SENSITIVITY AND PERFORMANCE CHARACTERIZATION OF AMMONIUM DINITRAMIDE (ADN)

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This paper gives some data on the sensitivity and performance of ADN. The ADN used in this work was synthesised at FOA and in a pilot plant at Bofors Explosives AB. The work performed was impact test, friction test, bullet impact test, detonation velocity, detonation pressure and some simple experiments with melt casting. The performance was also calculated with the Cheetah code, using different methods and compared with the experimental results.

INTRODUCTION

Ammonium Dinitramide, or ADN ($NH_4N(NO_2)_2$), is an energetic material which is a potential replacement for ammonium perchlorate (NH_4ClO_4 or AP) in composite propellants. It is also a candidate oxidizer for underwater explosives. It has additional potential as an ingredient in LOVA propellants and as a melt cast matrix for high explosives. Since ADN does not contain chlorine, a composite rocket propellant containing ADN and a polymer binder will produce minimal smoke, and will be more environmentally friendly compared with propellants based on AP. However, there are some drawbacks: ADN is relatively shock sensitive, and is also sensitive to light and moisture. Moreover, ADN has, until now, been very expensive to produce. Earlier work on ADN has mainly been focussed on its synthesis[1,2], thermal stability and decomposition[2–5] and its use as a propellant[4]. Very little has been published on its shock sensitivity or detonation characteristics. This paper presents a study of the sensitivity and thermal sensitivity of ADN, as well as some performance data (e.g. detonation velocity and detonation pressure). It also gives some data on pressability of ADN. In this paper, data from the following tests and studies are presented: Drop weight test, friction test, temperature of ignition, small scale gap test (SSGT), bullet impact, detonation velocity and detonation pressure, and a comparison with thermochemical calculations (Cheetah 1.40)[6]. The paper also presents a comparison of the detonation performance of ADN with that of explosives such as TNT and RDX as well as some potential melt cast compositions such as ADN/RDX or ADN/CL-20.

SYNTHESIS

The ADN for this work was synthesised at FOA and in a pilot plant at Bofors by a new and simple method[7], much less expensive than the one previously available. The particle shape from the synthesis could best be described as fluffy flakes and needles, see figure 1a. The crystal density of ADN was measured with a helium pycnometer and by x-ray powder diffraction and found to be 1.82 g/cm^3. In order to get better particle shapes for propellant use, a melt method for prilling ADN was tested. This method produced nicely rounded particles with a diameter of about 200 μm, see figure 1b. The heat of formation was measured using a bomb calorimeter and found to be -148 kcal/mol.

SENSITIVITY TESTS

The impact sensitivity as well as the friction sensitivity of ADN was measured[8–10]. The impact sensitivity was measured with a 2 kilogram drop weight using a BAM drop weight apparatus. The results are based on tests on both sides of the 50% probability level using

