion of nitrated diphenylamine-sulphonic acid with sodium polysulphide. | 1898. | Dahl & Co.<br>Ger. Pat. 102821. | **Appearance of dyestuff**: dark brown lumps.—**In water**: brown solution.—**On addition of hydrochloric acid**: brown precipitate.—**In conc. sulphuric acid**: brown solution.—**Dyes**: unmordanted cotton brown, fast to milling and light. |
| Fusion of *p*-nitrophenol with caustic soda, sulphur, and copper sulphate. | 1895. | R. Lepetit.<br>Fr. Pat. 255473$^{96}$.<br>Ger. Pat. 101577$^{96}$.<br>Ital. Pat. LXXVIII. 356. | **Appearance of dyestuff**: black coke-like mass.—**In water**: green solution, which on exposure to air deposits an insoluble green precipitate.—**On addition of hydrochloric acid**: black precipitate with evolution of hydric sulphide.—**Dyes**: unmordanted cotton dull green. Very fast to light, washing, and alkalies, but not to acids. |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 678 | **Immedial Black V.*** [*C.*] | | | |
| 679 | **Thional Black.** [*Lev.*] | | | |
| 680 | **Auronal Black.** [*T.M.*] | | | |
| 681 | **Cross Dye Blacks.** [*R.H.*]<br>**Sulpho Blacks.** [*R.H.*]<br>**Cross Dye Navy.** | | | |
| 682 | **Immedial Sky Blue.** [*C.*] | Probably dimethyl-amido-oxy-phenazthionium-sulphide. | | *Probably:*  $(CH_3)_2N\,[4]\,C_6H_3\left<\begin{matrix}[1]\\ N\\ [2]\\ S\end{matrix}\right>C_6H_2\left\{\begin{matrix}[4]\,OH\\ [5]\,S\end{matrix}\right.$ |
| 683 | **Fast Black B.** [*B.*] | | | |
| 684 | **Fast Black BS.** [*B.*] | | | |
| 685 | **Kryogene Blue G & R.** [*B.*]<br>**Kryogene Brown.** [*B.*] | | | |
| 686 | **Printing Blue for Wool.** [*B.*] | | | |
| 687 | **Printing Black for Wool.** [*B.*] | | | |

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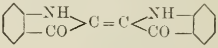
* To the class of sulphide dyestuffs belong also a large number of recently-introduced products such as **Sulphur Black T** [*A.*], **Thionol Black** [*G.*], These colouring matters all dye directly in fast shades from a sulphide bath. Their constitution is not known, but

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Fusion of dinitro-oxydiphenylamine (from chlorodinitrobenzene and *p*-amidophenol) with sodium polysulphide. | 1897. | KALISCHER.<br>L. CASSELLA & Co.<br>Eng. Pat. 25234$^{97}$.<br>Ger. Pat. 103861$^{97}$.<br>Fr. Pat. 271909$^{97}$. | **Appearance of dyestuff**: grayish black powder.—**In water**: bluish black solution.—**On addition of hydrochloric acid**: blackish brown precipitate.—**On addition of caustic soda**: greenish black precipitate.—**In conc. sulphuric acid**: dark violet solution.—**Dyes**: unmordanted cotton from a sodium sulphide bath a deep bluish black, rendered somewhat faster and deeper by fixation (with a chromium salt). The colour is very fast to milling, light, and acids. By oxidation of the (unfixed) colour on the fibre by hydrogen peroxide, or by air and steam, it is converted into an indigo blue (IMMEDIAL BLUE). |
| From *p*-nitrobenzeneazo-*o*-nitrophenol or a mixture of equal mols. of the latter and benzene-azo-*o*-nitrophenol by fusion with sodium polysulphide. | 1900. | C. MENSCHING.<br>LEVINSTEIN Ltd.<br>Eng. Pat. 18756$^{00}$.<br>Ger. Pat. appl. L14963. | **Appearance of dyestuff**: black powder.—**In water and alcohol**: insoluble.—**In aqueous caustic soda**: blue solution.—**In aqueous sodium sulphide**: blue black solution.—**Dyes**: unmordanted cotton from a sulphide bath a deep black, fast to washing, light, and acids. |
| Fusion of dinitro-*p*-amidodiphenylamine (from chlorodinitrobenzene and *p*-phenylene diamine) with sodium polysulphide. | 1901. | WEILER TER-MEER & Co.<br>Eng. Pat. 19267$^{01}$.<br>Fr. Pats. 310713$^{01}$ & additions ; 313052. | **Appearance of dyestuff**: black powder.—**In aqueous sodium sulphide**: blue solution.—**In conc. sulphuric acid**: blue to bluish green solution.—**Dyes**: unmordanted cotton from a sodium sulphide bath a blue black ; fast to washing, light, acids, and alkalies. |
| Fusion of a variety of amido compounds and phenols with sodium polysulphide. | 1890. | TURNER & TURNER.<br>READ HOLLIDAY & SONS.<br>Eng. Pats. 11370$^{90}$ & 17740$^{98}$. | **Appearance of dyestuff**: black lumps.—**In water**: olive green to dark blue solution.—**On addition of hydrochloric acid**: brown precipitates.—**In conc. sulphuric acid**: olive green, blue black, or blue solution ; violet precipitates on dilution.—**Dyes**: unmordanted cotton very fast dark blue to black shades. |
| Fusion of dimethyl-*p*-amido-*p*-oxy-diphenylamine with sodium polysulphide at 110° to 115°. | 1900. | R. HERZ.<br>L. CASSELLA & Co.<br>Eng. Pat. 16247$^{00}$.<br>Fr. Pats. 303524 & 313306.<br>Am. Pat. 693632.<br>J. Soc. Dyers, 1901, 120, 292. | **Appearance of dyestuff**: coppery powder.—**In aqueous caustic soda or sodium sulphide**: blue solution.—**In conc. sulphuric acid**: pure blue solution.—**Dyes**: unmordanted cotton a bright pure blue from a sulphide bath. Very fast to milling, light, acids, and alkalies. |
| Action of sodium sulphide in aqueous solution upon 1 : 8-dinitronaphthalene. | 1893. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 10996$^{93}$.<br>Am. Pats. 545336 & 545337.<br>Ger. Pat. 84989$^{93}$.<br>Fr. Pat. 237610$^{94}$. | **Appearance of dyestuff**: blackish blue paste.—**In water or alcohol**: insoluble.—**In caustic soda or sodium carbonate**: insoluble cold, violet solution on long boiling.—**On addition of hydrochloric acid to the aqueous solution**: greenish black precipitate with evolution of hydric sulphide.—**In conc. sulphuric acid**: slightly soluble with dull green colour.—**Dyes**: unmordanted cotton a fast black from an alkaline bath. Oxidising agents convert it into a fast brown. |
| Action of alkalies upon Fast Black B (No. 683). | 1894. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 22603$^{94}$.<br>Am. Pat. 546576$^{95}$.<br>Ger. Pat. 88847$^{94}$.<br>Fr. Pat. 243142$^{94}$. | **Appearance of dyestuff**: blue black paste.—**In water or alcohol**: bluish violet solution.—**On addition of hydrochloric acid**: colour precipitated.—**In conc. sulphuric acid**: dull green solution.—**Dyes**: unmordanted cotton from a cold concentrated bath a fast deep black. |
| Fusing with sodium polysulphide the product obtained by reduction of 1 : 8-dinitronaphthalene by sodium sulphide in presence of sodium sulphite. | 1897. | R. BOHN & M. H. ISLER.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 9338$^{98}$.<br>Am. Pat. 632170.<br>Fr. Pat. 277530.<br>Ger. Pats. 88236 ; 92471 ; 92472 ; & 103987. | **In water or alcohol**: insoluble.—**In caustic soda**: bluish green to olive green solution.—**On addition of hydrochloric acid to the alkaline solution**: blue precipitate.—**In conc. sulphuric acid**: dull bluish green to brown solution.—**Dyes**: unmordanted cotton from a cold bath blue or brown. |
| Reduction of 1 : 8-dinitronaphthalene with sodium sulphide in presence of sodium sulphite and caustic soda. | 1895. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 20250$^{96}$.<br>Am. Pat. 609327.<br>Ger. Pats. 88236$^{95}$ & 92471$^{96}$.<br>Fr. Pat. 255452. | **Appearance of dyestuff**: violet black metallic powder.—**In water**: violet solution.—**On addition of caustic soda**: bluish green solution.—**In conc. sulphuric acid**: blue solution with green fluorescence.—**Dyes**: unmordanted wool violet blue. Employed in wool printing. |
| Reduction of a mixture of 1 : 5- and 1 : 8-dinitronaphthalene by means of glucose in alkaline solution in presence of sodium sulphite. | 1896. | R. BOHN.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. 20250$^{96}$.<br>Am. Pat. 609327.<br>Ger. Pats. 88236 & 92472.<br>Fr. Pat. 255452. | **Appearance of dyestuff**: bluish black powder.—**In water**: easily soluble with violet colour.—**On addition of caustic soda**: dull bluish green solution.—**In conc. sulphuric acid**: blue solution with moss green fluorescence.—**Dyes**: wool violet black from acid bath. Employed in wool printing. |

**Katigene Black** [*By.*], **Pyrrol Black** [*L.*] **Sulphanil Black** [*K.*], **Pyrogene Blacks and Blues** [*I.*], **Melanogen Blue** [*M.*], **Thiogene Blue** [*M.*], etc. all of them are prepared by the action of sodium polysulphide upon various amido-oxy derivatives of diphenylamine.

