# DETONATION PROPERTIES AND REACTION RATE MODELING OF MELT CAST AMMONIUM DINITRAMIDE (ADN)

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The detonation curvature and detonation velocity of melt cast Ammonium Dinitramide, or ADN ($NH_4N(NO_2)_2$), have been measured at charge diameters of 25 to 100mm. The detonation velocities were as follows: 25 mm, no detonation; 40 mm, 4.3 mm/μs; 60 mm, 5.4 mm/μs; 100 mm, 6.0 mm/μs; all at a density of 1.72 g/cc. The detonation curvature was 59, 76, and 137 mm, respectively. A cylinder test with 51.95 mm inner diameter, 5 mm thickness and 300 mm length was also conducted. This paper also presents a method for melt casting ADN witch enables the melt casting of multi-kg charges at up to 99% of TMD. A comparison with thermo-chemical calculations (Cheetah 2.0) shows a large discrepancy and the conclusion is that ADN is a strongly non-ideal explosive or even a non-CJ explosive.

## 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 as an ingredient in 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. Earlier work on ADN has mainly been focussed on its synthesis[1,2], thermal stability and decomposition[3-6], and its use as a propellant[4]. Very little has been published on its shock sensitivity or detonation characteristics[7-9].

ADN can be characterized by equations of states (EOS) for the reaction products and the unreacted explosive together with a reaction rate law. The EOS for the reaction products can be derived from a cylinder test for the high-pressure regime coupled with thermo-chemical calculations with Cheetah for the low-pressure regime. Once the equations of states are known, the reaction

**TABLE 1. DENSITIES OF PRESSED AND MELT CAST ADN COMPOSITIONS.**

| HE | Density (kg/m$^3$) | % of TMD |
|---|---|---|
| Pure ADN, cast, ambient pressure | 1660 | 92 |
| Pure ADN, cast, vacuum | 1640 | 90 |
| ADN/MgO 99/1, cast, ambient pressure | 1760 | 97 |
| ADN/MgO 99/1, cast, vacuum | 1740 | 95 |
| Pure ADN, pressed, 80 MPa, 25 mm diameter | 1580 | 87 |
| Pure ADN, pressed, 80 MPa, 40 mm diameter | 1660 | 92 |
| Pure ADN, pressed, 90 MPa, 10 mm diameter | 1670 | 93 |

rate law can be calibrated from measurements of detonation front curvature versus detonation velocity.

This paper presents a study of detonation front curvature and detonation velocity for ADN for charge diameters in the interval of 25-100 mm, as well as a comparison with some performance data (e.g. detonation velocity and detonation pressure). A cylinder test has also been performed. This paper also presents a melt casting technique for ADN compositions. A comparison between the experimental detonation velocity and detonation pressure, with thermo-chemical calculations (Cheetah 2.0[11]) was also performed.

No attempt to calibrate an EOS for inert ADN has been made.

## EXPERIMENTAL

### Materials

This study was performed on melt cast ADN compositions using ADN from NEXPLO Bofors AB, Sweden. A method for melt casting of ADN and ADN/Al in batches of up to 6 kg has been developed[12]. ADN proved to be relatively easy to cast when 1% of magnesium oxide (MgO) was added as nucleation kernels and stabilizer. Densities for melt cast ADN/MgO 99/1 were up to 97% of the Theoretical Maximum Density (TMD) and the densities for ADN/Al/MgO (64/35/1) were between 95 and 99% of the TMD. It was found that melt casting in vacuum produced charges with lower densities. Sedimentation of Al in the melt was prevented by selecting a suitable particle size for Al. No gelling agents or other additives were used. A number of basic parameters of importance to melt casting ADN were also determined; Shrinkage on solidification 14%, Liquid density (at 100 ºC) 1560 kg/m$^3$, Heat capacity (Cp, solid) 1.8 ± 0.2 J/g, Heat of fusion 130 ± 5 J/g. Examples of achieved densities for both pressed and melt cast charges are given in Table 1.

After preliminary work with small charges the casting process was scaled up to 6 kg charges. This involved taking into account the physical properties of ADN.