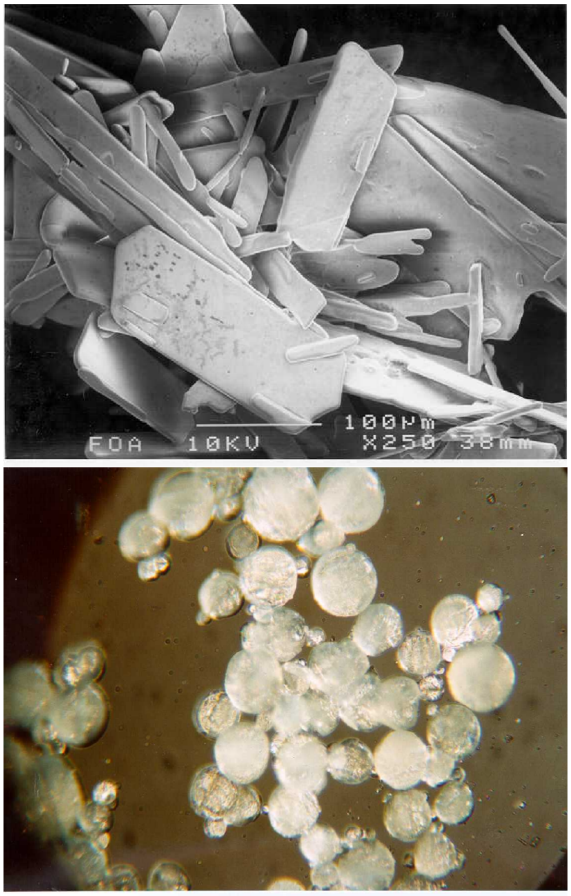

FIGURE 1. ADN PARTICLE SHAPES: A) RE-CRYSTALLIZED, B) PRILLED.

the up-and-down method. The friction sensitivity was measured with a BAM friction apparatus, using the same technique. The results of these tests are given in table 1, where data for RDX is also given for comparison.The friction sensitivity of ADN is much lower than that of RDX. The impact sensitivity of ADN is of the same magnitude as that of RDX, but varies a great deal with the shape of the particles. Prilled ADN, for instance, has a much lower sensitivity than RDX, which indicates that sensitivity to impact, as measured by drop weight test, is greatly dependent on the shape of the ADN particles. The reaction of ADN is also less violent than that of RDX.

IGNITION TEMPERATURE TEST

The sensitivity to thermal ignition was measured, using Wood's metal bath technique. The ignition temperature was found to be 160°C. The ignition temperature measured for ADN is relatively low; RDX tested in the same apparatus and under the same conditions, gave a temperature of ignition of 215°C. The data are shown in figure 2. From these measurements the activation energy was also determined to be $E_a = 127$ kJ/mol.

SMALL SCALE GAP TEST (SSGT)

The results from the SSGT test could not be evaluated as the ADN initiated and burned from the bottom up. This was due to the inert shock travelling through ADN being reflected at the witness-plate. This is a clear indication that under these test conditions, ADN exhibits non-ideal behaviour.

MELT CASTING

At first, small samples of ADN were put into test tubes of glass, submerged in oil and put into an oven under vacuum at a temperature of 97°C and 2 hours. The tube was removed from the oven and placed in insulating material. This was then placed on a tray with some water, just reaching the bottom of the test-tube. In this way the solidification was seeded from the bottom. Similar to TNT there was a crimp-hole forming from the top. The cylinder was turned in a lathe and the density was

TABLE 1. SENSITIVITY DATA FOR ADN AND SELECTED EXPLOSIVES.

Explosive	Drop height (cm)	Friction Test (kp)	Bullet Impact Test (m/s)	Comments
ADN (powder)	31	> 35	309-316	See fig. 1 a
prilled ADN	59	> 35		See fig. 1 b
RDX	38	12		
RDX (98/1/1) pressed			434-474	
TNT (powder)	>120	> 35	364-405	

measured to be 1.67 g/cm3. Without vacuum the density became 1.54 g/cm3. The turning went without problems, although the melt cast ADN was brittle.

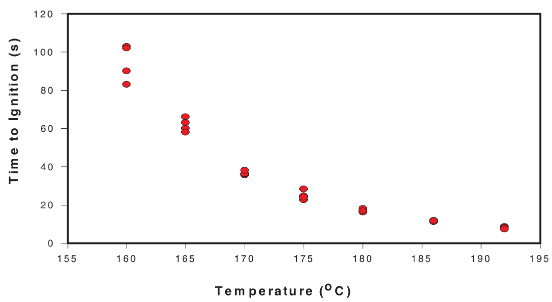

FIGURE 2. TIME TO IGNITION USING WOOD'S METAL BATH.