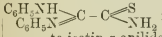
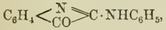
| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 688 | **Anthraquinone Black.** [*B.*] | | | |

## XXI. INDIGO

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 689 | **Indigo.**<br>(Natural indigo from Bengal, Java, Kurpah, Guatemala, Madras, etc.)<br>**Indigo Pure BASF.** [*B.*]<br>**Indigo.** [*M.*] [*G.*] | Indigotine. | $C_{16}H_{10}N_2O_2$ |  |

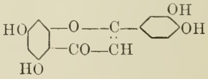
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Fusion of 1 : 5-dinitroanthraquinone with sodium polysulphide. | 1895. | M. H. ISLER.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $15242^{95}$.<br>Am. Pat. 597983.<br>Ger. Pats. $91508^{95}$ & $95484^{96}$.<br>Fr. Pat. 249511. | **Appearance of dyestuff**: black powder.—**In water**: easily soluble with bluish green colour.—**On addition of hydrochloric acid**: colour precipitated.—**In conc. sulphuric acid**: gray black solution.—**Dyes**: unmordauted cotton direct black from an alkaline or sulphide bath. |

## GROUP.

| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| *Natural.*<br>Steeping the leaves of indigo-bearing plants (Indigofera tinctoria, etc.) in water, and oxidation of the extract by air. | | J. BRIDGES-LEE.<br>On Indigo Manufacture (Thacken & Co., London, 1892).<br>C. RAWSON.<br>J. Soc. Chem. Ind. 1899, 467.<br>J. Soc. Dyers, 1899, 166.<br>J. Soc. Arts, 1900, April 6.<br>W. GALLENKAMP.<br>Chem. Ztg. 1901, 197.<br>HOOGEWERFF & TER MUELEN.<br>J. Soc. Chem. Ind. 1900, 1100.<br>BRÉAUDAT & MOLISCH.<br>Rev. Gén. d. Mat. Color. 1900, 253.<br>CALMETTE.<br>Fr. Pats. $301826^{00}$ & addn.<br>GUEGNIER.<br>Fr. Pat. $302169^{00}$.<br>R. MELDOLA.<br>J. Soc. Arts, 1901, 397. | **Appearance of dyestuff**: the natural indigo forms blue lumps or cubes, with a coppery fracture. According to the quality and source it contains from 30 to 80% of pure indigo. The synthetic indigo comes into commerce as a dark blue powder (Indigo Pure powder), as a reddish blue paste (Indigo Pure paste 20%), and as a very fine dark blue paste (Indigo Pure for printing, and Indigo Pure S, 20% paste).—**In water or alcohol**: insoluble.—**In aniline, nitrobenzene, or phenol**: violet blue solution.—**With hydrochloric acid or caustic soda**: no change.—**On heating the dry colour**: it forms a violet vapour and sublimes in glistening dark violet crystals.—**In conc. sulphuric acid**: yellowish green solution, becoming blue on warming.—**Reducing agents**: dissolve it as the leuco compound ("Indigo White").—**Employment**: cotton, wool, and silk are dyed from a vat containing the leuco compound, by alternate steeping and exposure to air. Designs are produced upon indigo dyed cloth by printing an oxidising discharge (*e.g.* chromate or ferricyanide). It is also employed in calico printing by direct application in the form of a paste mixed with caustic soda to cloth prepared with glucose (Schlieper & Baum process), or by production on the fibre from Kalle's Indigo Salt (orthonitrophenyllactic-methyl-ketone).—**Fastness**: indigo, applied by dyeing or printing to cotton, wool, or silk, is very fast to light, washing, and other agents.—**Patents for methods of application**: Eng. Pats. $1294^{97}$; $2021^{97}$; $509^{98}$; $6546^{98}$; and $2689^{00}$. |
| *Synthetic.*<br>(1) Action of acetone and caustic soda upon *o*-nitrobenzaldehyde. | 1882. | A. BAEYER & V. DREWSEN.<br>Ber. **15**, 2856.<br>J. Soc. Chem. Ind. 1882, 131.<br>Eng. Pat. $1266^{82}$.<br>Am. Pats. 257814 & 257815.<br>Ger. Pat. $19768^{82}$. | |
| (2) Fusion of phenyl-glycine (from aniline and chloracetic acid) with caustic alkalies. | 1890. | K. HEUMANN.<br>Ber. **23**, 3043, 3289.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $8726^{90}$.<br>Am. Pat. $622189^{99}$.<br>Fr. Pat. $206567^{90}$.<br>Ger. Pats. $54626^{90}$ & $63310^{91}$. | |
| (3) Fusion of phenyl-glycine with sodium amide or with caustic alkalies and sodium amide. | 1901. | HOMOLKA.<br>DEUTSCHE GOLD & SILBER SCHEIDE ANSTALT, AND MEISTER, LUCIUS, & BRÜNING.<br>Eng. Pats. $13059^{01}$ & $16875^{01}$.<br>Ger. Pat. appl. D12245.<br>Fr. Pat. $312763^{01}$ & additions. | |
| (4) Fusion of phenyl-glycine-*o*-carboxylic acid (from anthranilic acid and chloracetic acid) with caustic alkalies. | 1890.<br>1894. | HEUMANN.<br>KNIETSCH & SEIDEL.<br>Ber. 1890, 3431; 1900, Hofmann number (Brunck).<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pats. $10509^{90}$; $9291^{94}$; & $55966^{98}$.<br>Am. Pats. 534560 & 546165.<br>Ger. Pats. $56273^{90}$; $85494^{94}$; & $105569^{98}$.<br>Fr. Pat. $206982^{90}$ & additions.<br>J. Soc. Chem. Ind. 1901, 332, 554, 802; J. Soc. Dyers, 1901, 138. | |
| (5) Action of yellow ammonium sulphide upon hydrocyancarbodiphenylimide (from diphenylthiourea and carbon disulphide), condensation of the thioamide  $\begin{matrix}C_6H_5NH\\C_6H_5N\end{matrix}\!\!>\!C-C\!<\!\begin{matrix}S\\NH_2\end{matrix}$ formed, to isatin-α-anilide  $C_6H_4\!<\!\begin{matrix}N\\CO\end{matrix}\!>\!C\cdot NHC_6H_5$, by means of conc. sulphuric acid, and reduction of the latter to indigo. | 1899. | SANDMEYER.<br>J. R. GEIGY & CO.<br>Eng. Pats. $15416^{99}$; $15497^{99}$; & $6036^{00}$.<br>Am. Pat. 647280.<br>Fr. Pat. 291416.<br>Ger. Pats. 113848 ; 113978 ; 113979 ; 113980 ; 113981 ; 115169 ; 115464 ; 115465 ; 116563 ; 119280 ; 119831 ; 123887 ; 125916. | |

| No. | Commercial Name. | Scientific Name. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 690 | **Indigo Salt T.**<br>[*K.*] | *o*-Nitrophenyllactic-methyl-ketone. | $C_{10}H_{11}NO_4$ | $C_6H_4\left\{\begin{matrix}[1]\,CH\,(OH)\cdot CH_2\cdot CO\cdot CH_3\\ {[2]}\,NO_2\end{matrix}\right.$ |
| 691 | **Indigo White BASF.**<br>[*B.*]<br>**Indigo Vat.**<br>[*M.*] | Leucindigotine. | $C_{16}H_{12}N_2O_2$ | $C_6H_4\left\{\begin{matrix}[1]\,NH\\ {[2]}\,CO\end{matrix}\right.>CH\cdot CH<\left.\begin{matrix}NH\,[1]\\ CO\,[2]\end{matrix}\right\}C_6H_4$ |
| 692 | **Indigo Carmine.**<br>**Indigo Extract.**<br>**Indigotine.**<br>[*B.*] | Sodium salt of indigotine disulphonic acid or the free acid. | $C_{16}H_8N_2O_8S_2Na_2$ | $C_6H_3(SO_3Na)<\begin{matrix}NH\\ CO\end{matrix}>C=C<\begin{matrix}NH\\ CO\end{matrix}>C_6H_3(SO_3Na)$ |
| 693 | **Indigotine P.**<br>[*B.*] | Sodium salt of indigotine tetrasulphonic acid. | $C_{16}H_6N_2O_{14}S_4Na_4$ | $C_6H_2(SO_3Na)_2<\begin{matrix}NH\\ CO\end{matrix}>C=C<\begin{matrix}NH\\ CO\end{matrix}>C_6H_2(SO_3Na)_2$ |
| 694 | **Methyl Indigo B.**<br>[*Mo.*] | *o*-Methylindigotine. | $C_{18}H_{14}N_2O_2$ | $C_6H_3\left\{\begin{matrix}[1]\,CH_3\\ {[2]}-NH\\ {[3]}-CO\end{matrix}\right.>C=C<\left.\begin{matrix}H_3C\,[1]\\ NH-[2]\\ CO-[3]\end{matrix}\right\}C_6H_3$ |
| 695 | **Methyl Indigo R.**<br>[*Mo.*] | *p*-Methylindigotine. | $C_{18}H_{14}N_2O_2$ | $C_6H_3\left\{\begin{matrix}[1]\,CH_3\\ {[4]}-NH\\ {[3]}-CO\end{matrix}\right.>C=C<\left.\begin{matrix}H_3C\,[1]\\ NH-[4]\\ CO-[3]\end{matrix}\right\}C_6H_3$ |

