

## Objectives

- Extrapolation of data beyond its measured range and its quality.
- Prediction of the behaviour of explosives at lower temperatures.

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## Explosives

### 1. Introduction

An explosion is a physical or chemical phenomenon in which energy is released in a very short time, usually accompanied by formation and vigorous expansion of a very large amount of hot gas:

1. Mechanical explosions are caused by the sudden breaking of a vessel containing gas under pressure
2. Chemical explosions are caused by decomposition or very rapid reaction of a product or a mixture
3. Nuclear explosions are caused by fission or fusion of atomic nuclei
4. Electrical explosions are caused by sudden strong electrical currents that volatilize metal wire (exploding wire)

Only chemical explosions are treated in this article.

For an explosion to occur, the reaction must be exothermic ; a large amount of gas must be produced by the chemical reaction and vaporization of products ; and the reaction must propagate very fast. For example, gasoline in air burns at a rate of ca.  $10^{-6}$  m/s ; a solid propellant, at ca.  $10^{-2}$  m/s ; and an explosive detonates at a rate of ca.  $10^3 - 10^4$  m/s (detonation velocity).

The two different modes of decomposition are deflagration and detonation. Deflagration exhibits two characteristics : 1) the combustion is very rapid (1 m/s up to a few hundred meters per second) and 2) the combustion rate increases with pressure and exceeds the speed of sound in the gaseous environment, but does not exceed the speed of sound in the burning solid. The materials are often powdered or granular, as with certain pyrotechnics and black powder. Detonation is chemically the same as deflagration, but is characterized by a shock wave formed within the decomposing product and transmitted perpendicularly to the decomposition surface at a very high velocity (several thousand meters per second) independent of the surrounding pressure (see Chap. 2. Physical Properties and Chemical Reactions).

Explosive substances can be divided into three classes. Members of the first class detonate accidentally under certain conditions. These are explosible substances, some of which are used in industry as catalysts (e.g., peroxides), dyes, and fertilizers. This class includes products or mixtures whose formation must be avoided or controlled, e.g., firedamp, or peroxides in ethers. In the second class are products normally used for their quick burning properties but which may detonate under some circumstances, e.g., pyrotechnic compositions, propellants, and some kinds of hunting powder. In the third class are substances intentionally detonated for various purposes.

For reasons of safety, acquaintance with the first group of materials is necessary. The second group is described elsewhere (Propellants; Pyrotechnics). Pure substances and mixtures of the third class are described here.

The distinctions between these three classes are not clear-cut because most explosives burn smoothly if they are not confined. However, if some fine hunting powder burns under certain confined conditions, combustion may become detonation. Dry nitrocellulose fibers can easily detonate, but this tendency is significantly lower in

the gelatinized form. Some compositions, such as mixtures of cyclotrimethylenetrinitramine (RDX) with a binder, can be used as a propellant, gunpowder, or high explosive, depending on the type of initiation.

The third class consists of primary and secondary explosives. Primary explosives (initiator explosives) detonate following weak external stimuli, such as percussion, friction, or electrical or light energy. Secondary explosives are much less sensitive to shock. However, they can detonate under a strong stimulus, such as a shock wave produced by a primary explosive, which may be reinforced by a booster composed of a more sensitive secondary explosive. The various secondary explosives are used militarily or industrially as shown in Figure (1).

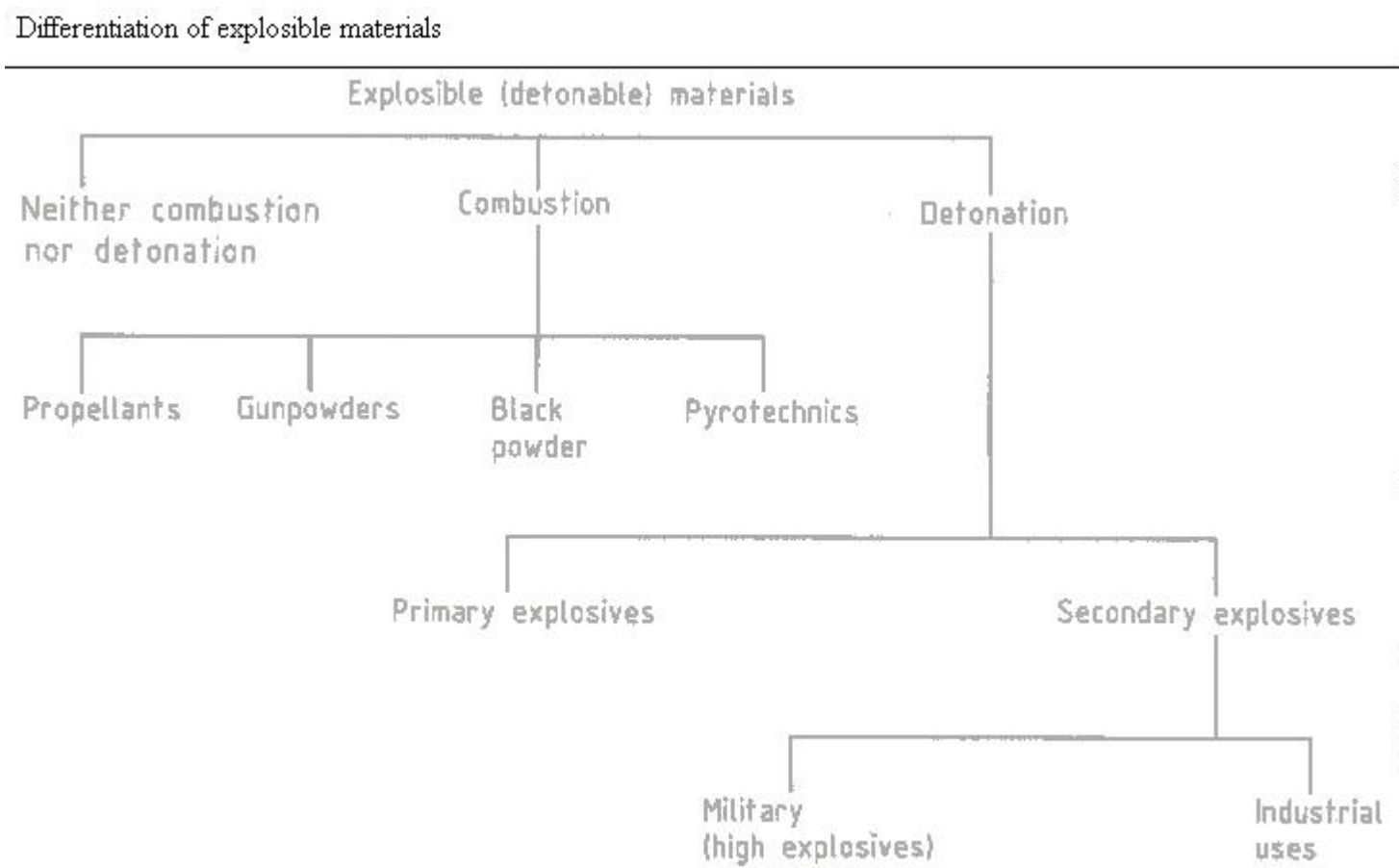


Figure 1

**Functions and Constraints.** Explosives can be either pure substances or mixtures. They function in such systems as munitions, where they are a component of a complex firing system or as firing devices in quarries or metal forming equipment. With such systems, the ingredients must fulfill one or more functions, while meeting various constraints arising in manufacture or use. Therefore, tests that represent these functions and constraints are required.

When an explosive detonates, it generates a shock wave, which may initiate less sensitive explosives, cause destruction (shell fragments, blast effect, or depression effect), split rocks and soils, or cause formation of a detonation wave. A detonation wave of special geometry (hollow charge effect) may modify materials by very rapid generation of high pressure ; for example, shaped charges, metal hardening, metal-powder compaction, or transformation of crystalline forms. A shock wave may be used to transmit signals, e.g., for safety devices or in seismic prospecting.

In general, constraints are related to safety, stability, compatibility with other elements of the system, vulnerability, toxicity, economics, and, more recently, environmental and disposal problems [21].

**History** [1][2][3][4]. Explosives were probably first used in fireworks and incendiary devices. The admixture of saltpeter with combustible products such as coal and sulfur produced black powder, for which a fabrication process was described by the Chinese in 808 A.D. [82]. Its use as an explosive charge in a shell — also by the Chinese — was recorded as early as 1044 A.D., but in Europe only around 1580 (siege of Berg-op Zoom). However, the difficulties of initiation upon impact against the target were not overcome until 1820 when fulminate caps were developed. In the early 1600s, black powder was used for the first time to break up rocks in a mine in Bohemia. This technique spread throughout western Europe during the 1600s. Ammonium perchlorate was discovered in 1832.

The development of organic chemistry after 1830 led to new products, although their explosive properties were not always immediately recognized. These include nitrocellulose and nitroglycerin.

The very important contributions of ALFRED NOBEL (1833 – 1896) include the use of mercury fulminate for the initiation of explosives (1859 – 1861), the development of dynamites (1873), and the addition of 8 % nitrocellulose to nitroglycerin (blasting gelatine, 1876).

Many new products were developed between 1865 and 1910, such as nitrated explosives, mixtures in situ of an oxidizer and a fuel, explosives safe in the presence of firedamp, chlorate explosives, and liquid oxygen explosives. Organic nitro compounds for military uses included tetryl, trinitrophenol, and trinitrotoluene.

Between the two world wars, RDX, pentaerythritol tetranitrate (PETN), and lead azide were produced. After 1945 cyclotetramethylenetetranitramine (HMX), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and hexanitrostilbene (HNS) were developed (see Chap. 5. Secondary Explosives), as well as "fuel – air explosives." Ammonium nitrate – fuel oil (ANFO) explosives and slurries were developed for industrial uses ; some were improved by adding bubbles or micropores.

In the 1880s BERTHELOT described the phenomenon of detonation. About the same time the hollow-charge effect was discovered, and the foundations of the hydrodynamic theory of detonation were established. In 1906, the first accurate measurements of velocities of detonation were made. After World War II, the science of detonation was further developed and perfected [17].

Recently, new explosive compositions of low vulnerability (LOVA = low vulnerability ammunitions) are being developed. Major efforts are being made to use predicted properties (e.g., density, DHf, sensitivity, thermal stability) to avoid unnecessary experiments [18][19][20], [87], [94].