DETONATION CHARACTERISTICS

Experimental Set-up

The detonation velocities were determined using cylinders of three different diameters of pressed ADN. These were lightly confined in tubes of Plexiglass, and further enclosed in a larger diameter tube of Plexiglass containing silica gel, see figure 3. Silica-gel was used because of ADN's high sensitivity to moisture. The cylinders of ADN were pressed axially to a density of 1.568 g/cm3, with a diameter of 25.1 mm, length 25 mm. and a density of 1.658 g/cm3, for diameter 43.9 mm, length 40 mm. The difference in density was due to problems with the tooling for 25.1 mm diameter. A booster of pressed tetryl was used for initiation of ADN. It had a density of 1.45 g/cm3 which roughly corresponds to a detonation pressure of 100 kbar. By doing this we ensured that no over-driven detonation occurred in ADN. Thin, lacquered copper wires were inserted transversally between each cylinder. This resulted in seven measurement locations along the charge axis. One of them served as a reference point. Towards the charges end a manganin gauge was mounted between the two last cylinders for measurement of detonation pressure. These gauges were thin foils, low impedance (0.05 ohm) types, and the active element is 1 mm square. The instruments were triggered using an ionisation pin mounted in the tetryl booster.

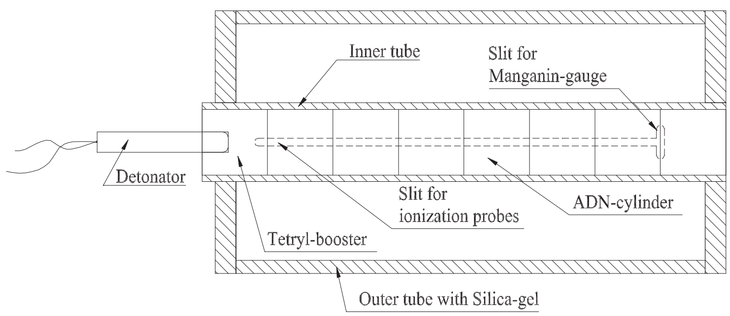

FIGURE 3. EXPERIMENTAL SET-UP FOR RECORDING DETONATION VELOCITY AND PRESSURE.

Detonation Velocity

The results from the 25.1 and 43.9 mm charges are shown below in table 2 and table 3, respectively.

A 10 mm charge, similar in design to those described above, was also fired in an effort to determine the critical diameter, but no reaction at all could be measured. We can therefore assume that the critical diameter is $10 < d_{crit} < 25.1$ mm.

Detonation Pressure

As mentioned earlier an effort to measure the detonation pressure was performed. The pressure profiles are shown in figures 4 and 5. For the 25.1 mm charge the radius of the reaction-zone is small, subjecting the gauge to transversal strain as well, hence the shape of the curve. A CJ-pressure of around 180 kbar could only

TABLE 2. RAW-DATA FROM 25.1 MM ADN CHARGE (ρ = 1.568).

Height of cylinder [mm]	Time [µs]	Velocity [mm/µs]
25.46	5.021	5.071
25.85	5.181	4.989
25.10	4.993	5.027
25.12	5.022	5.002
24.79	4.925	5.034
24.72	4.991	4.953

$D_m = 5.013$, $\sigma = 0.0407$

TABLE 3. RAW-DATA FROM 43.9 MM ADN CHARGE ($\rho = 1.658$).

Height of cylinder [mm]	Time [µs]	Velocity [mm/µs]
40.15	7.519	5.340
39.91	7.580	5.265
40.00	7.501	5.333
39.63	7.599	5.215
39.55	7.599	5.205
40.33	7.752	5.203