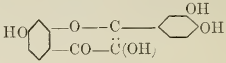
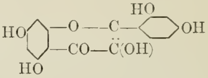
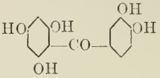
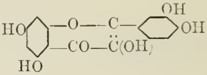
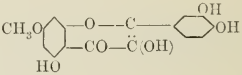
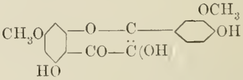
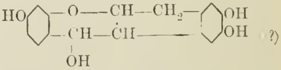
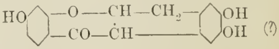
## XXII. NATURAL

| No. | Commercial Name. | Dyeing Principle. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 696 | **Weld Extract.**<br>**(Wau.)**<br>**(Gaude.)** | Luteolin or tetraoxyflavone. | $C_{15}H_{10}O_6$ | *Luteolin :*<br><br> |

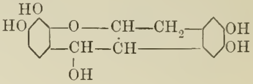
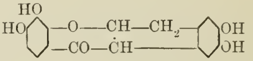
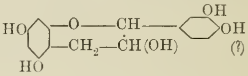
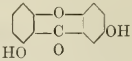
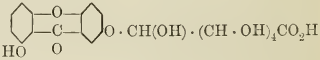
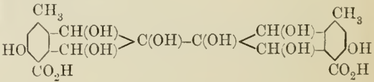
| Method of Preparation. | Year of Discovery. | Discoverer. Patents. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|---|
| Action of dilute caustic soda upon a solution of *o*-nitrobenzaldehyde in acetone. | 1882.<br>1892. | BAEYER & DREWSEN.<br>Ber. **15**, 2857.<br>EUGEN FISCHER & OPPERMANN (method of employment).<br>Chem. Ztg. 1893, 1069.<br>KALLE & CO.<br>Ger. Pat. $73377^{93}$. | **Appearance of dyestuff**: yellow crystalline solid.—**In water**: insoluble.—**In aqueous sodium bisulphite**: dissolves at 35° to 45°, but again separates if the solution is heated to a higher temperature.—**Alkalies**: convert it into indigo blue.—**Employment**: in calico printing, the compound being applied dissolved in bisulphite, and converted into indigo by subsequent treatment with alkalies. |
| Treatment of indigo with reducing agents. | 1805. | PROUST. | **Appearance of dyestuff**: white paste, becoming blue on exposure to air.—**In water**: insoluble.—**In alcohol**: soluble with a blue fluorescence.—**On addition of hydrochloric acid**: no change.—**In caustic soda**: dissolves to a yellowish green solution.—**Employment**: for preparing indigo vats or indigo printing. |
| (1) Sulphonation of indigo with slightly fuming sulphuric acid.<br>(2) Action of fuming sulphuric acid upon phenylglycine or its carboxylic acid. | 1740.<br>1890.<br>1890. | BARTH.<br>CROM, BERZELIUS, & DUMAS.<br>Ann. **22**, 72.<br>B. HEYMANN.<br>Ber. **24**, 1476 & 3066.<br>FR. BAYER & CO.<br>Ger. Pat. 63218.<br>R. KNIETSCH.<br>Ber. **24**, 2086.<br>BAD. ANIL. & SODA FABRIK.<br>Eng. Pat. $8726^{90}$.<br>Am. Pat. 524256.<br>Ger. Pat. $68372^{91}$.<br>Fr. Pat. 206567.<br>See also Ber. **34**, 1860. | **Appearance of dyestuff**: blue, brown, or reddish brown paste or powder.—**In water**: blue solution.—**In alcohol**: slightly soluble.—**On addition of hydrochloric acid**: bluish violet solution; blue on dilution.—**On addition of caustic soda**: olive or green solution; on dilution yellowish green.—**In conc. sulphuric acid**: bluish violet solution; blue on dilution.—**Dyes**: wool blue from an acid bath. |
| Sulphonation of indigo with sulphuric anhydride of 50% $SO_3$ at 70° to 80°. | | TH. REISSIG.<br>JUILLARD.<br>Bull. Soc. Chim. [3] 7, 619. | **Appearance of dyestuff**: violet powder or copper red lumps.—**In water**: easily soluble.—**In alcohol**: insoluble.—**On addition of hydrochloric acid**: blue solution with red dichroism.—**On addition of caustic soda**: red; yellow on dilution.—**In conc. sulphuric acid**: blue solution; on dilution blue with red dichroism.—**Dyes**: wool bluish violet from an acid bath. |
| Condensation of nitrotoluic aldehyde $C_6H_3(NO_2)(CH_3)(CHO)$ [2 : 1 : 3] with acetone and alkali in presence of air. | 1898. | KOETSCHET.<br>SOC. CHIM. DES USINES DU RHÔNE.<br>Eng. Pat. $25634^{98}$.<br>Am. Pat. 662075. | **In alcohol or acetone**: somewhat soluble.—**Dyes**: cotton greenish blue from a reduced vat. |
| Condensation of nitrotoluic aldehyde $C_6H_3(NO_2)(CH_3)(CHO)$ [4 : 1 : 3] with acetone and alkali in presence of air. | 1898. | KOETSCHET.<br>SOC. CHIM. DES USINES DU RHÔNE.<br>Eng. Pat. $25634^{98}$.<br>Am. Pat. 662075. | **In alcohol or acetone**: nearly insoluble.—**Dyes**: cotton reddish blue from a reduced vat. |

## DYESTUFFS

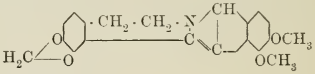
| Source and Method of Preparation. | Investigators. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|
| An extract of the dried herbaceous plant, Reseda luteola or "Dyer's Rocket," which was formerly much cultivated in many parts of Europe.<br>Luteolin was obtained synthetically by Kostanecki. | CHEVREUL, Ann. chim. phys. [2], **82**, 53.<br>MOLDENHAUER, Ann. **100**, 180.<br>SCHUTZENBERGER & PARAFF, Jahresb. 1861, 707.<br>HLASIWETZ & PFAUNDLER, Ann. **112**, 107.<br>HERZIG, Ber. **29**, 1013; **30**, 656.<br>PERKIN, J. Chem. Soc. 1896, 206, 799.<br>v. KOSTANECKI, Ber. **33**, 3410. | **Appearance and properties of dyestuff**: pure luteolin crystallises in small yellow needles ($+1\frac{1}{2}H_2O$) of m.p. about 320°, sparingly soluble in water, readily in alcohol, and in aqueous alkalies with a yellow colour. It is an adjective dyestuff giving fast yellow shades upon alumina, chrome, or tin mordants.—**Employment**: weld is now only used to a small extent for dyeing silk and wool mordanted with alumina or tin. |

| No. | Commercial Name. | Dyeing Principle. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 697 | **Young Fustic.**<br>**Cotinin.**<br>**(Bois jaune de Hongrie.)**<br>**(Fisetholz.)** | Fisetin or trioxyflavonol. | $C_{15}H_{10}O_6$ | *Fisetin :*  |
| 698 | **Fustic**<br>(chips or extract).<br>**Old Fustic.**<br>**(Bois Jaune.)**<br>**(Gelbholz.)** | Morin or tetraoxyflavonol<br>and<br>Maclurin or pentaoxybenzophenone. | *Morin :* $C_{15}H_{10}O_7$<br>*Maclurin :* $C_{13}H_{10}O_6$ | *Morin :*  <br>*Maclurin :*  |
| 699 | **Quercitron**<br>(ground bark or extract).<br>**Flavine.** | Quercitrin (glucoside)<br>and<br>Quercetin or tetraoxyflavonol. | *Quercitrin :* $C_{21}H_{22}O_{12}$<br>*Quercetin :* $C_{15}H_{10}O_7$ | *Quercetin :*  |
| 700 | **Persian Berries**<br>(crushed or extract).<br>**Yellow Berries.**<br>**(Kreuzbeeren.)**<br>**(Gelbbeeren.)**<br>**Rhamnine.** | Rhamnetin or quercetin-monomethyl ether, Rhamnazin or quercetin-dimethyl ether<br>and<br>Quercetin<br>(all present as glucosides). | *Rhamnetin :* $C_{16}H_{12}O_7$<br>*Rhamnazin :* $C_{17}H_{14}O_7$ | *Rhamnetin :*  <br>*Rhamnazin :*  |
| 701 | **Brazil Wood**<br>(chips and extract).<br>**Red Wood.**<br>**Sapan Wood.**<br>**Peach Wood.**<br>**(Bois de Fernambouc.)**<br>**(Rothholz.)** | Brazilin (leuco compound)<br>and<br>Brazilein (dyestuff proper). | *Brazilin :* $C_{16}H_{14}O_5$<br>*Brazilein :* $C_{16}H_{12}O_5$ | *Brazilin :*  <br>*Brazilein :*  |