### Detonation front curvature and velocity

A series of experiments has been conducted where the detonation front curvature and detonation velocity was measured for a range of charge diameters. Four charges with diameters 25, 40, 60 and 100 mm were shot in order to measure how the detonation velocity and the curvature of the detonation front depend on the charge diameter. The 25-mm charge did not detonate, which indicates that the critical diameter for cast ADN is between 25 and 40 mm. The charges were cast in thin-walled

PMMA cylinders. The charges were initiated with a plane-wave lens to ensure that the curvature did not originate from geometrical effects. At the opposite end, an array of piezo-electric pins was placed to measure the detonation front curvature. At the cylinder wall, seven equidistant short-cut wires were assembled to register the arrival time of the detonation front. The set-up is presented in Figures 1 and 2.

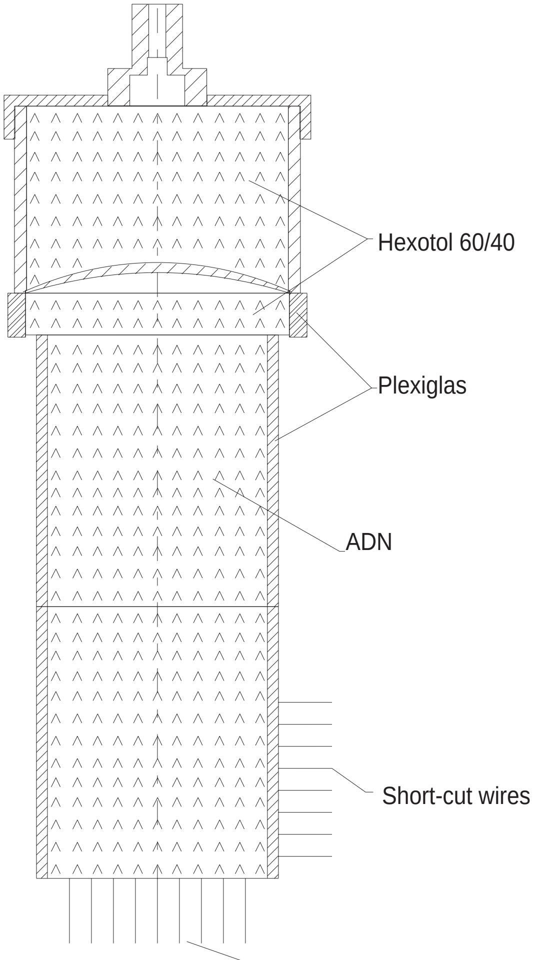

**FIGURE 1. EXPERIMENTAL SET-UP FOR CURVATURE AND DETONATION VELOCITY MEASUREMENTS.**

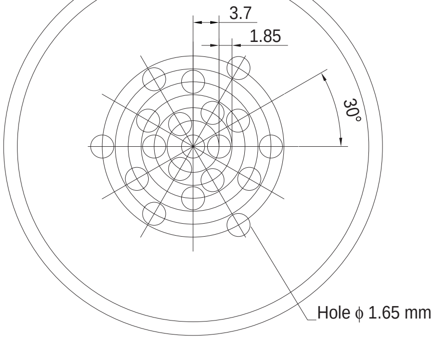

**FIGURE 2. PIEZO-PIN PLACEMENT FOR DETONATION CURVATURE MEASUREMENTS.**

The detonation velocity was obtained by fitting a straight line to the measured arrival times using a least square approximation (Figure 3). The radius of curvature was deduced by fitting the measured detonation front lags to a spheroid with semi-axes *a* and *b*;

$$\frac{(x-x_0)^2}{a^2}+\frac{(y-y_0)^2}{a^2}+\frac{(z-z_0)^2}{b^2}=1 \qquad (1)$$

The center of the spheroid was not fixed to the cylinder axis to account for possible obliquity in the shock front. In Equation (1), *z* denotes the coordinate along the cylinder axis and $(x_0, y_0, z_0)$ denotes the center of the spheroid. The radius of curvature on the center of the axis is given by $R_c = a^2/b$. Figure 4 shows the fits of the measured lags for the three different charges diameters and the results are summarized in Table 2.