[21] Life Cycle of Energetic Materials, Conferences Proceedings (1993, 1994, 1996), Los Alamos Lab.

## **2. Physical Properties and Chemical Reactions**

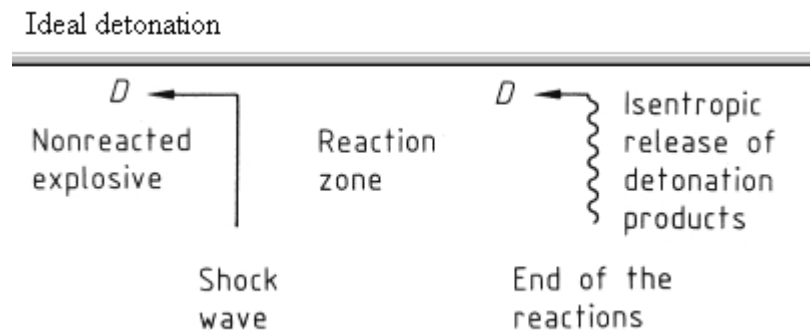
### **2.1. Detonation**

The detonation process needed for most uses is characterized by a shock wave that initiates chemical reactions as it propagates through the explosive charge. The shock wave and reaction zone have the same supersonic velocity ; a fraction of the chemical energy is used to support the shock.

#### **2.1.1. Ideal Detonation**

A model of ideal detonation (ID) is shown in Figure (2), with steady flow to the end of the reaction zone.

Stationarity requires the plane corresponding to the end of the reactions to be locally sonic. This condition, termed the Chapman – Jouguet (CJ) condition [23], [24], yields the relation  $D = u + c$  needed to solve the equations of conservation of flow (where  $D$  = detonation velocity,  $u$  = particle velocity, and  $c$  = sound velocity).



**Figure 2**

The structure of the reaction zone of the ID plane detonation can be ignored, and the mechanical and thermodynamic data can be calculated by solving equations between the nonreacted and fully reacted states. The description of the ideal detonation is given by the model [25][26][27] represented in Figure (3) by the  $p - V$  plane (Fig. (3) A) and the pressure  $p$  vs. distance  $x$  profile at a given instant of time (Fig. (3) B). This model relates the explosive at rest ( $V_0$ ), the shocked nonreacted explosive (ZND spike (\*)), and the end of the reaction zone (CJ plane ( $\wedge$ )).

In Figure (3) A the three states are located on a straight line (Rayleigh line), with slope equal to  $-D^2/V_0^2$ . The loci of the shocked states are termed Hugoniot curves :  $H_0$  for the unreacted explosives, and  $H$  for the completely reacted explosives. Some relations at the CJ plane can be expressed as a function of  $D$  and the polytropic coefficient of the detonation products :

$$\Gamma = \left( \frac{\partial \log \hat{\varrho}}{\partial \log \hat{V}} \right)_s$$

The notation  $(\cdot)_s$  represents the derivative along the isentrope at the CJ point.

$$\hat{u} = \frac{D}{\Gamma + 1} \quad \hat{p} = \varrho_0 \frac{D^2}{\Gamma + 1}$$

$$\hat{c} = \frac{\Gamma}{\Gamma + 1} D \quad \hat{\varrho} = \varrho_0 \frac{\Gamma + 1}{\Gamma}$$

where  $\varrho$  = density

These relations are valid for most condensed organic explosives  $\Gamma \approx 3$ , with the assumptions that  $p_0 = 0$  and  $u_0 = 0$ .

### 2.1.2. Deflagration and Detonation

In a thermodynamic diagram such as [Figure \(3\)](#) A, there is another point that satisfies the Chapman – Jouguet condition in the region  $p < p_0$  (not drawn in the figure). It represents the Chapman – Jouguet deflagration, in contrast to the detonation :

Detonation	Deflagration
$\hat{p} > p_0$	$\hat{p} < p_0$
$\hat{u} > 0$	$\hat{u} < 0$
$\hat{V} < V_0$	$\hat{V} > V_0$

Unlike the detonation wave, the deflagration wave is subsonic, and consequently a precursor shock is propagated in front of the reaction zone. Its intensity and velocity depend on the chemical energy released and on the boundary conditions ; in contrast to detonation, a specific explosive does not provide a unique solution for deflagration.

A precursor shock that is strong enough can, in addition to compressing the explosive, also heat it sufficiently to initiate reactions just behind its front ; a progressive buildup of a completely stationary process identical with the ZND model of the detonation is observed. Consequently, a detonation is equivalent to a shock followed by a deflagration.

[23] D. L. Chapman, Phil. Mag. 47 (1899) 90.

## 2.2. Prediction of Detonation Data

### 2.2.1. Complete Calculation

[28]

The quantities  $D$ ,  $p$ ,  $\hat{A}$ ,  $V$ , and  $T$  in the Chapman – Jouguet state are needed to evaluate further the effectiveness of the explosive on the surroundings in a given action. The calculation of these quantities requires

the equation of decomposition, the heats of reaction, and an equation of state for the reaction products, which may be theoretical (virial expansion) [29] , [30] , semiempirical [31], empirical [32], or a constant  $\gamma$  law. In addition, the equilibrium constants for the reaction given as a function of  $V$  and  $T$  are needed.

For organic explosives, the distinction between oxygen-positive or weakly oxygen-negative explosives, which give only gaseous products, and the strongly oxygen-negative explosives, which also give free carbon, is important. In fact, the assignment to one class or the other is determined by the values of the equilibrium constants for  $(V, T)$  determined after a first calculation.

Inasmuch as  $(V, T)$  are a function of the loading density  $r_0$  , some explosives, for instance, pentaerythritol tetranitrate (PETN), produce free carbon at high loading densities and only gaseous products at moderate values of  $r_0$  . Because of the complexity of the calculation, the number and formulation of the equations depend on the final result.

The thermochemical equations are solved with a priori  $(V, T)$  pairs to give gas product composition. The mechanical equations are then applied at the Chapman – Jouguet plane with the geometric condition represented on Figure (3) A : at the CJ point, the isentropic and the Hugoniot curves have the same tangent, with a slope equal to  $-D^2/V_0^2$ .

Development of the ideal detonation

A) The  $p$ - $V$  plane; B) The pressure vs. distance profile;  $p$  pressure;  $V$  specific volume;  $D$  detonation velocity;  $H_0$  Hugoniot curve of nonreacted explosives;  $H$  Hugoniot curve of reaction products; (0) explosive at rest; (1) reaction zone of length  $a$ , an arbitrary quantity; (2) isentropic release of the detonation product

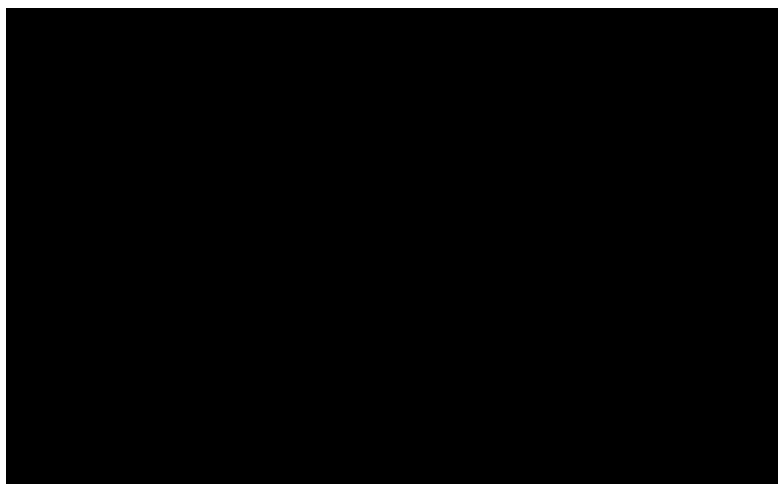


Figure 3

### 2.2.2. Approximation Methods

A first prediction of the CJ data can be given by using methods valid for condensed explosives. Chemical Potential. For many organic explosives,  $D$  and  $p$  can be expressed simply as a function of a parameter  $F$  defined as [33] :

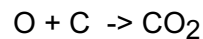
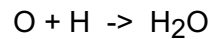
$$\Phi = N\sqrt{\bar{M}_r Q}$$

$N$  = number of moles of gaseous products per gram

$\bar{M}_r$  = average molecular mass of these products, g/mol

$Q$  = enthalpy of the explosive minus the enthalpy of the products, J/g

The calculation of  $\Phi$  is made under the assumption that :



i.e., the formation of water is considered before the formation of carbon oxides.

The following relations are then proposed :

$$D = A(1 + B \varrho_0)\sqrt{\Phi}$$

$$\hat{p} = K \varrho_0^2 \Phi$$

A good fit with experimental data is found for organic explosives by setting

$$A = 1.01 \quad B = 1.3 \quad K = 15.58$$

This method, which requires only a knowledge of the equation of decomposition, is useful for comparing organic explosives.

**Rothstein Method.** An empirical correlation has been found between the detonation velocity  $D$  and a parameter  $F$ , which is a function of the explosive molecule [34].

$$D(\varrho_0) = \frac{F - 0.26}{0.55} - 3(\varrho_{TM} - \varrho_0)$$

$\varrho_{TM}$  = theoretical density

Molecular masses and atomic composition for explosive mixtures must be derived as sums of mass-average molecular mass and of elemental mole fractions. The prediction of the detonation velocity is ca. 95 % accurate.

[28] D'Altonique Th'orique, Edition de l'Ecole Nationale Sup. des Techniques Avanc'ees, Paris 1981.