| Source and Method of Preparation. | Investigators. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|
| The wood (or extract therefrom) of the Venetian sumach, Rhus cotinus, a tree belonging to the family of Terebinthaceæ, growing in Southern and Eastern Europe, the Levant, Jamaica, etc. | J. Schmid, Ber. **19**, 1734.<br>Herzig, Mon. f. Chem. **12**, 177, 190 ; **14**, 39 ; **15**, 688 ; **17**, 421 ; Ber. **28**, 293.<br>Perkin, J. Chem. Soc. 1895, 648 ; 1896, 1303.<br>v. Kostanecki, Ber. **28**, 2302. | **Appearance and properties of dyestuff:** the colouring matter is contained in the wood as a tannic glucoside, "Fustin tannide," which crystallises in easily soluble yellowish white needles. It is readily hydrolysed to fisetin, which when pure forms small lemon yellow needles or prismatic crystals $(+6H_2O)$ of m.p. above 360° ; insoluble in cold water, very slightly in hot, readily in alcohol. Is a mordant dyestuff.—**Employment:** young fustic has a limited use for dyeing wool orange and scarlet (chrome or tin mordant) and for dyeing leather. It is tolerably fast to milling and soap, but very fugitive to light. |
| The wood (or extract therefrom) of the Morus tinctoria, a tree belonging to the family of the Urticaceæ, growing in North, Central, and South America, Cuba, Jamaica, etc. | Wagner, J. pr. Chem. **51**, 82 ; Ann. **76**, 347 ; **80**, 315.<br>Hlasiwetz & Pfaundler, Ann. **127**, 351.<br>Benedikt & Hazura, Mon. f. Chem. **5**, 165, 667 ; Ber. **8**, 606.<br>Perkin, J. Chem. Soc. 1895, 649 ; 1896, 792.<br>Ciamician & Silber, Ber. **27**, 1627 ; **28**, 1393.<br>v. Kostanecki, Ber. **27**, 1994. | **Appearance and properties of dyestuff:** pure morin forms glistening colourless needles of m.p. 285°, very sparingly soluble in water, more readily in alcohol. It gives deep yellow solutions in aqueous alkalies, and is an adjective dyestuff producing various shades of yellow with alumina, tin, and chrome mordants, olive shades with iron and copper. Pure maclurin crystallises in pale yellow prismatic crystals $(+H_2O)$ of m.p. 200°, rather sparingly soluble in water, easily in alcohol. It is a very weak dyestuff. Combines with diazo compounds.—**Employment:** fustic is chiefly used in wool dyeing for yellows and mixed shades (upon a chrome or alumina mordant). Also as a bottom for black. |
| The ground bark (or extract therefrom) of the Quercus tinctoria, an oak indigenous to North America.<br>"Flavine, yellow shade," is prepared by extracting the bark with water under pressure.<br>"Flavine, red shade," is obtained by boiling the alkaline extract with dilute sulphuric acid.<br>The former, therefore, chiefly consists of quercetrin, the latter of querectin. | Bancroft, introduction in 1775.<br>Bolley, Ann. **37**, 101 ; **115**, 57.<br>Rigaud, Ann. **90**, 283.<br>Hlasiwetz & Pfaundler, J. pr. Chem. **94**, 65.<br>Liebermann & Hamburger, Ber. **12**, 1178 ; **17**, 1680.<br>Herzig, Mon. f. Chem. **5**, 72 ; **6**, 863 ; **9**, 537 ; **12**, 172 ; **14**, 53 ; **15**, 697.<br>Perkin & Pate, J. Chem. Soc. 1895, 647.<br>v. Kostanecki, Ber. **28**, 2302. | **Appearance and properties of dyestuff:** usually employed as a thick extract or as an olive yellow to brown powder ("Flavine"). Pure quercitrin crystallises from water in pale yellow needles $(+H_2O)$ of m.p. 168°. It is readily hydrolysed by acids to quercetin. Quercetin forms fine yellow crystals, slightly soluble in water, readily in alcohol and aqueous alkalies forming yellow solutions. It is an adjective dyestuff giving the following colours with metallic mordants:—alumina, greenish yellow; chrome, dull yellow; tin, bright orange; iron, olive to greenish black.—**Employment:** extensively used in calico printing and wool dyeing for production of yellows and browns (chiefly upon chrome or iron and alumina mordants). Also for toning logwood blacks. |
| The dried berries (or extract therefrom) of various species of Rhamnus (Rhamnus tinctoria, infectoria, oleoides, alaterna, etc.) trees of the Buckthorn family growing in Asia Minor. | Kane, Phil. Mag. **23**, 3 ; J. pr. Chem. **29**, 481.<br>Galatly, Edin. New Phil. J. **7**, 252.<br>Schützenberger, Ann. chim. phys. [4] **15**, 118 ; Bull. Soc. Chim. **10**, 179.<br>Liebermann & Hörmann, Ann. **196**, 299.<br>Herzig, Mon. f. Chem. **6**, 889 ; **9**, 548 ; **12**, 172.<br>Perkin & others, J. Chem. Soc. 1895, 496, 650 ; 1897, 818. | **Appearance and properties of dyestuff:** the glucoside of rhamnetin, xanthorhamnin, forms easily soluble golden yellow microscopic crystals, having no dyeing power itself, but readily hydrolysed to the dyestuff rhamnetin. The latter is a deep yellow crystalline powder, very sparingly soluble in water, but dissolving with a yellow colour in alkalies. Rhamnazin (also present as glucoside) crystallises in bright yellow needles of m.p. 215°, sparingly soluble in alcohol, soluble with an orange yellow colour in aqueous alkalies. Both rhamnetin and rhamnazin are adjective dyestuffs, the latter being much the weaker.—**Employment:** Persian berries are largely used for cotton printing in conjunction with a tin, chrome, or alumina mordant, giving valuable bright yellow to orange shades, those upon chrome being very fast to soap and chlorine. |
| The wood of several species of Cæsalpinia, leguminous trees growing in the Tropics, Central and South America, the Antilles, Africa, Asia, and the West Indies.<br>The extract is prepared by boiling out the wood with water and concentration in vacuo. | Chevreul, Ann. chim. phys. **66**, 225.<br>Liebermann & Burg, Ber. **9**, 1883.<br>Schall & Dralle, Ber. **17**, 375 ; **20**, 3365 ; **21**, 3009 ; **22**, 1547 ; **23**, 1430 ; **25**, 18 : **27**, 524.<br>Hummel & Perkin, Ber. **15**, 2343.<br>Buckha & Erck, Ber. **17**, 683 ; **18**, 1138.<br>Fuerstein & v. Kostanecki, Ber. **32**, 1024.<br>Herzig, Mon. f. Chem. **12**, 187 ; **14**, 56 ; **15**, 139 ; **16**, 913.<br>Gilbody, Perkin, & Yates, J. Chem. Soc. 1901, 1396. | **Appearance and properties of dyestuff:** pure brazilin crystallises from water in transparent yellowish or colourless needles $(+H_2O)$. Its alkaline solution rapidly oxidises in the air to a carmine red solution of brazilein. The latter crystallises in gray silvery plates, sparingly soluble in water, easily in alkalies. It is an adjective dyestuff, giving red lakes with chromium, aluminium, and tin mordants.—**Employment:** chiefly as extract of Brazil wood for cotton printing (with metallic mordants). Also upon chromed wool. Owing to deficient fastness to soap, alkalies, and acids its employment is limited and rapidly decreasing. |

| No. | Commercial Name. | Dyeing Principle. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 702 | **Logwood**<br>(chips or extract).<br>**Campechy Wood.**<br>**(Bois de Campêche.)**<br>**(Blauholz.)**<br>**Hematine Paste & Powder.**<br>**Noir reduit.**<br>**Steam Black.** | Hæmatoxylin (leuco compound) and Hæmatein (dyestuff proper). | *Hæmatoxylin :*<br>$C_{16}H_{14}O_6$<br>*Hæmatein :*<br>$C_{16}H_{12}O_6$ | *Hæmatoxylin :*<br><br>*Hæmatein :* (?)<br> |
| 703 | **Cutch.**<br>**Catechu.**<br>**Gambier.**<br>**Japan Earth.**<br>**(Cachou.)**<br>**(Katechu.)** | Catechin and Catechu-tannic acid, together with some Quercetin. | *Catechin :*<br>$C_{15}H_{14}O_6$ |  |
| 704 | **Indian Yellow.**<br>**Purree.**<br>**Piuri.** | Magnesium salt of Euxanthic acid together with some Euxanthone. | *Euxanthone :*<br>$C_{13}H_8O_4$<br>*Euxanthic acid :*<br>$C_{19}H_{18}O_{11}$ | *Euxanthone :*<br><br>*Euxanthic acid :*<br> |
| 705 | **Sandal Wood.**<br>**Barwood.**<br>**Camwood.** | Santaline or santalic acid (?). | | Unknown. |
| 706 | **Cochineal.**<br>**Cochinille.**<br>**Carmine.**<br>**Carmine Lake.** | Carminic acid. (Carmine lake consists substantially of the aluminium salt of carminic acid.) | $C_{22}H_{24}O_{12}$ | *Carminic acid :*<br><br>(?) |
| 707 | **Turmeric.**<br>**(Curcuma.)**<br>**(Safran d'Inde.)** | Curcumine. | $C_{21}H_{20}O_6$ | Unknown. |