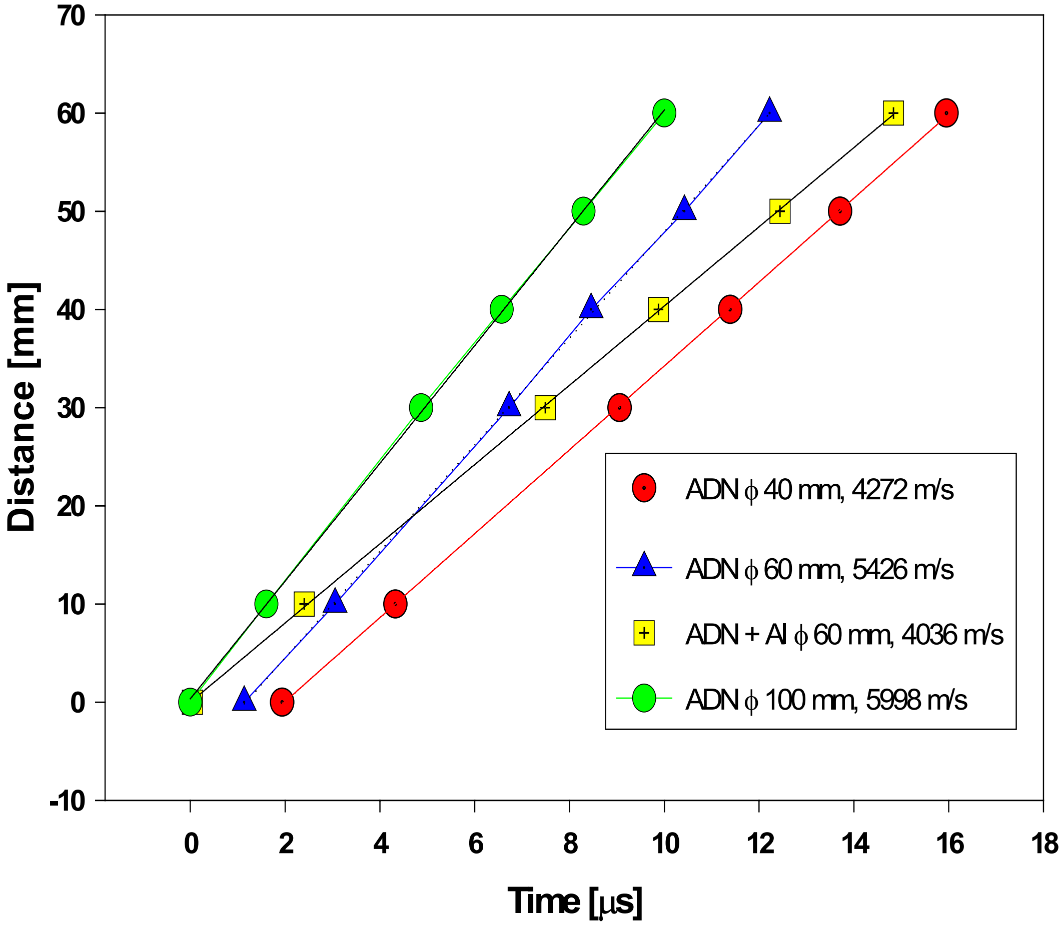

**FIGURE 3. DETONATION VELOCITY OF ADN AND ADN/AL FOR VARIOUS CHARGE DIAMETERS.**

**TABLE 2. DETONATION FRONT VELOCITY $D_0$ AND RADIUS OF CURVATURE ($R_c$) AT THE CYLINDER AXIS FOR DIFFERENT CHARGE DIAMETERS (D).**

| *d* (mm) | $D_0$ (m/s) | *a* (mm) | *b* (mm) | $R_c$ (mm) |
|---|---|---|---|---|
| 40 | 4250 | 17.75 | 5.374 | 58.6 |
| 60 | 5430 | 159.8 | 335.7 | 76.0 |
| 100 | 5990 | 61.03 | 27.17 | 137.1 |

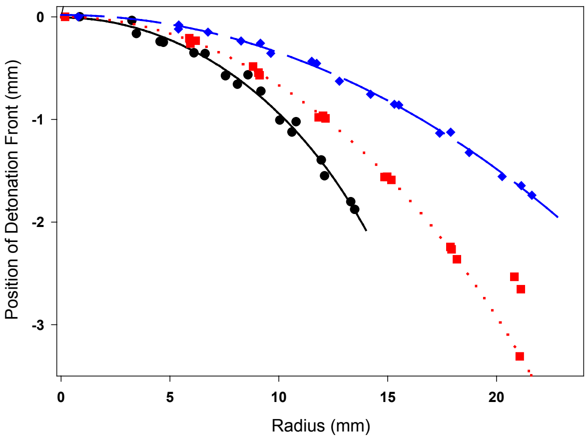

**FIGURE 4. ADN DETONATION FRONT CURVATURE FOR VARIOUS CHARGE DIAMETERS.**
**(● 40 MM; ■ 60 MM ♦ 100 MM)**

The detonation velocity for the three diameters was almost linear in the inverse squared charge diameter, as shown in Figure 5. Assuming a linear behavior, the extrapolated detonation velocity for an infinite charge is approximately 6300 m/s.