$D_m = 5.260$, $\sigma = 0.0630$

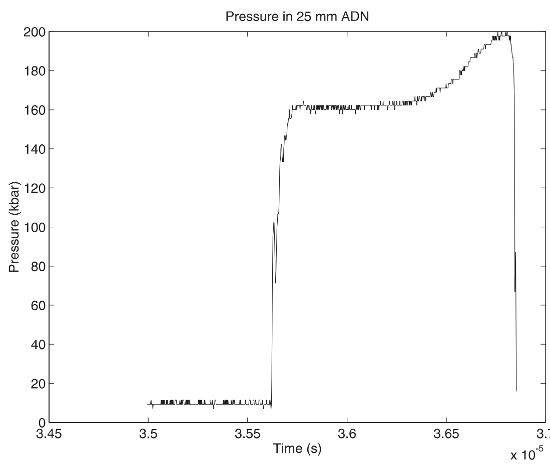

FIGURE 4. PRESSURE PROFILE FROM 25.1 MM CHARGE. THE GAUGE IS SUBJECTED TO BOTH AXIAL AND TRANSVERSAL STRAIN BECAUSE OF THE SMALL RADIUS OF THE REACTION ZONE.

be estimated from the curve from the 43.9 mm charge by inserting an approximation of the ideal behaviour of a shock-front.

THERMOCHEMICAL CALCULATIONS

Since ADN melts at a temperature as low as 93°C, it has potential use as a matrix component in a melt cast composition with other explosives. As can be seen in table 4 ADN gives, together with HMX, RDX or CL-20, rather high increase in performance, and some tests of these compositions will be as useful in practice as in theory, should be performed.

In Table 5 is shown a comparison of the experimental results with thermo-chemical calculations (Cheetah 1.40). As can be seen here we have a large discrepancy between the experimental and the theoretical value. The best value of the detonation velocity was obtained if we suppressed the formation of water. This gave rise to a large increase in the formation of NO_x compounds. This is also in accordance with the experiments, where an odour of nitric acid and NO_x compounds was found. The suppression of water caused the CJ-pressure to decrease to almost half the experimental value.

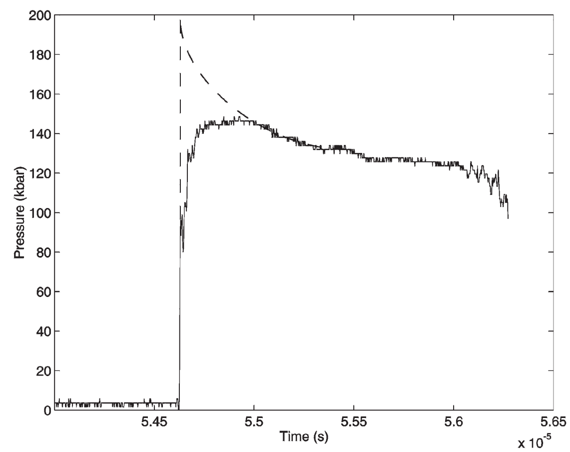

FIGURE 5. PRESSURE PROFILE FROM 43.9 MM CHARGE. THE DASHED LINE REPRESENTS THE IDEAL BEHAVIOUR OF A SHOCK-FRONT.

TABLE 4. CALCULATED PERFORMANCE (TMD 100%, BKW EOS, BKWC LIBRARY, CHEETAH 1.40).

Explosive	D_{CJ} (m/s)	P_{CJ} (GPa)	Expansion Energy for $V/V_0 = 2.2$
HMX/TNT (70/30)	8460	32.25	84% of HMX
HMX/ADN (80/20)	9.485	39.20	100% of HMX
HMX/ADN (60/40)	9.674	39.00	97% of HMX
RDX/ADN (70/30)	9290	35.90	94% of HMX
CL-20/ADN (70/30)	10070	43.00	110% of HMX
CL-20	10030	47.75	119% of HMX

DISCUSSION

Detonation Velocity

The difference in mean density compared to mean velocities is both about 5%, suggesting that the detonation velocitiy is mostly dependent on density. By assuming this we get, so far, a horizontal line in a velocity versus inverse radius diagram. This, together with what we know of critical diameter, suggests a prompt step in such a diagram from detonation to no detonation at the critical diameter.

TABLE 5. CALCULATED DETONATION PARAMETERS (BKW EOS, BKWS LIBRARY, CHEETAH 1.40).