| Source and Method of Preparation. | Investigators. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|
| The wood of the Hæmatoxylon campechianum, a tree growing in Central America, Cuba, Hati, Jamaica, Domingo, Martinique, etc.<br>The extract is prepared by boiling out the wood with water and concentrating in vacuo. | Chevreul, Ann. chim. phys. [2] **82**, 53, 126.<br>O. L. Erdmann, J. pr. Chem. **26**, 193 ; **36**, 205 ; **75**, 318.<br>Hesse, Ann. **109**, 332.<br>E. Erdmann & Schultz, Ann. **216**, 234.<br>Rheim, Ber. **4**, 329.<br>Herzig, Mon. f. Chem. **16**, 906 ; **19**, 738 ; **20**, 461.<br>Hummel & A. G. Perkin, Ber. **15**, 2337.<br>Gilbody, W. H. Perkin, & Yates, J. Chem. Soc. 1901, 1396 ; Proc. 1899, 27 ; 1900, 105. | **Appearance and properties of dyestuff:** logwood extract is a brown treacly liquid or semi-solid mass, soluble in alkalies to a purple solution. Pure hæmatoxylin forms colourless crystals $(+3H_2O)$ slightly soluble in cold, easily in hot water. Its alkaline solution rapidly oxidises in the air to a bluish violet solution of hæmatein. The latter forms in reddish crystals with green metallic lustre, sparingly soluble in hot water to a yellowish brown solution. It is an adjective dyestuff, giving with metallic mordants the following colours:—alumina, blue ; chrome, blackish blue ; iron, black ; copper, greenish black ; tin, violet.—**Employment:** chiefly for dyeing blacks, with a chrome mordant for wool, with an iron mordant for silk, and with a chrome or an iron and alumina mordant for cotton. Also as a substitute or bottom for indigo blues. In calico printing logwood blacks are produced by printing the extract together with a chrome mordant and an oxidising agent, or by applying a ready-prepared chrome lake dissolved in sodium bisulphite ("Noir reduit"). |
| The dried sap of various species of Acacia or Mimosa, leguminous trees growing in the East Indies. Also from areca or betel nut (Bengal cutch) and from species of Uncaria belonging to the family of Cinchonaceæ (Gambier cutch). | Berzelius, Jahresb. **14**, 235.<br>Svanberg, Wachenroder, & others, Ann. Pharm. **24**, 215 ; **31**, 72 ; **37**, 306, 320, 336.<br>Neubauer & others, Ann. **96**, 337 ; **128**, 285 ; **134**, 118.<br>Etti, Ann. **186**, 327 ; Mon. f. Chem. **2**, 547.<br>Liebermann & Fauchert, Ber. **13**, 694.<br>Perkin & Yoshitake, J. Chem. Soc. 1902, 1160. | **Appearance and properties of dyestuff:** pure catechin crystallises in fine white silky needles, sparingly soluble in cold water, very easily in hot, readily soluble in alcohol. It has a slightly acid astringent taste. It dissolves in aqueous alkalies, forming very oxidisable solutions, and combines with diazo compounds.—**Employment:** cutch is extensively used for production of fast browns upon cotton by dyeing or printing and subsequent fixation with bichromate or with copper salts. Also in conjunction with mordant colours, *e.g.* logwood, for various other shades (black, olive, etc.), and for dyeing and weighting silk (iron mordant). |
| Prepared at Monghyr in Bengal by heating the urine of cows fed on the leaves of the Mango. | Gräbe, Ann. **254**, 267 ; Ber. **15**, 1675 ; **16**, 862 ; **19**, 2607 ; **20**, 2331.<br>Erdmann, J. pr. Chem. **33**, 190 ; **37**, 385.<br>Stenhouse, Ann. **60**, 423.<br>Baeyer, Ann. **155**, 257.<br>v. Kostanecki & others, Ber. **19**, 2918 ; **24**, 3983 ; **26**, 71 ; **27**, 1989. | **Appearance and properties of dyestuff:** Indian yellow appears in commerce in the form of round balls of a brown or greenish colour. Pure euxanthic acid crystallises from alcohol in pale yellow glistening plates of m.p. 156°, soluble in hot water, sparingly in cold. It is split up by hydrolysis into glycuronic acid and euxanthone. It is a mordant dyestuff. Euxanthone, which crystallises in yellow needles of m.p. 240°, sparingly soluble in water, is a much weaker colouring matter than euxanthic acid.—**Employment:** as a painter's pigment, chiefly used in fresco painting. Not employed in dyeing. |
| The rasped or powdered wood of various species of Pterocarpus and Baphia, trees belonging to the family of Dalbergieæ growing in Africa, the East Indies, Ceylon, etc. | Pelletier, Ann. chim. phys. [2] **51**, 193.<br>Bolley, Ann. **62**, 150.<br>Leo Meyer, Ann. **72**, 320.<br>Weyermann & Häffely, Ann. **74**, 226.<br>Franchimont, Ber. **12**, 14. | **Appearance and properties of dyestuffs:** the dyeing principles of these woods are not known with certainty, and require reinvestigation. They are adjective dyestuffs giving red lakes with alumina, chrome, tin, and iron ; and also dyeing wool directly.—**Employment:** sandalwood, barwood, and camwood have a limited employment for dyeing wool by the "saddening" method (alumina, chrome, tin, or iron mordant), and as a bottom for indigo. Also used for dull reds upon cotton (tin mordant). They are fast to acids, but sensitive to alkalies and light. |
| The dried bodies of the female cochineal insect, Coccus cacti, which lives upon plants belonging to the family of Opuntia or Prickly Pear growing in Mexico and Central America. Contains about 10% of true colouring matter. Carmine is obtained by precipitating cochineal extracts with acid salts. | Pelletier & Caventon, Ann. chim. phys. [2] **8**, 250.<br>Warren de la Rue, Ann. **64**, 1.<br>Schützenberger, Ann. chim. phys. [3] **54**, 52.<br>Liebermann, Ber. **18**, 1969 ; **30**, 688, 1731 ; **31**, 2080 ; Ann. **163**, 105.<br>Will & Leymann, Ber. **18**, 3180.<br>v. Miller & Rohde, Ber. **26**, 2647 ; **30**, 1760.<br>Schunck & Marchlewski, Ber. **27**, 2980. | **Appearance and properties of dyestuff:** pure carminic acid crystallises in bright red prisms, tolerably soluble in water, less in alcohol. The aqueous solution is yellowish red, becoming crimson on addition of alkalies. It is an acid compound and a mordant dyestuff giving scarlet and crimson lakes with tin and alumina respectively, and a green lake with uranium.—**Employment:** for dyeing a scarlet upon wool (tin mordant) which is very fast to light, air, etc., but not to soap. Formerly used in calico printing (albumin colours) and for silk dyeing (alumina or tin mordant). Still much employed for preparation of pigments, etc. |
| The ground root of Curcuma tinctoria, a plant belonging to the ginger tribe, growing in India, China, Cochin-China, and the East Indies. | Vogel, Ann. **44**, 297.<br>Daube, Ber. **3**, 609.<br>Iwanof-Gejewski, Ber. **3**, 625 ; **5**, 1103 ; **6**, 196.<br>Kachler, Ber. **3**, 713.<br>Ciamician & Silber, Ber. **30**, 192.<br>Jackson, Am. Chem. Soc. **4**, 77 & 360 ; Ber. **14**, 485.<br>Radcliffe, J. Soc. Dyers, 1897, 25. | **Appearance and properties of dyestuff:** turmeric powder contains 3 or 4% of pure curcumine. The latter crystallises in bright red needles or yellow prisms with a blue reflex. It melts at 178°, and is insoluble in water, readily soluble in alcohol. Dissolves in aqueous alkalies to a brownish red solution, and gives a red compound with boric acid which is changed to blue by alkalies.—**Employment:** dyes cotton direct with a mordant a bright greenish yellow. Still used in dyeing to a small extent (chiefly for shading) in spite of its want of fastness to light, soap, and alkalies. Also employed for colouring butter, cheese, curry-powder, wood, wax, etc. |

| No. | Commercial Name. | Dyeing Principle. | Empirical Formula. | Constitutional Formula. |
|---|---|---|---|---|
| 708 | **Safflower.**<br>**Bastard Saffron.**<br>**(Safflor.)** | Carthamine and a yellow dyestuff. | *Carthamine:*<br>$C_{14}H_{14}O_7$ | Unknown. |
| 709 | **Annatto.**<br>**(Orlean.)** | Bixin. | $C_{28}H_{34}O_5$ | Unknown. |
| 710 | **Archil**<br>(extract or powder).<br>**Orchil.**<br>**Cudbear.**<br>**(Orseille.)**<br>**(Pourpre Français.)** | Alkali salt of orcein. | $C_{14}H_{14}N_2O_6$<br>(?) | Unknown; possibly an oxazine derived from orcinol. |
| 711 | **Berberine.** | Berberine. | $C_{20}H_{17}NO_4$ |  |