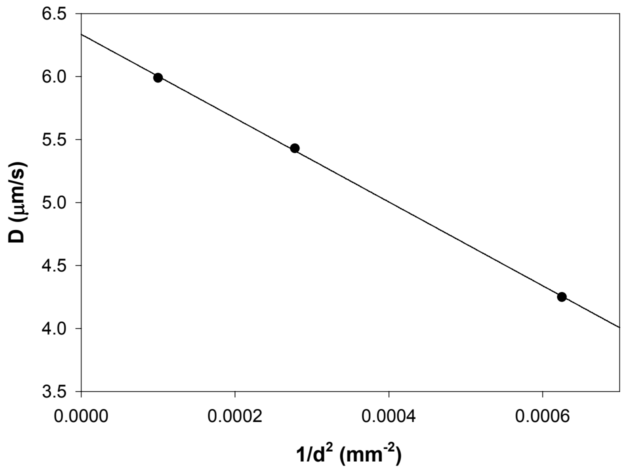

**FIGURE 5. DETONATION VELOCITY AS A FUNCTION OF CHARGE DIAMETER.**

## Cylinder test

In the cylinder test a cylinder of OFHC copper with 51.95 mm inner diameter, 5 mm thickness and 300 mm length was used. The density of the ADN sample was 1.72 g/cc. The charge was initiated with a plane-wave lens to obtain as close to ideal detonation conditions as possible. At 150 mm distance from the bottom, 22 piezo-pins were mounted perpendicular to the cylinder axis to measure the cylinder wall velocity. The distances between the pins and the outer cylinder surface varied between 0.1 mm and 60 mm, corresponding to a maximal volume expansion of 11 times the original volume. The set-up is shown in Figure 6.

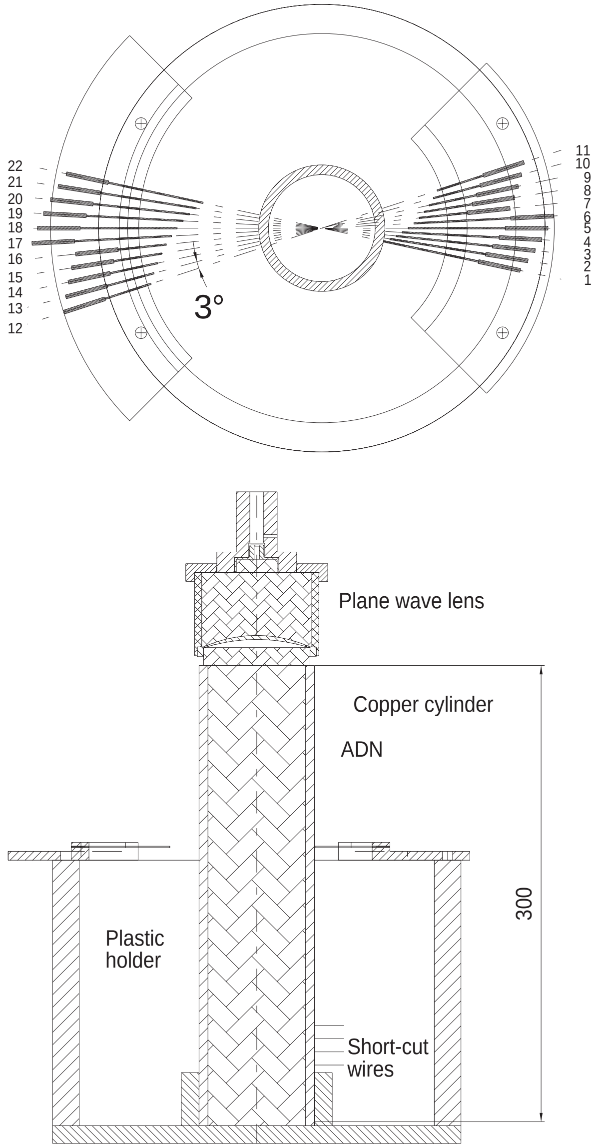

**FIGURE 6. EXPERIMENTAL SET-UP FOR THE CYLINDER TEST.**

The measured arrival times of the cylinder wall are presented in Table 3. The signal from the piezo-pin closest to the cylinder was missing, which makes it difficult to estimate the jump-off velocity. Some scatter in the data can be observed when numerically differentiating the distance with respect to time. The wall velocity increases initially and then starts to oscillate around a nearly constant value of 1.2 mm/µs.