### 2.3. Nonideal Detonation Waves and Explosives

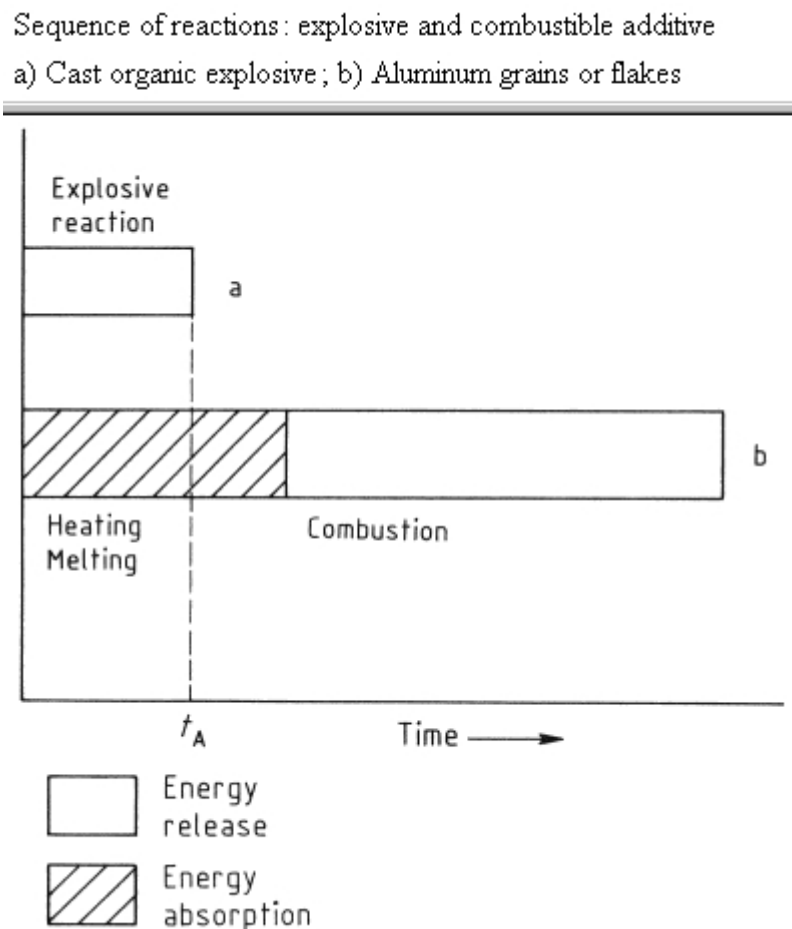
A detonation wave is nonideal if the geometry and dimensions of the charge are such that the reaction zone is affected by lateral shock or rarefaction waves. Consequently, the nonideality depends strongly on the dimensions of the charge and the explosive composition characterized by a given reaction zone length.

An explosive composition consisting of components with different reaction kinetics does not satisfy the ideal detonation model, which assumes all the exoenergetic reactions to be completed simultaneously in the sonic Chapman – Jouguet plane. Such compositions are nonideal explosives. The ideal detonation model applies

only as an approximation to most multicomponent explosives ; however, with data on reaction kinetics under pressure often lacking, calculations are commonly based on the ideal detonation model.

### 2.3.1. Nonideal Explosive Compositions

An example of an organic explosive with a metallic nonexplosive additive is a dispersion of aluminum grains or flakes in a cast organic explosive. The process sequence is shown in Figure (4). The energy effectively supporting the detonation wave has been delivered at time  $t_A$  . The absorption of energy by aluminum reduces  $p$  and  $D$ , but the late combustion of the aluminum allows the pressure to be sustained behind the CJ plane, thereby increasing the total impulse transmitted to the surroundings.



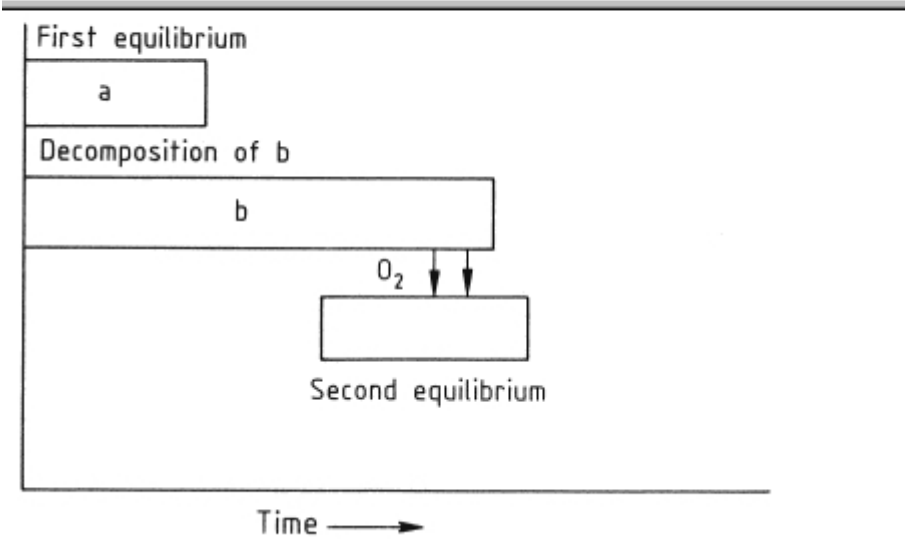
**Figure 4**

The possible sequence of an organic explosive (a) with a negative oxygen balance cast or pressed with a binder containing oxygen (b) is shown in Figure (5). The relatively slow decomposition of the binder produces oxygen gas, which shifts the reaction of the organic explosive toward better oxygen balance, thus increasing energy production.



Sequence of reactions: explosive and oxygen-rich binder

a) Negative-oxygen-balance explosive; b) Oxygen-containing binder



**Figure 5**

A typical example of a mixture of two explosive components with different reaction kinetics is a mixture of trinitrotoluene (TNT) and ammonium nitrate (AN). The slower reaction of AN produces energy and an excess of oxygen, which shifts the equilibrium of the TNT reaction to a higher energy release. Because the detonation of the nonideal explosives involves heat transfer between components, the specific surface areas become important. Moreover, because the total reaction zone is relatively long, detonation depends on the dimensions of the charges.

### 2.3.2. Detonation of Cylindrical Cartridges

In the detonation of cylindrical cartridges, the reactive flow is two-dimensional, stationary, and relatively easy to model. Many military or engineering applications use cylindrical geometry.

The basic phenomenon is the interaction of the inwardly propagating rarefaction fan, originating at the outer surface as it is reached by the shock wave, with the reaction zone. The first consequence of this interaction is freezing of the reactions by cooling, which reduces the released energy. A second effect is a curvature of the detonation front and a loss in energy through a diverging flow. The reaction zone length and the radius of the cartridge are two quantities that play opposite roles in the process.

The experimental determination of the detonation velocity as a function of the diameter produces a curve limited in two ways :

1. As the diameter increases, the detonation velocity  $D$  approaches a constant value  $D_i$  equal to that of the ideal detonation wave.
2. Below a given diameter  $d$ , called the critical diameter,  $d_{cr}$ , the detonation is no longer self-supporting and fails.

Many analytical expressions  $D/D_i(d)$  have been proposed in which the explosive is characterized by its ideal reaction zone length. The function  $D(d)$  and the critical diameter  $d_{cr}$  depend on both the length and the structure of the reaction zone, i.e., on factors that affect this zone, such as the loading density  $\rho_0$ , grain size  $g$ , initial temperature  $t_0$ , and composition, especially in the case of mixtures.

As an example of the effects of these factors on ideal explosive compositions, the influence of  $\rho_0$  is shown in Figure (6) for the conventional military composition 60 RDX/40 TNT (composition B) [35]. In the case of energy-rich explosives, the effect of the cylinder diameter increases with decreasing density, whereas the critical diameter decreases with increasing density and increasing temperature [36]. The influence of mean grain size, e.g., that of powdered TNT, is shown in Figure (7) [28], and most nonideal explosive compositions and some pure explosives exhibit a particular behavior (see Chap. 6. High Explosive Mixtures).

Detonation velocity  $D$  vs. diameter  $d$  for two densities  $\rho$  of 60 wt% RDX–40 wt% TNT

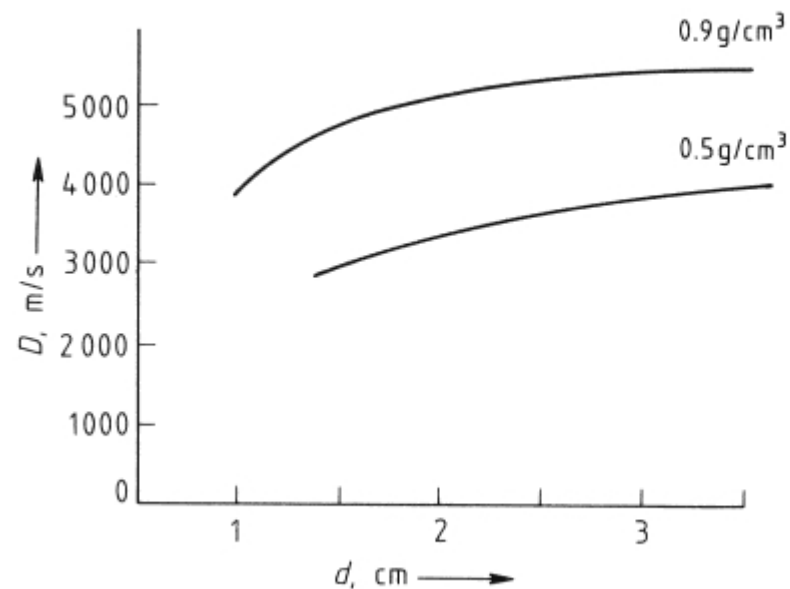


Figure 6

Detonation velocity  $D$  vs. diameter  $d$  for several grain sizes  $g$  of powered TNT

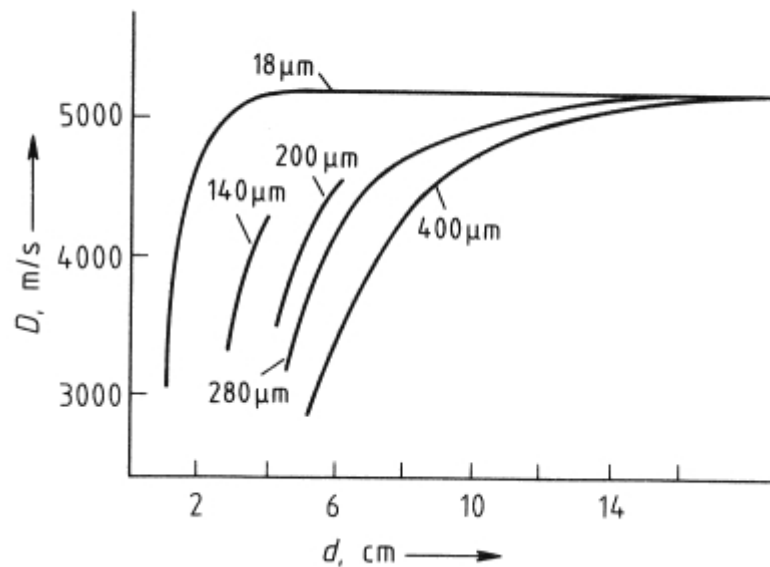


Figure 7

### 2.3.3. Low- and High-Order Detonation Velocity

Some explosives exhibit two different detonation velocities, depending on the diameter of the cartridge and the initial ignition energy. Such explosives always have a relatively low energy and loading density, with great sensitivity to shock waves [35]. Conventional examples are the dynamites and highly porous explosives [37].