| Source and Method of Preparation. | Investigators. Literature. | Behaviour with Reagents. Shade and Dyeing Properties. Method of Employment. |
|---|---|---|
| The dried petals of Carthamus tinctorius or Dyer's Thistle, which grows in many parts of Europe, Persia, Egypt, and South America. | Salvetat, Ann. chim. phys. [3] **25**, 337.<br>Schlieper, Ann. **58**, 357.<br>Malin, Ann. **136**, 117. | **Appearance and properties of dyestuff:** carthamin forms dark red crystalline crusts, sparingly soluble in water, easily in alcohol. Dissolves in alkalies with a deep yellowish red colour.—**Employment:** dyes silk and cotton direct red without a mordant, but owing to its extreme fugitiveness no longer used in dyeing. Under the names of "Rouge végétale," "Safflower Carmine," etc., it is employed as a cosmetic and as a pigment. |
| The seed of the Bixa Orellana, a tree growing in Central America, the East Indies, and the Antilles. | Kerndt, Jahresb. 1849, 475.<br>Piccard, Dingl. **162**, 139.<br>Bolley & Mylius, J. pr. Chem. **93**, 359.<br>Etti, Ber. **7**, 446 ; **11**, 864.<br>Zwick, Ber. **30**, 1972.<br>v. Kostanecki & Maron, Ber. **31**, 728. | **Appearance and properties of dyestuff:** pure bixin forms dark red metallic glistening microscopic plates of m.p. 175°, insoluble in water, soluble in aqueous alkalies, sparingly soluble in alcohol. It dissolves in conc. sulphuric acid with a cornflower blue colour which on dilution becomes dark green.—**Employment:** annatto dyes cotton (direct or upon a tin mordant) a bright orange, fast to soap and acids, but very fugitive to light. It is chiefly used for colouring butter, cheese, etc., very little for dyeing. |
| From various species of lichen belonging to the families of Roccella and Lecanora by treatment with ammonia and air. Orcein is also formed from isolated orcinol by the same treatment. | Thillaye, Chandois, & Martin, Pol. Centralbl. 1854, 493 & 1326.<br>Guinon, Rép. de chim. app. par Persoz, I., 189.<br>Gerhardt & Laurent, Ann. chim. phys. [3] **24**, 315.<br>Robiquet, Ann. chim. phys. [2] **47**, 238.<br>Liebermann, Ber. **7**, 247 ; **8**, 1649.<br>Zulkowski & Peters, Mon. f. Chem. **11**, 227. | **Appearance and properties of dyestuff:** orcein is a carmine red crystalline powder, insoluble in water, soluble in alcohol to a carmine red solution. Dissolves in aqueous alkalies with a bluish violet colour.—**Employment:** for dyeing wool and silk (with or without a mordant). The bluish red so obtained is very level and "bloomy," but not fast to light. It is now largely replaced by level dyeing azo colours. |
| Occurs in the root of the common barberry (Berberis communis) and in many other plants, *e.g.* Columbo root (Cocculus palmatus), Hydrastis Canadensis, Coptis tecta, Woodumpar, etc. | Chevalier & Pelletan, J. chim. med. (1826) **2**, 314.<br>Buchner & Herberger, Ann. **24**, 228.<br>Fleitmann, Ann. **59**, 160.<br>Perrins, Ann. (1861) Suppl. 2, 176.<br>W. H. Perkin, J. Chem. Soc. 1889, 63 ; 1890, 992.<br>A. G. Perkin, J. Chem. Soc. 1895, 413 ; 1897, 1198. | **Appearance and properties of dyestuff:** pure berberine crystallises from water in glistening yellow needles (+6$H_2O$), readily soluble in hot water and alcohol, and having a very bitter taste. It dissolves in conc. sulphuric acid with a yellow colour which on warming becomes olive green. It is the only natural basic colouring matter, forms golden yellow stable salts with acids, and dyes cotton mordanted with tannin.—**Employment:** to a small extent for dyeing silk and leather yellow. |

# A Cross-Index of Green-Schultz and Schultz-Green Numbers

By H. WALES

*(Sixtieth Contribution from the Color Laboratory, U. S. Bureau of Chemistry, Washington, D. C.)*

THE following tables giving the numbers in Schultz's Farbstofftabellen 1914 edition, which correspond to the numbers in Green's Systematic urvey of the Organic Colouring Matters, 1908 edition, have been prepared for use in the Color Laboratory, U. S. Bureau of Chemistry. Several Schultz dyes are given in footnotes in Green. In such cases the Green number is given in italics.

## GREEN-SCHULTZ NUMBERS

| Green Nos. | Schultz Nos. |
|---|---|
| 1 | 5 |
| 2 | — |
| 3 | 6 |
| 4 | 7 |
| 5 | — |
| 6 | — |
| 7 | 31 |
| 8 | 137 |
| 9 | — |
| 10 | 35 |
| 11 | 36 |
| 12 | — |
| 13 | 37 |
| 14 | 38 |
| 15 | 39 |
| 16 | 32 |
| 17 | 33 |
| 18 | 34 |
| 19 | — |
| 20 | 40 |
| 21 | 41 |
| 22 | 43 |
| 23 | 47 |
| 24 | 48 |
| 25 | 49 |
| 26 | 58 |
| 27 | — |
| 28 | 52 |
| 29 | 53 |
| 30 | 54 |
| 31 | 56 |
| 32 | 57 |
| 33 | 55 |
| 34 | 59 |
| 35 | — |
| 36 | 61 |
| 37 | 65 |
| 38 | 67 |
| 39 | 60 |
| 40 | 62 |
| 41 | 69 |
| 42 | — |
| 43 | 70 |
| 44 | — |
| 45 | 71 |
| 46 | — |
| 47 | 74 |
| 48 | 75 |
| 49 | 76 |
| 50 | 77 |
| 51 | 78 |
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| 58 | 104 |
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| 67 | 114 |
| 68 | 116 |
| 69 | 84 |
| 70 | 86 |
| 71 | 94 |
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| 74 | 100 |
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| 82 | 125 |
| 83 | 126 |
| 84 | 143 |
| 85 | 144 |
| 86 | 145 |
| 87 | 138 |
| 88 | 139 |
| 89 | 142 |
| 90 | — |
| 91 | 140 |
| 92 | 141 |
| 93 | 146 |
| 94 | 23 |
| 95 | 134, 136 |
| 96 | — |
| 97 | 151 |
| 98 | 150 |
| 99 | — |
| 100 | — |
| 101 | 160 |
| 102 | 161 |
| 103 | 163 |
| 104 | 167 |
| 105 | 166 |
| 106 | 169 |
| 107 | 168 |
| 108 | 170 |
| 109 | — |
| 110 | 171 |
| 111 | 172 |
| 112 | 174 |
| 113 | 176 |
| 114 | 175 |
| 115 | — |
| 116 | 177 |
| 117 | 178 |
| 118 | 186 |
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| 120 | 203 |
| 121 | 204 |
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| 123 | 158 |
| 124 | 25 |
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| 127 | — |
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| 130 | 194 |
| 131 | — |
| 132 | 182 |
| 133 | — |
| 134 | 208 |
| 135 | 209 |
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| 141 | 220 |
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| 148 | 228 |
| 149 | 240 |
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| 151 | 235 |
| 152 | 233 |
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| 154 | 236 |
| 155 | 230 |
| 156 | 231 |
| 157 | 237 |
| 158 | 238 |
| 159 | 248 |
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| 161 | 246 |
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| 163 | 247 |
| 164 | 251 |
| 165 | — |
| 166 | — |
| 167 | 252 |
| 168 | 253 |
| 169 | 255 |
| 170 | 254 |
| 171 | — |
| 172 | 245 |
| 173 | 243 |
| 174 | 244 |
| 175 | 274 |