The detonation velocity was measured by four short-cut wires placed 10 mm apart from each other just above the bottom of the cylinder. The detonation velocity was determined to be 5605 m/s, which is much lower than the extrapolated infinite size value 6300 m/s.

**TABLE 3. MEASURED ARRIVAL TIMES OF THE CYLINDER WALL.**

| Distance (mm) | Time (µs) | Distance (mm) | Time (µs) |
|---|---|---|---|
| 3.0 | 39.251 | 33.0 | 65.935 |
| 6.0 | 42.339 | 36.0 | 68.361 |
| 9.0 | 44.860 | 39.0 | 70.928 |
| 12.0 | 47.866 | 42.0 | 73.393 |
| 15.0 | 50.499 | 45.0 | 75.792 |
| 18.0 | 53.028 | 48.0 | 78.315 |
| 21.0 | 55.622 | 51.0 | 80.798 |
| 24.0 | 58.133 | 54.0 | 83.182 |
| 27.0 | 60.647 | 57.0 | 85.784 |
| 30.0 | 63.260[†] | 60.0 | 88.174 |

[†] Averaged over two opposite piezo-pins at the same distance.

## THERMOCHEMICAL CALCULATIONS

It is interesting to compare the experimental results with results from a thermo-chemical code. Cheetah 2.0[11] with the BKW EOS and the BKWS product library was used for this comparison. The calculations were performed using the default heat of formation and theoretical maximum density for ADN, which are –135.0 kJ/mol and 1.808 g/cc respectively. A calculation of the CJ state using the density 1.72 g/cc gives a detonation velocity of 7.62 mm/µs and a CJ-pressure of 21 GPa. The calculated detonation velocity is 21% higher than our estimated infinite size value. In earlier experiments[2], the pressure profile for a 43.9 mm charge of pressed ADN was measured using a manganin gauge. The pressure profile is shown in Figure 7. Although no distinct spike can be observed, a 21 GPa CJ-value seems unlikely.

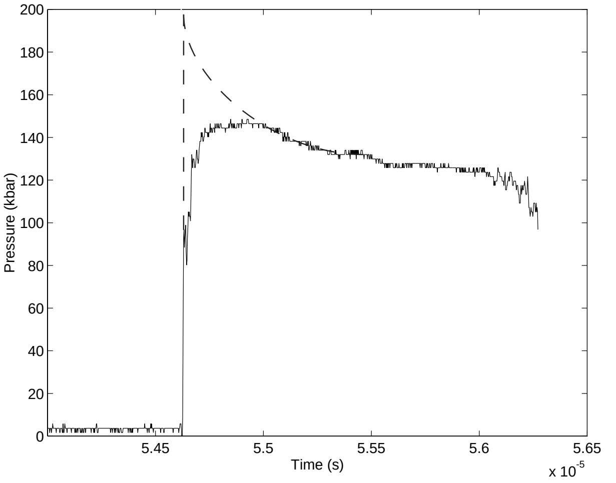

**FIGURE 7. PRESSURE PROFILE FROM 43.9 MM PRESSED ADN CHARGE. THE DASHED LINE REPRESENTS THE IDEAL BEHAVIOR OF A SHOCK-FRONT (FROM REF 8).**

The experimental wall velocity, defined by $u = d(R - R_0)/dt$ (which is different from the particle velocity), can be related to a PETN-standard by[1]

$$u(\exp) = u(\text{PETN})\sqrt{E_d / E_d(\text{PETN})} \qquad (2)$$

where $E_d$ is the detonation energy. A cylinder run in Cheetah calculates the ratio between the detonation energy in ADN and PETN. The Cheetah calculated wall velocities are compared to the experimental values in Table 4. The calculated velocities are approximately 10% higher than the experimental values.

**TABLE 4. MEASURED AND CALCULATED WALL VELOCITY USING CHEETAH 2.0 FOR DIFFERENT SPECIFIC VOLUMES V.**

| $v/v_0$ | $E_d/E_d$(PETN) | $u$(PETN)[†] [mm/µs] | $u$(calc) [mm/µs] | $u$(exp) [mm/µs] |
|---|---|---|---|---|
| 2.20 | 0.61 | 1.575 | 1.23 | 1.12 |
| 4.10 | 0.58 | 1.720 | 1.31 | 1.18 |
| 6.50 | 0.57 | 1.775 | 1.34 | 1.20 |

[†] From Ref. 10 for a full wall 1 inch cylinder.