The high sensitivity to shock waves tends to allow the detonation to be sustained. This is true even when the development of the reactions is seriously limited by the size of the cartridge. Thus, under steady conditions, a state of shock plus reaction would correspond to that appearing in a transient regime in the buildup of heterogeneous explosives to detonation.

### 2.3.4. The Effect of Confinement

Confinement usually delays the arrival of the expansion waves on the axis. A confined charge is equivalent to a charge having a large diameter. However, two anomalous effects should be noted: if the velocity of sound in the confinement exceeds the detonation velocity for the given diameter, a foreshock is propagated ahead of the wave. This foreshock can accelerate the wave (increase the density) or stop the detonation, i.e., desensitize a porous explosive by compaction, the explosive becoming homogenous. An analogous desensitizing effect can be generated if there is an air gap between the explosive and the container. The expanding reaction products adiabatically compress the porous explosive. This effect can stop the detonation of mining charges embedded in boreholes.

[35] C. H. Johansson, P. A. Persson : Detonics of High Explosives, Academic Press, London-New York 1970.

## 2.4. The Buildup of Detonation

### 2.4.1. Combustion – Deflagration – Detonation Transition (DDT)

Deflagration can generate a shock wave, which is propagated in the unreacted medium, and if strong enough, can initiate reactions and become a detonation wave. This transition can occur only if the explosive charge is confined or is of such a size that expansion waves do not prevent formation of a shock wave. Accident reports have shown that DDT affects a variety of explosives and propellant charges.

However, different phenomena, which depend on the mechanical properties of the medium, may occur [38] , [39] : if the explosive is porous or exhibits poor mechanical behavior, the gas formed and subjected to pressure is injected between the grains or into cracks, increasing the combustion surface. The resulting acceleration stops only when detonation occurs. The path versus time of the observed ionization front is continuous. In the case of explosives stiff enough to withstand an elastic wave, a steady deflagration develops as soon as the pressure makes the medium impervious to the gas. The transition to detonation occurs as the pressure of the gas formed behind the deflagration zone becomes high enough to generate a shock wave. Detonation occurs when the shock wave reaches the front of the deflagration wave. As a consequence, a discontinuity is observed in the path versus time of the ionization front.

#### 2.4.2. Shock-to-Detonation Transition (SDT)

If the end of an explosive charge is subjected to a shock wave, the steady detonation appears only at a distance  $s$  and with a delay  $t$  inside the explosive charge [40] . For a given composition,  $s$  and  $t$  are inversely proportional to the intensity of the shock wave. There are two SDT processes : one for homogeneous (for instance, a liquid) and one for heterogeneous composition.

**Homogeneous Explosives.** The shock wave (a) in Figure (8) propagated at constant velocity initiates decomposition reactions that are first completed along the entrance side (b) at time  $t$ , the detonation appearing at point A. The detonation wave (c) travels in a compressed medium heated by shock wave (a). Therefore, the detonation wave (c) travels with a velocity exceeding the normal detonation velocity, which is attained at point B (wave d) as soon as wave c has reached wave a.

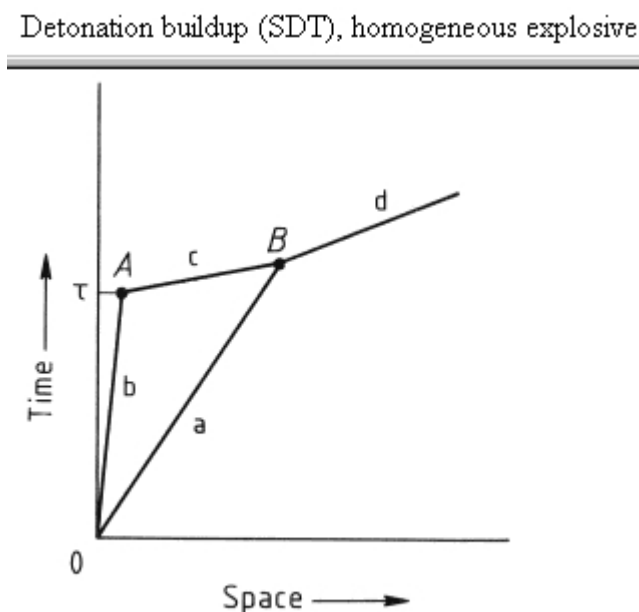
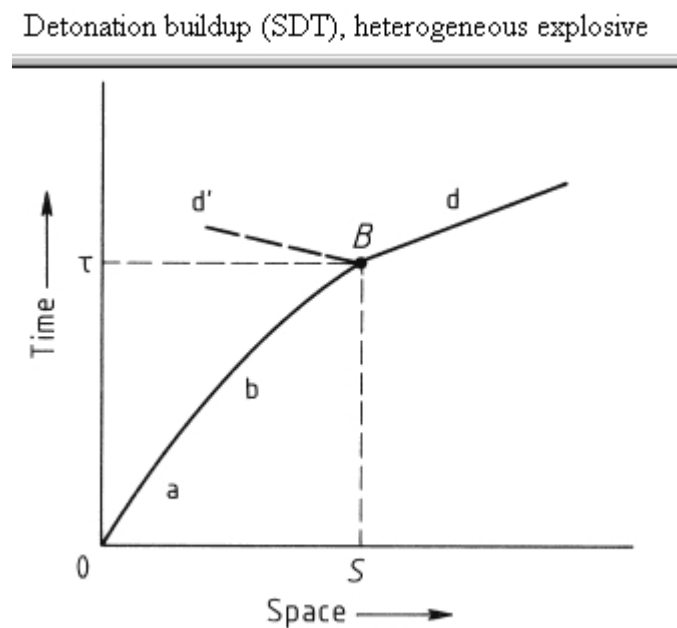


Figure 8

**Heterogeneous Explosives.** In Figure (9), the shock wave (a) is gradually accelerated by the energy released upon its passage. Its acceleration ends with the appearance of a detonation wave at point B. This wave is characterized by its luminosity, as seen on optical records. Sometimes a second wave starts from point B and moves backward in the explosive, which has reacted only partially (retonation wave). The macroscopic analysis can be explained by the microscopic heterogeneities of the explosive [41] .



**Figure 9**

The energy of the shock wave is converted into heat energy by the implosion of occluded gas bubbles, the impact of microjets, or the adiabatic shearing of the powder grains. All the observations allow for two successive phases, ignition and buildup, that are accommodated by numerical models assuming inward or outward combustion of the grains [42] .

#### **2.4.3. Shock and Impact Sensitivity**

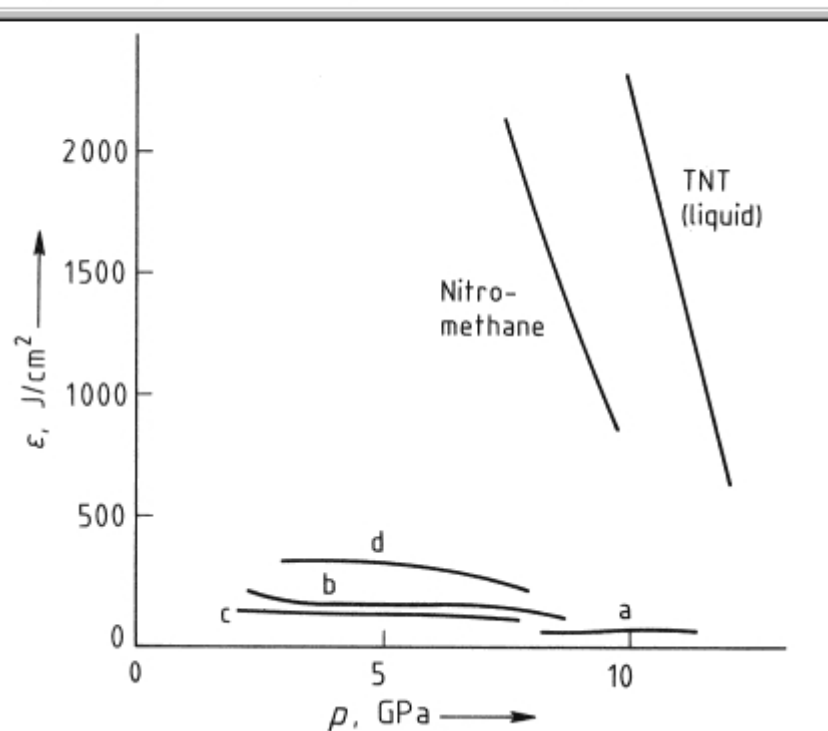
The sensitivity of the explosives to an applied load is measured by the maximum load at which no detonation occurs, or at which there is a 50 % occurrence of detonation, i.e., a 50 % chance of failure. The sensitivity to shock loading depends on the pressure  $p^*$  and its action time  $t^*$ . Sensitivity is defined with the aid of the curve  $p^*(t^*)$ , which separates detonation points from failure points.

$$\left(p^*\right)^2 \tau^* = \varepsilon$$

For a variety of explosives and for a certain pressure range, the sensitivity is defined by the relation , where  $\varepsilon$  is a constant that depends on the composition and exhibits the dimension surface energy per unit area [43] .

Figure (10) shows that the concept of the energy threshold is an acceptable approximation for solid-state compositions [44] . For liquid explosives, which exhibit different behavior, the relation  $t^*(p^*)$ , based on an Arrhenius-type kinetic theory (with initial temperature  $T^*$  expressed as a function of pressure  $p^*$ ) accurately reproduces the experimental findings. The critical time  $t^*$  is equal, for a given shock pressure, to the time of the shock-to-detonation transition (see Fig. (8)). Except for primary explosives, the sensitivity to shock-wave action and the shock-to-detonation transition are both dependent on the homogeneity of the composition. Sensitivity is affected by grain size [95] and internal grain defects [96]. The reaction of an explosive to impact loading depends on several factors. If the projectile is a large plate, the reaction is identical with that observed in the preceding case : the shock wave induced by the impact depends on the velocity and acoustic impedance, whereas the action time is proportional to the plate thickness. In tests of sensitivity to shock-wave action, the impacting plates are driven by explosives. If the projectile is a small sphere or cylinder, the interaction with the target becomes complex [40]. If the shock wave cannot induce a shock – detonation transition, it degenerates into an adiabatic compression. Frictional and shearing effects can cause ignition. Finally, a phenomenon analogous to the deflagration – detonation transition (see Section 2.4.1. Combustion – Deflagration – Detonation Transition (DDT)) is observed, in which the mechanical properties of the explosive play a part.