| Green Nos | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. |
|---|---|---|---|---|---|---|---|
| 176 | — | 243 | 313 | 310 | 408 | 377 | 473 |
| 177 | 262 | 244 | 320 | 311 | 410 | 378 | 479 |
| 178 | 263 | 245 | 321 | 312 | 411 | 379 | 477 |
| 179 | — | 246 | 322, 378, 409 | 313 | 417 | 380 | 480 |
| 180 | 275 | 247 | 324 | 314 | 412 | 381 | 481 |
| 181 | Sulphonated 275 | 248 | 327 | 315 | 418 | 382 | 482 |
| 182 | 276 | 249 | 328 | 316 | 421 | 383 | 486 |
| 183 | 266 | 250 | 329 | 317 | 423 | 384 | 485 |
| 184 | 269 | 251 | 333 | 318 | 419, 422, 424 | 385 | 487 |
| 185 | 267 | 252 | 326 | 319 | 426 | 386 | 488 |
| 186 | — | 253 | 334 | 320 | 413 | 387 | 489 |
| 187 | 270 | 254 | 337 | 321 | 414 | 388 | — |
| 188 | 272 | 255 | 354 | 322 | 416 | 389 | — |
| 189 | 271 | 256 | 352 | 323 | 428 | 390 | — |
| 190 | 294 | 257 | 353 | 324 | 427 | 391 | — |
| 191 | 296 | 258 | 331 | 325 | 429 | 392 | — |
| 192 | — | 259 | 356 | 326 | 430 | 393 | 491 |
| 193 | — | 260 | 357 | 327 | 380 | 394 | 1 |
| 194 | — | 261 | 358 | 328 | 303 | 395 | — |
| 195 | 297 | 262 | 355 | 329 | 304 | 396 | 2 |
| 196 | 279 | 263 | — | 330 | 305 | 397 | 3 |
| 197 | 283 | 264 | — | 331 | — | 398 | 4 |
| 198 | 291 | 265 | 360 | 332 | 301 | 399 | 9 |
| 199 | 292 | 266 | — | 333 | 302 | 400 | 9 |
| 200 | 290 | 267 | — | 334 | — | 401 | 10 |
| 201 | 284 | 268 | 376 | 335 | — | 402 | 10 |
| 202 | 285 | 269 | 394 | 336 | — | 403 | 12 |
| 203 | 286 | 270 | 392 | 337 | — | 404 | 18 |
| 204 | 287 | 271 | 395 | 338 | — | 405 | 11 |
| 205 | — | 272 | 362 | 339 | — | 406 | 11 |
| 206 | 431 | 273 | — | 340 | — | 407 | 13 |
| 207 | 432 | 274 | 374 | 341 | — | 408 | 13 |
| 208 | 433 | 275 | 373 | 342 | — | 409 | 15 |
| 209 | 434 | 276 | 393 | 343 | — | 410 | — |
| 210 | 295 | 277 | 363 | 344 | — | 411 | 14 |
| 211 | 300 | 278 | 364 | 345 | — | 412 | 205 |
| 212 | — | 279 | 365 | 346 | — | 413 | 207 |
| 213 | 483 | 280 | 366 | 347 | — | 414 | 206 |
| 214 | 484 | 281 | 370 | 348 | — | 415 | 16 |
| 215 | — | 282 | 367 | 349 | 444 | 416 | 17 |
| 216 | 350 | 283 | 369 | 350 | 445 | 417 | 770 |
| 217 | 315 | 284 | 371 | 351 | 440 | 418 | 769 |
| 218 | — | 285 | 372 | 352 | 439 | 419 | 772 |
| 219 | 317 | 286 | 375 | 353 | 438 | 420 | 931 |
| 220 | 342 | 287 | 377 | 354 | 447 | 421 | 771 |
| 221 | 351 | 288 | 381 | 355 | 446 | 422 | 773 |
| 222 | — | 289 | 382 | 356 | 451 | 423 | 774 |
| 223 | — | 290 | — | 357 | 450 | 424 | 775 |
| 224 | — | 291 | 387 | 358 | 452 | 425 | 493 |
| 225 | 340 | 292 | 388 | 359 | 456 | 426 | 494 |
| 226 | 343 | 293 | 391 | 360 | 436 | 427 | 495 |
| 227 | 344 | 294 | 386 | 361 | 437 | 428 | 499 |
| 228 | 347 | 295 | 397 | 362 | 442 | 429 | 496 |
| 229 | 348 | 296 | 396 | 363 | 448 | 430 | 500 |
| 230 | 349 | 297 | 399 | 364 | 443 | 431 | 497 |
| 231 | 345 | 298 | 398 | 365 | 449, 454, 457 | 432 | 501 |
| 232 | 346 | 299 | 404 | 366 | 453 | 433 | 502 |
| 233 | — | 300 | — | 367 | 455 | 434 | 504 |
| 234 | 319 | 301 | 401 | 368 | 461 | 435 | 505 |
| 235 | 314 | 302 | — | 369 | 459 | 436 | 506 |
| 236 | 306 | 303 | 402 | 370 | 460 | 437 | — |
| 237 | — | 304 | 403 | 371 | 478 | 438 | — |
| 238 | 310 | 305 | — | 372 | 474 | 439 | 546 |
| 239 | 309 | 306 | 406 | 373 | 475 | 440 | 549 |
| 240 | 307 | 307 | 405 | 374 | 467 | 441 | 544 |
| 241 | 316 | 308 | — | 375 | 468 | 442 | 545 |
| 242 | 312 | 309 | 407 | 376 | 470 | 443 | 509 |

| Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. |
|---|---|---|---|---|---|---|---|
| 444 | 549 | 511 | 586 | 578 | — | 645 | — |
| 445 | 510 | 512 | 587 | 579 | 669 | 646 | 656 |
| 446 | 523 | 513 | 588 | 580 | 670 | 647 | 657 |
| 447 | 511 | 514 | 589 | 581 | 678 | 648 | 658 |
| 448 | 512 | 515 | 590 | 582 | — | 649 | — |
| 449 | 513 | 516 | 591 | 583 | — | 650 | 659 |
| 450 | 514 | 517 | 592 | 584 | 679 | 651 | 660 |
| 451 | 515 | 518 | 593 | 585 | 680, 683 | 652 | 661 |
| 452 | 516 | 519 | 594 | 586 | 682 | 653 | 662 |
| 453 | 518 | 520 | 595 | 587 | — | 654 | — |
| 454 | 517 | 521 | 596 | 588 | 703, 704, 705 | 655 | 663 |
| 455 | — | 522 | 598 | 589 | 684 | 656 | 667 |
| 456 | 520 | 523 | 597 | 590 | 685 | 657 | 665 |
| 457 | 521 | 524 | — | 591 | 687 | 658 | 618 |
| 458 | 540 | 525 | 599 | 592 | 686 | 659 | 616 |
| 459 | — | 526 | 601 | 593 | 688 | 660 | 198 |
| 460 | 519 | 527 | 601 | 594 | 689 | 661 | 51 |
| 461 | — | 528 | 602 | 595 | 691 | 662 | 614, 615 |
| 462 | 524 | 529 | 603 | 596 | 692 | 663 | 617 |
| 463 | 525 | 530 | 605 | 597 | 696 | 664 | 611 |
| 464 | 527 | 531 | 604 | 598 | 701 | 665 | 610 |
| 465 | 526 | 532 | 606 | 599 | 697 | 666 | 612 |
| 466 | 528 | 533 | 607 | 600 | 698 | 667 | 613 |
| 467 | 529 | 534 | 778 | 601 | 699 | 668 | 706 |
| 468 | 530 | 535 | 785 | 602 | 700 | 669 | 707 |
| 469 | 532 | 536 | 784 | 603 | 671 | 670 | 717 |
| 470 | 548 | 537 | 783 | 604 | 672 | 671 | 718 |
| 471 | 534 | 538 | 782 | 605 | 673 | 672 | 732 |
| 472 | 561 | 539 | 787 | 606 | 674 | 673 | 738 |
| 473 | 547 | 540 | 788 | 607 | 675 | 674 | 721 |
| 474 | 533 | 541 | 799 | 608 | 676 | 675 | 715 |
| 475 | 531 | 542 | 789 | 609 | — | 676 | 737 |
| 476 | 535 | 543 | — | 610 | — | 677 | 709 |
| 477 | 536 | 544 | — | 611 | 677 | 678 | 724 |
| 478 | 537 | 545 | 779 | 612 | — | 679 | 719 |
| 479 | 538 | 546 | 780 | 613 | 695 | 680 | 722 |
| 480 | 539 | 547 | — | 614 | 694 | 681 | 744 |
| 481 | — | 548 | 786 | 615 | 693 | 682 | 728 |
| 482 | — | 549 | 797 | 616 | 668 | 683 | 740 |
| 483 | 555 | 550 | 798 | 617 | 620 | 684 | 741 |
| 484 | 556 | 551 | — | 618 | 621 | 685 | 743 |
| 485 | — | 552 | 865 | 619 | 622 | 686 | 742 |
| 486 | 557 | 553 | 858 | 620 | 626 | 687 | 776 |
| 487 | 558 | 554 | — | 621 | 631 | 688 | 749 |
| 488 | 559 | 555 | — | 622 | 633 | 689 | 874 |
| 489 | 560 | 556 | 790 | 623 | 634 | 690 | 875 |
| 490 | 522 | 557 | — | 624 | 628 | 691 | 876 |
| 491 | 566 | 558 | 800 | 625 | 635 | 692 | 877 |
| 492 | 567 | 559 | 802 | 626 | 636 | 693 | 878 |
| 493 | 568 | 560 | 801 | 627 | 637 | 694 | 888 |
| 494 | — | 561 | 805 | 628 | 641 | 695 | — |
| 495 | 569 | 562 | 803 | 629 | 642 | 696 | 930 |
| 496 | 570 | 563 | 804 | 630 | 643 | 697 | 924 |
| 497 | 571 | 564 | 806 | 631 | 642 | 698 | 925 |
| 498 | 575 | 565 | 807 | 632 | 645 | 699 | 929 |
| 499 | 576 | 566 | 808 | 633 | 639 | 700 | 926 |
| 500 | — | 567 | 809 | 634 | — | 701 | 935 |
| 501 | 577 | 568 | — | 635 | — | 702 | 938 |
| 502 | 572 | 569 | 837 | 636 | 646 | 703 | 939 |
| 503 | 578 | 570 | 849 | 637 | 647 | 704 | 028 |
| 504 | 573 | 571 | 619 | 638 | 648 | 705 | 937 |
| 505 | 574 | 572 | — | 639 | 649 | 706 | 932 |
| 506 | 580 | 573 | 666 | 640 | 650 | 707 | 927 |
| 507 | 582 | 574 | 923 | 641 | 651 | 707 | 936 |
| 508 | 583 | 575 | — | 642 | 653 | 709 | 933 |
| 509 | 584 | 576 | 681 | 643 | 654 | 710 | 934 |
| 510 | 585 | 577 | 922 | 644 | 655 | 711 | — |