## CONCLUSIONS

There are large discrepancies between the thermo-chemical calculations and the experiments. Considering the usually good agreement between Cheetah-calculated and experimental detonation velocities for CHNO-explosives, the discrepancy for ADN is puzzling. Possible explanations for the discrepancy include:

- The product libraries in Cheetah are not calibrated for explosives producing a lot of oxygen and water
- CJ-theory is not applicable for ADN
- Size effects are not negligible even for 100 mm charges.

The pressure profile shown in Figure 7 indicates that a CJ-theory might not be appropriate, or that size-effects have to be considered. The pressure profile shows no spike and no expansion- (or Taylor-) wave structure behind the leading front, probably due to an extended reaction zone or considerable afterburning. However, provided the heat of formation value is correct, the discrepancy in wall velocity (which corresponds to the detonation energy) indicates that all the available energy is not released.

We have chosen not to calibrate an EOS to our experimental data for two reasons. Firstly, we would like to set the low-pressure tail from thermo-chemical calculations. Until the large deviation between experimental values and calculations has been explained, the correctness of such values will be questionable. Secondly, the cylinder data contains too few measurement points, especially near the cylinder wall, to give reliable wall velocities. Without a product EOS, calibration of a reaction rate law is of limited value.

### Future work

The detonation velocity in the cylinder test was low enough that CJ conditions at the front were probably never established. To obtain a high quality EOS from the cylinder data more data points are needed. Thus, a new cylinder test using a larger charge diameter and instrumented with a streak camera needs to be performed. To calibrate a reaction rate law to the front curvature experiments a shock Hugoniot for inert ADN also needed.

Further work has to be performed in order to explain the large discrepancy between thermo-chemical calculations and the experimentally determined detonation velocity.

## REFERENCES

1. Bottaro, J.C., P. E. Penwell, R. J. Schmitt: J. Am. Chem. Soc., vol. 119 (1997) p. 9405.
2. Bottaro, J.C., *et al.*, *Method of forming dinitramide salts*, U.S patent WO 91/19670, 1991.
3. Brill, T.B., P.J. Brush, and D.G. Patil, “Thermal Decomposition of Energetic Materials 58. Chemistry of Ammonium Nitrate and Ammonium Dinitramide Near the Burning Surface Temperature”, Combustion and Flame, vol. 92,. pp. 178-186, 1993

4. Östmark, H., N. Wingborg, and A. Langlet: "ADN: A new and High Performance Oxidizer for Solid Propellants." *16th International Symposium on Ballistics*. 1996, San Francisco, CA
5. Rossi, M.J., J.C. Bottaro, and D.F. McMillen: "The Thermal Decomposition of the New Energetic Material Ammonium Dinitramide ($NH_4N(NO_2)_2$) in Relation to Nitramide (NH2NO2) and NH4NO3." International Journal of Chemical Kinetics, vol. 25, pp. 549-570, 1993.
6. H. Östmark, U. Bemm, A. Langlet, R. Sandén and N. Wingborg: "The Properties of Ammonium Dinitramide (ADN): Part 1, Basic Properties and Spectroscopic Data" J. Energetic Materials vol. 18 p. 123, 2000.
7. Doherty, R. M., *et al*: "Detonation Velocity of Melt-Cast ADN and ADN/nano-diamond Cylinders" *Meeting of the APS Topical Group on the Shock Compression of Condensed Matter*, 27th of July - 1st of August 1997, Amherst, MA.
8. Karlsson, S and H. Östmark: "Sensitivity and Performance Characterization of Ammonium Dinitramide (ADN)", *Eleventh International Detonation Symposium*, pp.774-779. Snowmass 1998. ONR-33300-5
9. Miller P.J, C.D. Bedford and J.J. Davis: "Effect of Metal Particle Size on the Detonation Properties of Various Metallized Explosives", *Eleventh International Detonation Symposium,* pp.214-220. Snowmass 1998, ONR-33300-5
10. P. C. Souers, B. Wu, and L. C. Haselman, Jr.: *Detonation Equation of State at LLNL, 1995*, LLNL Report UCRL-ID-119262, February 1996.
11. Fried, L.E., *Cheetah 1.39 Users Manual*, 1996, Lawrence Livermore National Laboratory.
12. Hahma, A., H. Edvinsson and H. Östmark: "The Properties of Ammonium Dinitramide (ADN): Part 2, Melt Casting", to be published.