Initiation energy threshold vs. shock pressure  
a, b) HMX plus binder; c, d) Cast RDX compositions



**Figure 10**

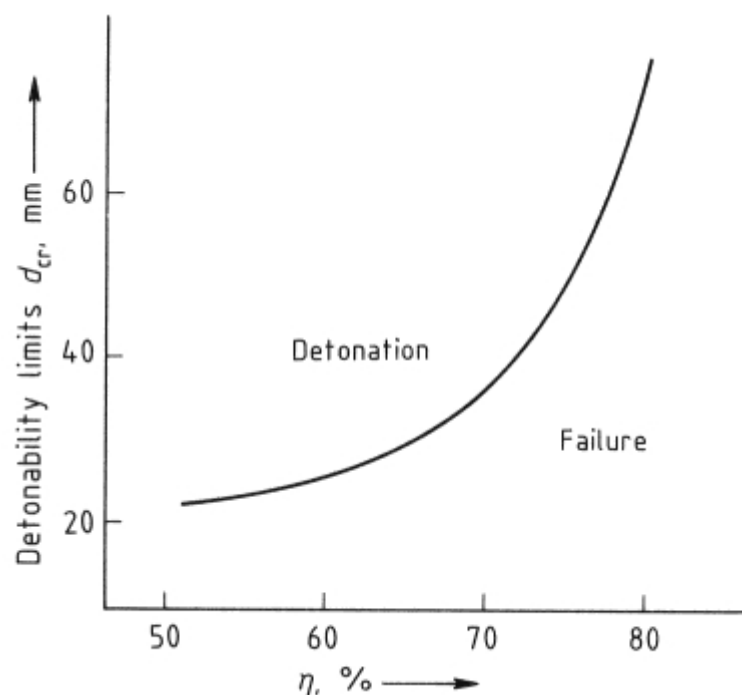
[38] R. R. Bernecker et al., Symposium (International) on Detonation, 7th, Office of Naval Research Report NSWC MP 82 – 334(1981).

## 2.5. Classification of Explosives

For many years the behavior of cylindrical cartridges, as described in Section 2.3.2. Detonation of Cylindrical Cartridges, was regarded as typical of ideal explosives. A detailed analysis has shown, however, that classification of explosives into two groups is possible, taking into account the influence of the loading density  $r_0$  on the detonation velocity as a function of the cartridge diameter and the critical diameter [45] .

The first group includes a variety of organic explosives : TNT, RDX, HMX, and their mixtures (see Chap. 5. Secondary Explosives). The second group includes mixtures of an explosive and a combustible nonexploding constituent (nonideal composition). This group also includes some pure explosives such as hydrazine mononitrate (HN), nitroguanidine (NG), ammonium nitrate (AN), dinitrotoluene (DNT), dinitrophenol (DNP), and ammonium perchlorate (AP). The behavior of the second group is illustrated for ammonium perchlorate in Figure (11).

Detonation behavior of ammonium perchlorate,  $\eta$  = percent of theoretical maximum density



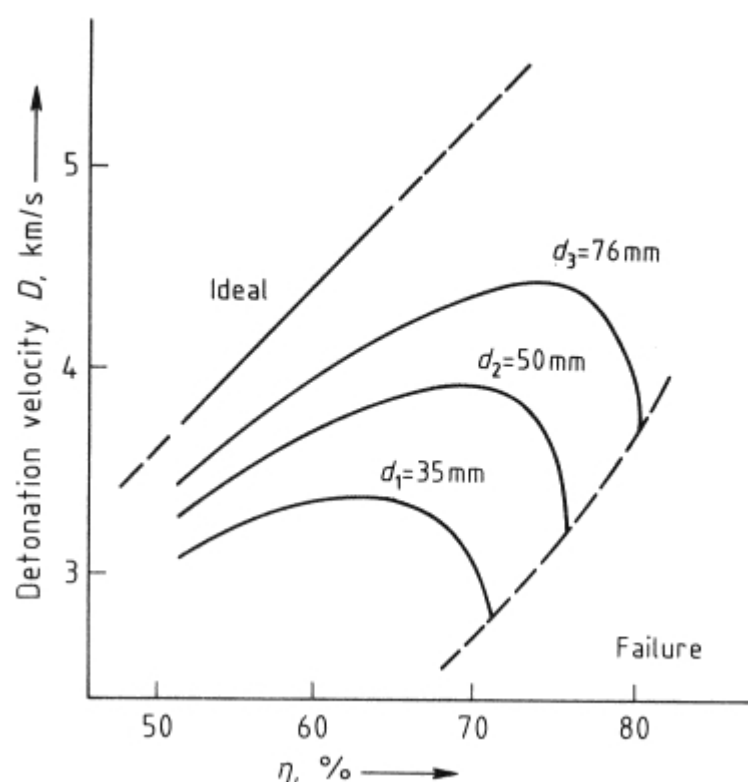


Figure 11

[45] D. Price, Symp. (Int.) Combust. 11th (1967) 963.

## 2.6. Functional Groups

Certain groups impart explosive potential.

### 2.6.1. Nitro Group

The nitro group is present in the form of salts of nitric acid,  $\text{ONO}_2$  derivatives (nitrate esters),  $\text{CNO}_2$  derivatives (aliphatic or aromatic nitro compounds), and  $\text{NNO}_2$  derivatives (N-nitro compounds such as nitramines, nitroureas, etc.).

**Salts of Nitric Acid.** Salts of nitric acid include the alkali metal and alkaline earth metal nitrates, ammonium nitrate, and the nitrates of methylamine, urea, and guanidine. These are usually low-density, water-soluble, sometimes hygroscopic compounds. With the exception of some salts of hydrazines, e.g., triaminoguanidine and hydrazine nitrates, they are insensitive to impact and friction.

**O-Nitro Derivatives, Nitrate Esters ( $\text{RONO}_2$ ).** The low molecular mass representatives are liquids or low-melting solids. They are sensitive to impact when the number of carbon atoms and  $-\text{ONO}_2$  groups are equal or nearly equal. Densities are in the medium range, except for symmetrical molecules such as pentaerythritol tetranitrate (PETN). Heat stability is moderate; they are subject to hydrolysis and autocatalytic decomposition.



**C-Nitro Derivatives (CNO<sub>2</sub>).** Aliphatic and cycloaliphatic nitro compounds differ greatly from the aromatic and heteroaromatic series. Members of the first group have limited explosive properties, except when the number of NO<sub>2</sub> groups equals or exceeds the number of carbon atoms, as in some gem-dinitro compounds and derivatives of nitroform, HC(NO<sub>2</sub>)<sub>3</sub>. The latter are often shock sensitive, with limited heat stability. The compounds RCF(NO<sub>2</sub>)<sub>2</sub> are stable to heat and rather insensitive [6] , [7] . Members of the second group containing two or three NO<sub>2</sub> groups per ring are valuable ; they are often dense and insensitive to impact, with good hydrolytic and thermal stability.

**N-Nitro Derivatives (NNO<sub>2</sub>).** N-Nitro derivatives are often difficult to synthesize. They exhibit high densities and detonation velocities, with some sensitivity to impact. RDX and HMX are representative.

### 2.6.2. Other Groups

Organic chlorates and perchlorates, peroxides, metal salts of some organic compounds (acetylides and nitronates), and some organic compounds with three-membered rings or chains of nitrogen atoms or triple bonds have only limited application, except as primary explosives. Most are very dangerous to handle.

Nitroso (NO) compounds are usually unstable. So-called hexanitrosobenzene is an exception ; however, it is actually not a nitroso compound but a furoxan derivative (benzotrifuroxan). It is of interest because it is free of hydrogen (zero-hydrogen explosive). Other furoxanes and also furazanes have explosive properties [83]

The difluoroamine group imparts explosive character, increased density and volatility, a lower melting point and detonation velocity, and often much higher impact sensitivity. These compounds resemble primary explosives.

Many metal azides are primary explosives. Some organic azido derivatives are being studied because of their high density and stability. However, polyazido compounds can be very sensitive.

[6] Kirk-Othmer, 9, 561 – 620, and 15, 841 – 853.

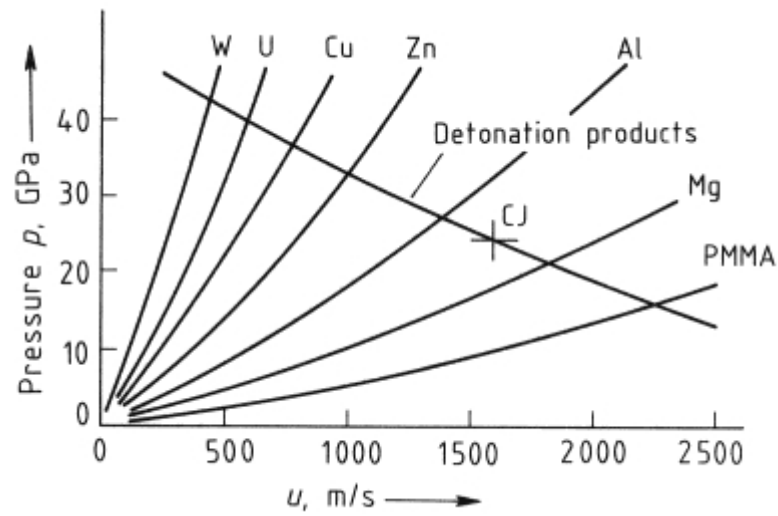
## 3. Application

### 3.1. Energy Transfer from the Explosive to the Surroundings

The energy available in the gaseous reaction products is transferred to the surroundings by shock waves. The mechanical effects depend on the geometry of the charge and the surroundings, on the distance from the charge, and on the acoustic impedance of the media. The explosive energy is used either to create compression and tension for engineering applications or to accelerate projectiles for military applications.