## SCHULTZ-GREEN NUMBERS

| Schultz Nos. | Green Nos. |
|---|---|
| 1 | 394 |
| 2 | 396 |
| 3 | 397 |
| 4 | 398 |
| 5 | 1 |
| 6 | 3 |
| 7 | 4 |
| 8 | — |
| 9 | 399, 400 |
| 10 | 401, 402 |
| 11 | 405, 406 |
| 12 | 403 |
| 13 | 407, 408 |
| 14 | 411 |
| 15 | 409 |
| 16 | 415 |
| 17 | 416 |
| 18 | 404 |
| 19 | — |
| 20 | — |
| 21 | — |
| 22 | — |
| 23 | 94 |
| 24 | — |
| 25 | 124 |
| 26 | — |
| 27 | — |
| 28 | — |
| 29 | — |
| 30 | — |
| 31 | 7 |
| 32 | 16 |
| 33 | 17 |
| 34 | 18 |
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| 37 | 13 |
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| 67 | 38 |
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| 71 | 45 |
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| 75 | 48 |
| 76 | 49 |
| 77 | 50 |
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| 79 | 54 |
| 80 | 52 |
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| 82 | 55 |
| 83 | 56, 57 |
| 84 | 69 |
| 85 | — |
| 86 | 70 |
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| 100 | 74 |
| 101 | 73 |
| 102 | 75 |
| 103 | 76 |
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| 107 | 66 |
| 108 | — |
| 109 | 62 |
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| 111 | 63 |
| 112 | 65 |
| 113 | 64 |
| 114 | 67 |
| 115 | — |
| 116 | 68 |
| 117 | — |
| 118 | — |
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| 134 | 95 |
| 135 | — |
| 136 | 95 |
| 137 | 8 |
| 138 | 87 |
| 139 | 88 |
| 140 | 91 |
| 141 | 92 |
| 142 | 89 |
| 143 | 84 |
| 144 | 85 |
| 145 | 86 |
| 146 | 93 |
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| 150 | 98 |
| 151 | 97 |
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| 158 | 123 |
| 159 | — |
| 160 | 101 |
| 161 | 102 |
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| 163 | 103 |
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| 174 | 112 |
| 175 | 114 |
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| 177 | 116 |
| 178 | 117 |
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| 182 | 132 |
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| 186 | 118 |
| 187 | 119 |
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| 190 | 126 |
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| 192 | 128 |
| 193 | 129 |
| 194 | 130 |
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| 198 | 660 |
| 199 | 125 |
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| 203 | 120 |
| 204 | 121 |
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| Schultz Nos. | Green Nos. |
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| 262 | 177 |
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| 266 | 183 |
| 267 | 185 |
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| 269 | 184 |
| 270 | 187 |
| 271 | 189 |
| 272 | 188 |
| 273 | — |
| 274 | 175 |
| 275 | 180 |
| 276 | 182 |
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| 286 | 203 |
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| 292 | 199 |
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| 294 | 190 |
| 295 | 210 |
| 296 | 191 |
| 297 | 195 |
| 298 | — |
| 299 | — |
| 300 | 211 |
| 301 | 332 |
| 302 | 333 |
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| 306 | 236 |
| 307 | 240 |
| 308 | — |
| 309 | 239 |
| 310 | 238 |
| 311 | — |
| 312 | 242 |
| 313 | 243 |
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| 315 | 217 |
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| 317 | 219 |
| 318 | — |
| 319 | 234 |
| 320 | 244 |
| 321 | 245 |
| 322 | 246 |
| 323 | — |
| 324 | 247 |
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| 326 | 252 |
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| 334 | 253 |
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| 337 | 254 |
| 338 | — |
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| 340 | 225 |
| 341 | — |
| 342 | 220 |
| 343 | 226 |
| 344 | 227 |
| 345 | 231 |
| 346 | 232 |
| 347 | 228 |
| 348 | 229 |
| 349 | 230 |
| 350 | 216 |
| 351 | 221 |
| 352 | 256 |
| 353 | 257 |
| 354 | 255 |
| 355 | 262 |
| 356 | 259 |
| 357 | 260 |
| 358 | 261 |
| 359 | — |
| 360 | 265 |
| 361 | — |
| 362 | 272 |
| 363 | 277 |
| 364 | 278 |
| 365 | 279 |
| 366 | 280 |
| 367 | 282 |
| 368 | — |
| 369 | 283 |
| 370 | 281 |
| 371 | 284 |
| 372 | 285 |
| 373 | 275 |
| 374 | 274 |
| 375 | 286 |
| 376 | 268 |
| 377 | 287 |
| 378 | 246 |
| 379 | — |
| 380 | 327 |
| 381 | 288 |
| 382 | 289 |
| 383 | — |
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| 385 | — |
| 386 | 294 |
| 387 | 291 |
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| 389 | — |
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| 393 | 276 |
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| 407 | 309 |
| 408 | 310 |
| 409 | 246 |
| 410 | 311 |
| 411 | 312 |
| 412 | 314 |
| 413 | 320 |
| 414 | 321 |
| 415 | — |
| 416 | 322 |
| 417 | 313 |
| 418 | 315 |
| 419 | *318* |
| 420 | — |
| 421 | 316 |
| 422 | *318* |
| 423 | 317 |
| 424 | 318 |
| 425 | — |
| 426 | 319 |
| 427 | 324 |
| 428 | 323 |
| 429 | 325 |
| 430 | 326 |
| 431 | 206 |
| 432 | 207 |
| 433 | 208 |
| 434 | 209 |
| 435 | — |
| 436 | 360 |
| 437 | 361 |
| 438 | 353 |
| 439 | 352 |
| 440 | 351 |
| 441 | — |
| 442 | 362 |
| 443 | 364 |
| 444 | 349 |
| 445 | 350 |
| 446 | 355 |
| 447 | 354 |
| 448 | 363 |
| 449 | 365 |
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| 453 | 366 |
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| 456 | 359 |
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| 462 | — |
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| 465 | — |
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| 467 | 374 |
| 468 | 375 |
| 469 | — |
| 470 | 376 |
| 471 | — |
| 472 | — |
| 473 | 377 |
| 474 | 372 |
| 475 | 373 |
| 476 | — |
| 477 | 379 |
| 478 | 371 |
| 479 | 378 |
| 480 | 380 |
| 481 | 381 |
| 482 | 382 |
| 483 | 213 |
| 484 | 214 |
| 485 | 384 |
| 486 | 383 |
| 487 | 385 |
| 488 | 386 |
| 489 | 387 |
| 490 | — |
| 491 | 393 |
| 492 | — |
| 493 | 425 |
| 494 | 426 |
| 495 | 427 |
| 496 | 429 |
| 497 | 431 |
| 498 | *444* |
| 499 | 428 |
| 500 | 430 |
| 501 | 432 |
| 502 | 433 |
| 503 | — |
| 504 | 434 |
| 505 | 435 |
| 506 | 436 |
| 507 | — |
| 508 | — |
| 509 | 443 |
| 510 | 445 |
| 511 | 447 |
| 512 | 448 |
| 513 | 449 |
| 514 | 450 |
| 515 | 451 |
| 516 | 452 |
| 517 | 454 |
| 518 | 453 |
| 519 | 460 |
| 520 | 456 |
| 521 | 457 |
| 522 | 490 |
| 523 | 446 |
| 524 | 462 |
| 525 | 463 |
| 526 | 465 |
| 527 | 464 |
| 528 | 466 |

| Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. | Schultz Nos. | Green Nos. |
|---|---|---|---|---|---|---|---|
| 529 | 467 | 597 | 523 | 665 | 657 | 733 | — |
| 530 | 468 | 598 | 522 | 666 | 573 | 734 | — |
| 531 | 475 | 599 | 525 | 667 | 656 | 735 | — |
| 532 | 469 | 600 | — | 668 | 616 | 736 | — |
| 533 | 474 | 601 | 526, 527 | 669 | 579 | 737 | 676 |
| 534 | 471 | 602 | 528 | 670 | 580 | 738 | 673 |
| 535 | 476 | 603 | 529 | 671 | 603 | 739 | — |
| 536 | 477 | 604 | 531 | 672 | 604 | 740 | 683 |
| 537 | 478 | 605 | 530 | 673 | 605 | 741 | 684 |
| 538 | 479 | 606 | 532 | 674 | 606 | 742 | 686 |
| 539 | 480 | 607 | 533 | 675 | 607 | 743 | 685 |
| 540 | 458 | 608 | — | 676 | 608 | 744 | 681 |
| 541 | — | 609 | — | 677 | 611 | 745 | — |
| 542 | — | 610 | 665 | 678 | 581 | 746 | — |
| 543 | 440 | 611 | 664 | 679 | 584 | 747 | — |
| 544 | 441 | 612 | 666 | 680 | 585 | 748 | — |
| 545 | 442 | 613 | 667 | 681 | 576 | 749 | 688 |
| 546 | 439 | 614 | 662 | 682 | 586 | 750 | — |
| 547 | 473 | 615 | 662 | 683 | 585 | 751 | — |
| 548 | 470 | 616 | 659 | 684 | 589 | 752 | — |
| 549 | 444 | 617 | 663 | 685 | 590 | 753 | — |
| 550 | — | 618 | 658 | 686 | 592 | 754 | — |
| 551 | — | 619 | 521 | 687 | 591 | 755 | — |
| 552 | — | 620 | 617 | 688 | 593 | 756 | — |
| 553 | — | 621 | 618 | 689 | 594 | 757 | — |
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