Density (g/cm^3)	Calculated		Experiments		Comments
	D_{CJ} (mm/μs)	P_{CJ} (GPa)	D_{CJ} (mm/μs)	P_{CJ} (GPa)	
1.820	7.960	23.6			
1.568	6.950	16.45	5.013 ± 0.06	(16.0)	25.1 mm (See text)
1.658	7.310	18.8	5.26 ± 0.08	18 ± 2	43.9 mm
1.658	5.275	8.95	"	"	water excluded

Detonation Pressure

The difference in shape of the pressure versus time curve for 25.1 mm and 43.9 mm charge is believed to be an anomaly. Assuming a spherical reaction-zone, of which the radius is smaller in the 25.1 mm charge, because we are close to the critical diameter. With such a small radius we subject the gauge not only to a head-on shock but also a transversal strain that influences the response of the gauge. In the case of 43.9 mm charge there is a more "normal" appearance of pressure versus time because the reaction-zone radius is larger resulting in less influence from lateral strain. We know from other experiments that the pressure peak in the beginning is often missing because of the response time of the measurement system. The ideal behaviour of a shock-front is represented by the dashed line in figure 5. From this we get an estimation of the CJ-pressure of about 180 kbar, ± 20 kbar.

Thermochemical Calculations

The calculated CJ-pressure using standard products is not far from the experiments, but the detonation velocity is. The conclusion will be that ADN behaves non-ideally and that its behaviour could not be fully predicted with ordinary thermochemical codes.

CONCLUSIONS

Some conclusions can be drawn from this initial study.

- ADN exhibits non-ideal detonation behavior.
- The detonation velocity for ADN was measured to be 5.26 ± 0.08 mm/μs, at a density of 1.658 g/cm^3.
- The detonation pressure is about 18 ± 2 GPa.
- The impact sensitivity of ADN was greatly dependent on particle shape.
- ADN is thermally less stable than RDX.

The results of this paper clearly indicate that ADN is a very promising candidate for a new oxidizer replacing AP, but that several important questions remain to be answered. It could also find use as an ingredient in melt cast explosives as a replacement for the often used TNT, giving melt cast charges a performance equal to that of pure HMX, CL-20 or other high performance ingredients. The reason for this is that the mixture will be oxygen and fuel balanced.

FUTURE WORK

More experiments have to be performed in order to determine the reaction-zone radius, reaction-zone length, detonation velocity as a function of density and inverse radius and critical diameter.

ACKNOWLEDGEMENT

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DISCUSSION

Chris Capellos
US-Army TACOM-ARDEC
Picatinny Arsenal, NJ

i. Which polymorph of CL-20 you were using in this experiments? Were you using the epsilon form?

ii. In the formulation CL-20/ADN, 70/30, what was the impact value?

iii. In pure CL-20 the Cheetah calculation I did agrees with the detonation pressure of 47.0 GPa you calculated. However, in your work the GPa for the 70/30 CL-20/ADN formulation the GPa reduces to 43 GPa. If the ADN does not stabilize the CL-20 what is the advantage of using ADN.

REPLY BY H. ÖSTMARK

i. Only calculations in Cheetah has been performed.

ii. ADN and CL-20 seems to form a complex that is very sensitive compared to lead-azide.

iii. You get a melt-castable formulation with a better oxygen-balance.

DISCUSSION

Divyakant Patel
US Army, CECOM-NVESD, Countermine
Fort Belvoir, VA 22060

i. How do you classify ADN-molecules, as a strong oxidizer or explosive molecule.

ii. How much cost 1 kg of Ammonium Dinitramide.

REPLY BY H. ÖSTMARK

i. Both as an oxidizer and a explosive molecule.

ii. We by our ADN at NEXPLO BOFORS AB, Sweden.

COMMENTS BY THE AUTHORS

The signals from the pressure-gauges may suggest that there is a chemical decomposition starting very fast so no von Neumann spike is to be found. This was proposed by L. Forbes and P. Urtiew, LLNL, during discussions at the symposium. The authors agree that this could be an explanation for the pressure profiles observed in figure 4 and 5.