#### 3.1.1. Shock and Blast Waves

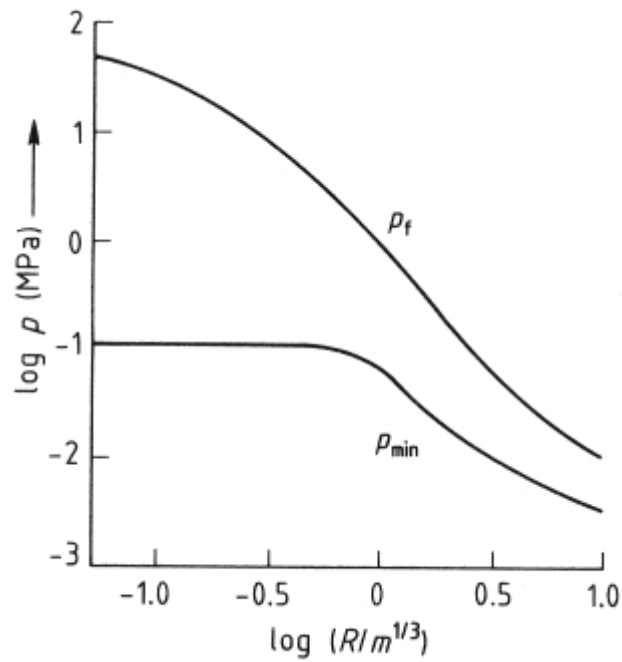
The highest dynamic pressures are produced at the exit end of the charge, where the detonation shock is transferred to the inert material. The shock pressure is a function of the shock impedance. It is defined by the so-called shock polar curve of the pressure ( $p$ ) vs. particle velocity ( $u$ ). By a graphical method (Fig. (12)) the induced pressure can be determined at the intersection of a shock polar curve with the detonation gas-product curve passing through the CJ point.



**Figure 12**

Even higher pressures can be obtained by using converging geometries or, indirectly, by a two-stage device. The explosive accelerates a thin metal plate, which generates an intense shock in the solid specimen as it strikes it in free flight. During wave propagation in the surrounding medium, the intensity of a shock wave decreases and the pressure profile changes. At a given distance from the charge, compression alternates with tension. The mechanical effects are a function of the maximum pressure and of the positive and negative impulses comprising the so-called blast wave. The maximum and minimum pressures are represented in Figure (13) as a function of the reduced distance  $R/m^{1/3}$  from the charge.

Front pressure  $p_f$  and minimum pressure  $p_{min}$  in air vs. reduced distance  $R/m^{1/3}$  from TNT in air, where  $R$  is the distance in meters and  $m$  the mass in kilograms.



**Figure 13**

### 3.1.2. Casing and Liner Acceleration

A casing or liner in contact with an explosive charge is accelerated by a three-step process :

1.  $u_1$  given by the shock wave
2.  $u_2 = 2 u_1$  given by reflection of the shock wave in a release wave at the free surface
3.  $u_3$  given by the further expansion of the gaseous detonation products

The Gurney formula gives an approximate  $u_3$  for a casing filled with an explosive characterized by the quantity  $E$ , which is given in J/kg [46] :

$$u_3 (\text{m/s}) = (2E)^{1/2} \left( \frac{M}{C} + \alpha \right)^{-1/2}$$

where

$M$  = mass of the casing, kg

$C$  = mass of the explosive, kg

$\alpha = 0.5$  for a cylindrical charge and

$\alpha = 0.6$  for a spherical charge

[46] S. J. Jacobs, Naval Ordnance Laboratory Technical Report 74 – 86.

### 3.2. High Compression of Solids

Explosives provide the most powerful means for compressing solids in spite of the fact that at high pressure the heating limits the volume reduction.

**Production of New Crystal Phases.** The large pressure generated by shock waves may be used to transform one crystal phase into another (polymorphic transformation). The best known example of this technique is the transformation of graphite into diamond. Unfortunately, the short duration of the shock limits this technique to the production of small crystals used as abrasives.

**Powder Compaction.** The compression of powders by shock waves produced by explosives creates high pressures and temperatures simultaneously, resulting in grain welding. The main problem, which has been solved only recently, is the explosion caused by the interaction of release waves, which follow the shock ; special geometries are required [47] . Rapidly solidified amorphous and metastable microcrystalline materials and ultrahigh-strength ceramics are expected to be produced by this technique.

**Shock Hardening.** The detonation of a thin sheet of explosive covering a piece of steel creates great surface hardness by a sequence of rapid compression, heating, and cooling.  
[47] M. L. Wilkins, UCRL Report 90 142 (1983).

### 3.3. Metal Forming and Welding

The detonation of an explosive charge is used to form a metal plate ; the shock wave is moderated by a liquid transmitting medium (Fig. (14)). Techniques of free forming (Fig. (14) A) or bulkhead forming (Fig. (14) B) may be used.

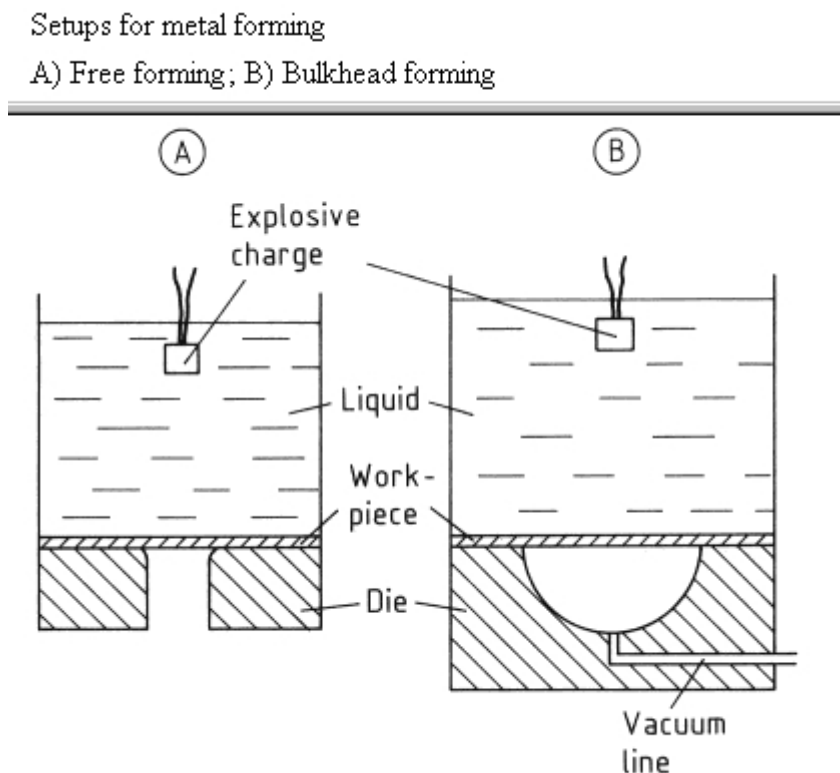
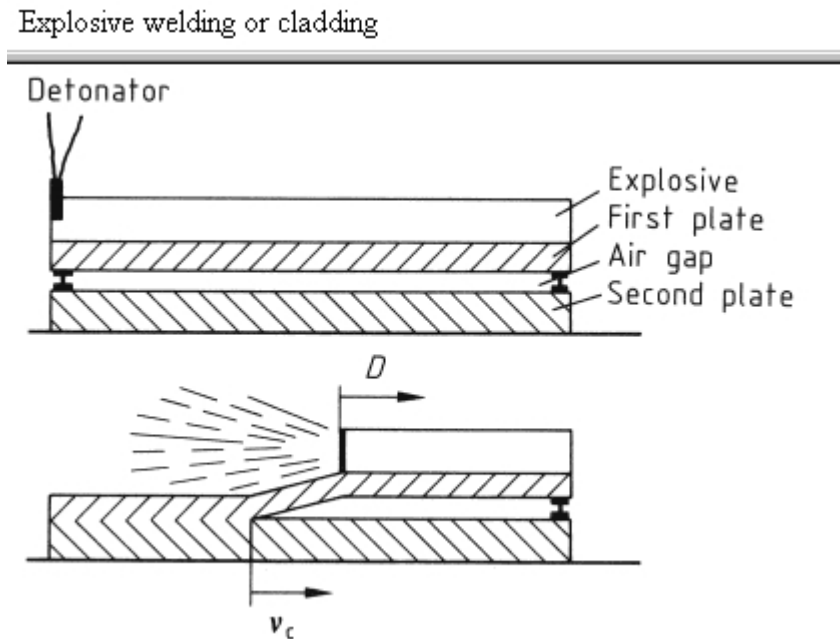


Figure 14

A grazing detonation may weld two metal plates with diffusion of metal through the interface (Fig. (15)) [48] . The required collision velocity,  $v_c$  , depends on the materials. This process is called explosive welding or cladding.



**Figure 15**

[48] V. D. Linse, H. E. Otto, P. Pocaliko : "Explosion Welding," Welding Handbook, vol. 3, Am. Welding Soc., Miami 1980.

### **3.4. Rock Blasting [35]**

In rock blasting the charges are placed in drill holes, which are usually parallel to the rock surface. With strong confinement, most of the explosive energy is usefully employed, even though much of it is released by afterburning. Equally good results are given by nitroglycerin in high (6000 – 8000 m/s) or low (2000 – 3000 m/s) explosives. Various types of wedge cuts are used for tunnel blasting.

[35] C. H. Johansson, P. A. Persson : Detonics of High Explosives, Academic Press, London-New York 1970.

### **3.5. Perforators, Shaped or Hollow Charges**

An explosive can be used to produce a thin, high-speed metallic projectile capable of perforating armor [49] . Nonmilitary applications include oil recovery.

A cavity in the explosive (Fig. (16)) is lined with a metal, usually copper. The detonation divides the liner into two parts that move along the axis at different velocities. Most of the mass of the liner forms the so-called slug at a velocity of several hundred meters per second. The remainder forms a thin projectile which is elongated because of the difference of velocity between the first formed elements near the apex ( $u_{jet\ max.} \approx 8000 - 11\ 000\ m/s$ ) and those formed last ( $u_{jet\ min.} = 1500 - 2000\ m/s$ ). The ultimate length of the projectile depends on the ductility of the liner and can be  $> 10$  times the diameter of the charge.

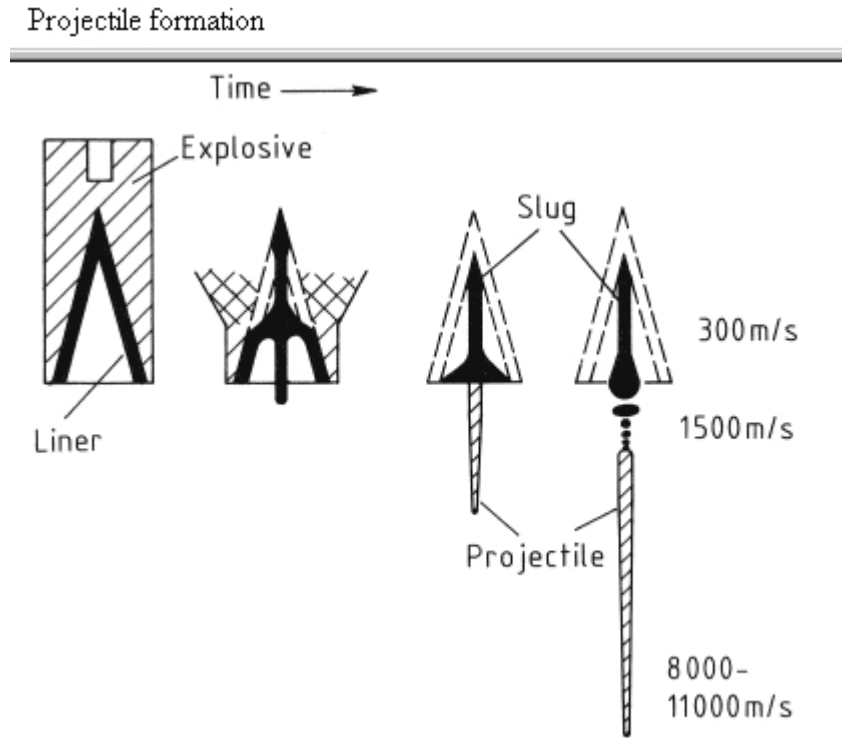


Figure 16

When the projectile strikes a solid or liquid target, it drills a deep, narrow hole. The hole depth  $P$  is given approximately by the expression

$$P = L \sqrt{\frac{\rho_j}{\rho_t}}$$

where  $L$  is the length of the projectile and  $\rho_j$  and  $\rho_t$  are the densities of the projectile and target.

[49] M. D'Aufforneaux, Sciences et Techniques de l'Armement, Paris 2 (1970) 293.

#### 4. Primary Explosives

Under low-intensity stimulus of short duration, primary explosives, even in thin layers, decompose and produce a detonation wave ; the activation energy is low. The stimulus may be shock, friction, an electric spark, or sudden heating. The deflagration – detonation transition occurs within a distance often too short to be measured. The released energy and the detonation velocity of primary explosives are small. Their formation is often endothermic.

The main function of primary explosives is to produce a shock wave when the explosive is stimulated by percussion, electrically, or optically (laser), thus initiating a secondary explosive. Primary explosives are the active detonator ingredients. Some are used in primer mixtures to ignite propellants or pyrotechnics. Because of their sensitivity, primary explosives are used in quantities limited to a few grams, and are manufactured under special precautions to avoid any shock or spark. To be used in industry, primary explosives must have limited sensitivity and adequate stability to heat, hydrolysis, and storage. Mercury fulminate, azides, and diazodinitrophenol are among the few products that meet these requirements and that can detonate a secondary explosive. Others, e.g., lead styphnate or tetrazene, initiate burning or act as sensitizers.

Properties of primary explosives are given in Table (1).

Properties of primary explosives						
Property	Mercury fulminate	Lead azide, pure	Silver azide	DDNP	Lead styphnate	Tetrazene
Properties of primary explosives						
Property	Mercury fulminate	Lead azide, pure	Silver azide	DDNP	Lead styphnate	Tetrazene
Crystal density, g/cm <sup>3</sup>	4.42	4.8	5.1	1.63	3.0	1.7
Detonation velocity, km/s	5.4	6.1 *	6.8 *	6.9	5.2	
at density	4.2	4.8	5.1	1.6	2.9	
Impact sensitivity, Nm	1–2	2.5–4	2–4	1.5	2.5–5	1
Friction sensitivity, N	8	0.1–1		20	8	10
Lead block test, cm <sup>3</sup> /10 g	ca. 130	110	115	325	130	130
Explosion temperature, ** °C	190–200	345	290	195	265–280	160

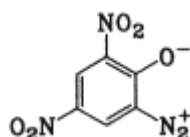
\* Theoretical. \*\* After 5 s.

**Table 1**

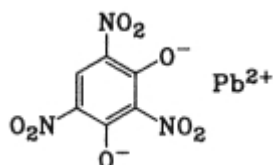
**Mercury fulminate [628-86-4]** , Hg(ONC)<sub>2</sub>, M<sub>r</sub> 284.65, was first prepared in the 1600s and was used by Nobel in 1867 to detonate dynamites. It is prepared by the reaction of mercury with nitric acid and 95 % ethanol, in small quantities because the reaction is difficult to control. Mercury fulminate is a gray toxic powder, which lacks the stability for storage. It reacts with metals in a moist atmosphere ; in most industrial countries its use has been abandoned.

**Lead azide [13424-46-9]**,  $\text{Pb}(\text{N}_3)_2$ ,  $M_r$  291.26, discovered by CURTIUS (1891) [13], was developed after World War I and is now the most important primary explosive. It is produced continuously by the reaction of lead nitrate or acetate with sodium azide in aqueous solution under basic conditions to avoid formation of hydrazoic acid, which explodes readily. The crystal size must be carefully controlled, large crystals being dangerous, by controlling the stirring and by using wetting agents. Demineralized water must be used. With thickeners such as dextrin, sodium carboxymethylcellulose, or poly(vinyl alcohol), purities from 92 % to 99 % are possible, the former containing 3 % dextrin and 4 – 5 %  $\text{Pb}(\text{OH})_2$ . The lower sensitivity of the 92 % lead azide to impact and friction compared to purer lead azides facilitates detonator loading. Lead azide has good stability to heat and storage. Contact with copper must be avoided because copper azide is extremely sensitive ; aluminum is preferred. Silver azide is used at high temperature or in miniaturized pyrotechnic devices. It is prepared from aqueous silver nitrate and sodium azide.

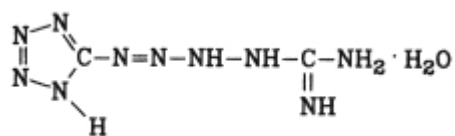
**Diazodinitrophenol [28655-69-8]**, DDNP,  $\text{C}_6\text{H}_2\text{N}_4\text{O}_5$ ,  $M_r$  210.06, is obtained by diazotizing picramic acid and purified by recrystallization from acetone. It is sparingly soluble in water, nonhygroscopic, and sensitive to impact, but not as sensitive to friction or electrostatic energy. It is less stable to heat than lead azide. It is most often used in the United States.



**Lead styphnate [15245-44-0]**, lead trinitroresorcinate,  $\text{C}_6\text{H}_2\text{N}_3\text{O}_8\text{Pb}$ ,  $M_r$  450.27, is produced continuously by the aqueous reaction of the magnesium salt with lead acetate, sometimes in the presence of agents that promote the formation of the correct crystalline form. Especially sensitive to electrostatic discharge, it is most frequently used to sensitize lead azide and in primer compositions to initiate burning.



**Tetrazene [31330-63-9]**,  $\text{C}_2\text{H}_8\text{N}_{10}\text{O}$ ,  $M_r$  188.07, is obtained by the reaction of sodium nitrite with a soluble salt of aminoguanidine in acetic acid at 30 – 40 °C. It decomposes in boiling water. Its greatest value is for the sensitization of priming compositions.



[13] H. D. Fair, R. F. Walker : Energetic Materials. Inorganic Azides, Plenum Press, New York 1977.

## 5. Secondary Explosives

### 5.1. Production

Common high explosives are usually made by liquid-phase nitration. The overall mechanism is believed to be ionic, with  $\text{NO}_2^+$  generally the reactive species. In some cases,  $\text{N}_2\text{O}_4$  may be added to a double bond or to an



epoxy group. It is also possible to nitrate gas-phase hydrocarbons. The most important nitrating agent is nitric acid.

Numerous end products of nitration are soluble in concentrated  $\text{HNO}_3$ , and may be recovered by dilution. However, dilution below ca. 55 wt % acid is not economic.

To increase the  $\text{NO}_2^+$  content (3 wt % in pure  $\text{HNO}_3$ ), lower the solubility of end products, reduce oxidative side reactions, and facilitate the treatment of spent acids, mixtures of sulfuric and nitric acids (mixed acid) are used. The water content of a mixed acid may be reduced by adding oleum. In 50 : 50 wt % mixed acid, the nitric acid is ca. 15 % dissociated.

However, sulfuric acid is difficult to remove from products by washing. Furthermore, some substances (e.g., nitramines, nitriles, etc.) are decomposed. Orthophosphoric acid or polyphosphoric acid may be used instead of sulfuric acid ; however, these phosphoric acids are more expensive and more difficult to recover.

Mild nitration or nitrolysis can be conducted in mixtures of nitric acid and acetic anhydride or acetic acid ; the reactive species may be  $\text{CH}_3\text{COONO}_2\text{H}^+$ . Mixtures of nitric acid and acetic anhydride containing between 30 and 80 wt %  $\text{HNO}_3$  can detonate [50] . A high concentration of acetic anhydride avoids this danger. Recently developed new nitration methods use  $\text{N}_2\text{O}_5$  as a solution in pure nitric acid ("nitric oleum") or in chlorinated solvents (e.g.,  $\text{CH}_2\text{Cl}_2$ ). Three processes for the production of nitric oleum are in operation or in development [85] :

1. Oxidative electrolysis of a  $\text{N}_2\text{O}_4 - \text{HNO}_3$  mixture
2. Ozonation of  $\text{N}_2\text{O}_4$
3. Distillation of an oleum ( $\text{H}_2\text{SO}_4 + \text{SO}_3$ ) –  $\text{NH}_4\text{NO}_3$  mixture [84]

Nitric oleum allows yields to be improved and permits some syntheses to be performed that are not possible by other routes ; the organic  $\text{N}_2\text{O}_5$  solutions allow nitration to be performed under very mild and selective conditions [16],[85]. These nitrating agents must be used at their site of production.

**Nitration.** Reaction is exothermic. Dilution of the nitric and mixed acids with water liberates heat [51]. Normally, nitration is rapid. However, 70 – 85 wt % nitric acid is also an oxidant, and for this reason the reaction is best conducted continuously to limit the contact time of the product with the reactive medium. If the medium is free of solid particles, a tubular reactor can be used ; otherwise, reactors in cascade with efficient stirring are employed. These reactors are made of highly polished stainless steel. Reactors and stirrers must be carefully designed to avoid dead zones and friction with crusts of explosives. Reactors are often provided with a valve that opens quickly to discharge reactants into a dilution vessel in an emergency.

**Product Isolation.** If a precipitate is not highly sensitive to friction, it may be centrifuged. For safe continuous filtration, the product must be stable in its mother liquor, and the filter design must avoid introduction of the explosive between moving and fixed parts. The precipitate is washed in two stages. The first uses only a small amount of water, which is recovered and mixed with spent acid. The acid is recovered from this mixture.

**Purification.** Treatment with boiling water is sometimes sufficient to hydrolyze impurities and wash out nitric acid. Crystallization eliminates sulfuric acid and produces the desired grain size. The solvent can be diluted with water or removed by steam distillation. Very fine crystals are obtained by dilution with high-speed stirring or by grinding in water or an inert liquid. A fluid energy mill may also be used. Size separation can be effected by sieving under flowing water or in a classifier. Drying is usually done as late as possible in the process.

**Recovery of Spent Acids.** Acid recovery in an explosive plant is of great importance in controlling production costs. These acids include 55 wt %  $\text{HNO}_3$ , 63 – 68 wt %  $\text{H}_2\text{SO}_4$  from nitric acid concentration, and spent  $\text{H}_2\text{SO}_4$  containing some nitric acid and nitration products.

To concentrate nitric acid, water is removed by countercurrent extraction with 92 – 95 %  $\text{H}_2\text{SO}_4$ . At the top, 98 – 99 %  $\text{HNO}_3$  is produced. At the bottom, 63 – 68 %  $\text{H}_2\text{SO}_4$  is obtained, which can be concentrated to 93 % by stripping with combustion gases, or to 96 – 98 % by vacuum distillation. Nitric acid can also be concentrated by distillation over magnesium nitrate.

Sulfuric acid is freed of nitric acid and nitro compounds by heating or steam injection.

**Pollution Problems.** Gaseous pollution may occur during nitrations, with evolution of red nitrous fumes. These can be absorbed in columns by recycling water or dilute nitric acid to provide 50 – 55 wt % acid.

Liquid and solid pollution is created by washing. Usually acids are transferred to decanting and settling basins, where product and other solid particles settle and liquids are neutralized. Some liquid wastes require special treatment ; for example, the red liquors from TNT are best destroyed by combustion.

**Safety** [9] , [11] . Accidents caused by detonation are usually very severe. In addition to the normal precautions required in acid handling, the production and use of explosives obviously involves special risks. Loss of life and destruction of property by an accidental explosion must be prevented at all costs, and the detonation of explosives stored near populated areas must be avoided. Minimum distances between plant and nearby structures are regulated.

The transmission of detonation by pipes or feeding devices must also be prevented by appropriate arrangements. The danger of detonation by an accidental fire can be mitigated by limiting vessel size. Detonations by shock and friction in pipes, pumps, or valves are prevented by suitable measures.

The following principles apply : partition of risks (e.g., specific buildings for specific operations) ; limitation of risks (limited number of persons present and limited quantities of explosives) ; and installation of two or three independent safety devices. Some of these measures are taken by the manufacturers under the supervision of professional organizations following government regulations.

[50] J. Dubar, J. Calzia, C.R. Seances Acad. Sci. SÃ©r. C 266 (1968) 1114 – 1116.

## 6. High Explosive Mixtures

Explosives are used for global or directed destruction (bombs, torpedoes, mines, reactive armors, and warheads) or for pyrotechnics. Among pure compounds, only TNT and trinitrophenol are sufficiently insensitive to be loaded in large quantities by casting. Small quantities of other pure compounds are sometimes used for detonators or cutting or transmitting cords.

For flexible wrapped cords, the pure explosive (e.g., PETN) flows continuously through a funnel to form a flowing stream that is wrapped in a thin plastic band. Thread is immediately woven on the plastic-enclosed explosive, and this is again encased with plastic by drawing through a die, which also helps adjust the loading density.

For metallic cords, the high explosive (PETN, RDX, HMX, or HNS) is introduced into a metallic tube (lead, copper, or silver), which is drawn through dies until the desired size and cross section are obtained.

**Loading Processes.** In casting processes, the explosive is employed as a solution or a liquid suspension ; it is cast into the shell or in the mold, where it crystallizes on cooling (physical process) or solidifies by the cross-

linking of a polymer (chemical process). In pressing processes, the explosive is introduced in granular form into a mold or shell and pressed with a piston at a pressure of 10 – 300 MPa ; conditions depend on the munitions size, the binder, and the required mechanical properties. Special shapes are prepared by laminating or calendering.

Flexibility is increased by the use of blends, which can enhance explosive performances while preserving safety and reducing cost. Special effects, such as delayed detonation, are possible with improved safety and high-temperature stability.

## **7. Industrial Explosives**

For more than 350 years explosives have been employed to mine ores and minerals. The annual consumption of explosives by each of the largest Western European consuming countries is around 40 000 t. World annual consumption of industrial explosives is at least  $5 \times 10^6$  t, 75 % of which is ammonium nitrate – fuel oil (ANFO).

During the first 250 years of this period, only black powders were known and used, but fundamental changes occurred in the 1860s (invention of dynamite and blasting cap by ALFRED NOBEL), 1950s (ANFO), and 1980s (emulsions). The search continues for less expensive products and safer techniques for production and field use in mines, quarries, and road, tunnel, and dam construction. At the same time, the introduction of new products is restrained by the cost of existing investments and by safety and environmental regulations.

## **8. Test Methods**

Tests of secondary explosives are designed to study detonation phenomena, to approve a product, and to verify that manufactured lots meet the requirements (i.e., quality control).

Detonation phenomena ( $10^{-9}$  to  $10^{-12}$  s) are observed by laser interferometry, streak cameras, and X-ray flashes, all electromagnetic methods. The very high instantaneous pressures (10 – 40 MPa) are measured, e.g., with low-impedance piezoresistive manganin gauges (Cu–Mn–Ni alloy) [74] or with fluorinated piezo polymers as shock sensors [93]. Phenomena are modelled based on Becker – Kistiakowsky – Wilson (BKW) [31] or Jones – Wilkins – Lee (JWL) [32] equations developed in the United States at the Los Alamos Scientific Laboratories (LASL) and the Lawrence Livermore National Laboratory (LLNL).

Tests to approve a product measure detonation velocity and pressure, energy released, ability to initiate or transmit detonation, and critical diameter. They also determine the safety characteristics in use, storage, and transportation.

The verification of a lot is usually based on the determination of physical properties (melting point, particle size, specific area) and chemical analysis. Safety and storage characteristics must match those of the approved product.

Codified tests for military use are published in the United States as military specifications (MIL), in France as Manuel des modes opératoires, in the Federal Republic of Germany as VTL, in the United Kingdom as DEF. STAN, and at NATO as STANAG. Industrial uses are the responsibility of the National Bureau of Standards in the United States, CERCHAR in France, and the Bundesanstalt für Materialprüfung (BAM) in the Federal Republic of Germany. Japan issues Japanese Industrial Standards [75]. Unified and standardized European explosives tests (EXTEST) are published in Explosifs (Belgium, 1960 – 1970), in Explosivstoffe (FRG, 1971 – 1973), in Propellants and Explosives (FRG, 1977 to 1981), and in Propellants, Explosives, Pyrotechnics (1982 to date).

[74] M. J. Ginsberg, A. R. Anderson, J. Wackerle, Symposium sur les jauges et matériaux piezoresistifs, 1st, Arcachon, France, 1981. L. M. Erickson et al., *ibid.*

## 9. Legal Aspects and Production

Governments regulate the possession, production, storage, packaging, shipping, and trading of explosives. Periodic inspections and labeling prevent theft. Tagging the explosive permits tracing its origin.

## 10. Toxicology and Occupational Health

**Raw Materials.** Both acids ( $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) and benzene derivatives (toluene and chlorobenzene) are of concern [4]. The usual safety measures must be followed to protect eyes, skin, and respiratory tract. Red fumes of nitrogen oxides, formed normally or by accident, can induce lung edema two days after exposure; the use of a gas mask is recommended.

**Explosives.** Some primary explosives are toxic (mercury fulminate and certain lead salts), but the toxic hazards are far below those arising from high sensitivities to detonation. Among the secondary explosives, nitroglycerin and other liquid nitrates exhibit hypotensive action accompanied by headaches and, in chronic cases, by methemoglobinemia. A tolerance to nitroglycerin can be developed. These substances are usually absorbed through the skin rather than by inhalation. For nitroglycerin and glycol dinitrate,  $\text{TLV} = 1.5 \text{ mg/m}^3$ . PETN, which like nitroglycerin is prescribed for heart diseases, has a very low vapor pressure and is not readily absorbed by the skin.

The toxic effects of TNT include blood changes, cyanosis, methemoglobinemia, and toxic hepatitis. It is introduced by inhalation, ingestion, and skin absorption; at inhalation level,  $\text{TLV} = \text{ca. } 1 \text{ mg/m}^3$ . Dust in the plant is to be avoided.

Tetryl and hexyl can induce an allergic dermatitis; sensitivity to hexyl is more widespread. For this reason there is a tendency to abandon the use of these explosives.

Both RDX and HMX have negligible vapor pressures. They do not penetrate the skin and their toxicity is very low. However, there have been reports of epileptiform convulsions, without liver involvement, or carcinogenic or mutagenic effects. Dust formation should be avoided and masks should be worn.

[4] B. T. Fedoroff et al.: Encyclopedia of Explosives and Related Items, U.S. Army and National Technical Information Service, Springfield, Va., 1960 – 1983.

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