ADN – The new oxidizer around the corner for an environmentally friendly smokeless propellant

Abstract: The search for a smokeless propellant has encouraged scientists and engineers to look for a chlorine-free oxidizer as a substitute for AP (ammonium perchlorate). Endeavors seemed to come to an end when ADN (ammonium dinitramide) appeared in the West in the early 1990s. Although some drawbacks soon became apparent by that time, the foremost obstacle for its use in rocket-motors came from the patent originally applied for in the United States in 1990. Furthermore, environmental concerns have also increased during these two decades. Ammonium perchlorate is believed to cause thyroid cancer by contaminating soil and water. In addition, AP produces hydrogen chloride during burning which can cause acid rain and ozone layer depletion. Unlike AP, ADN stands for both smokeless and green propellant. Since then, much progress has been made in its development in synthesis, re-shaping, microencapsulation and solid propellant. The high solubility of ADN in water has also allowed its application as liquid monopropellant. Tests have revealed Isp (specific impulse) superior to that normally observed with hydrazine, one of the most harmful and hazardous liquid propellants. With constraints of use, along with the patent near to expiry, scientists and engineers are rushing to complete developments and patents until then.

Keywords: ADN, Ammonium dinitrate, Smokeless propellant, green propellant, oxidizer.

INTRODUCTION

This text is intended to provide an overview of ADN and a comprehensive description of the recent achievements in its development to-date. A brief history is given from its origin in the former USSR, as a key component in the production of smokeless propellants, up until the aftermath of the end of the Cold War, when it proved to be a strategic component for smokeless and green propellants. A description of recent advances is made while addressing issues that emerged during the attempts to replace AP (ammonium perchlorate) in solid propellants and hydrazine in liquid monopropellants. With the information contained here, it is hoped to assist readers in assessing the future of ADN in the rocket motor industry for the coming years.

Although many routes for ADN (ammonium dinitramide) synthesis have been proposed so far, the only effective one for large-scale production uses sulfamate salts and nitrating acid. The shape of ADN crystals as synthesized is far from being round. In this sense, two techniques stand out in re-shaping these crystals, one by a prilling process and the other by emulsion crystallization. The shape of crystals plays a major role in the ADN loading (% weight) in solid propellants, which also helps to increase the propellant density. Microencapsulation is another breakthrough. After re-shaping the crystals into rounded grains, they are protected from wetting and reacting with the cure agent (chemical compatibility). Each particle is coated with a thin layer of polymer, which is also expected to reduce sensitivity and, to some extent, help to improve stability. Two methods are noteworthy, one by spray dryer and the other by a fluidized bed. Despite all the achievements so far, scientists continue to search for an ideal stabilizer. ADN-based propellants have exhibited higher burning rate with both binders, HTPB (hydroxyl-terminated poly-butadiene) and GAP (glycidyl-azide polymer). The ADN/HTPB-based propellants used to exhibit poorer mechanical properties when compared to the ADN/GAP-based one. These properties are also affected by microencapsulation, which has led to the development of techniques which depend on the material from which this coating is made. In addition, some achievements have been made in developing liquid monopropellants based on ADN. This new propellant is meant to replace hydrazine in liquid thruster.

HISTORY

Bottaro (1993), originally introduced ADN to the public in the West by applying for a patent in 1990. The patent was granted to SRI (Standford Research Institute) in 1993 for this subject matter, which also claimed to have conceived and first synthesized the ADN molecule. Meanwhile, Pak
(1993), of the LNPO Soyuz made public a paper at the AIAA Conference in the United States in 1993, in which he disclosed what is now accepted as being the origin of ADN in the former USSR (Union of Soviet Socialist Republics). One year later, Tartakovsky and Lukyanov (1994) reasserted the Soviet origin of ADN at the Fraunhofer-ICT Conference in Germany in 1994. Nowadays, it is acknowledged that ADN was first synthesized in the early 1970s in the USSR. After going through developments in the 1970s and 1980s, the Soviets started producing tons of ADN for tactical-rocket/missile during the 1980s. In the meantime, the Soviet union’s economy was growing worse during that decade, and finally disrupted the Cold War in the late 1980s. In the course of events, specialists in ADN moved abroad and lent assistance to local engineers. By that time, the Soviet’s plant was destroyed or dismantled and production was discontinued for good. In Sweden in 1996, FOI (Forskningsinstitut / Swedish Defense Research Agency) designed a new one-step process, and one year later, in 1997, Bofors inaugurated a plant and started producing ADN using the same FOI technology. SAAB AB purchased Bofors in 1999 and ultimately, Eurenco, a joint venture controlled by SNPE, took over AB Bofors in 2004. Thereafter Eurenco made ADN samples available for sale, which has stimulated engineers across the world to carry on developments. NASA/GRC (National Aeronautics and Space Administration / Glenn Research Center) has a requirement to produce ADN for solid rocket boosters. Even though NASA had started researching into ADN in 1990s, they interrupted this soon afterwards, due to the shortage of resources funded by AFOSR (Air Force Office of Scientific Research), and subsequently on account of the downturn in the American space program over the last two decades. However, in December 2008, they announced interest in acquiring items from FOI to produce ADN for the new ARES booster, the new vehicle that is meant to replace the Space Shuttle. Research into ADN is also under way in many countries e.g. Japan, India, China and more recently at AQI-IAE (Chemical Division - Institute of Aeronautics and Space) in Brazil.

**BACKGROUND**

**Structure**

Dinitramidic acid has a similar structure to ammonia. It has two NO₂ groups instead of the two hydrogen groups in the ammonia molecule.

\[
\text{NH}_4^+ \text{N} (\text{NO}_2)_2^- \quad (1)
\]

Dinitramidic acid

\[
\text{NH}_4^+ \text{N} (\text{NO}_2)_2^- + \text{H}^+
\]

Dinitramide anion

H

N

O

NO₂

NH₄⁺

N

O

NO₂

ammonia

dinitramidic acid

The two NO₂ groups exert strong inductive effect on the central nitrogen. As a result, the remaining hydrogen detaches as hydronium cation.

Dinitramide anion is more stable when compared to the acid form. Bottaro et al. (1997), have attributed the additional stability to the existence of the three resonance structures shown below (3):

\[
\quad \quad \quad (3)
\]

ADN is formed by one dinitramide anion and one ammonium cation. This salt is highly soluble in water at ambient temperature and slightly soluble at temperatures as low as -40° C. The dissociation is represented by:

\[
\text{NH}_4^+ \text{N} (\text{NO}_2)_2^- \leftrightarrow \text{NH}_4^+ + \text{N} (\text{NO}_2)_2^-
\]

**Physical & Chemical Properties**

ADN crystals grow as yellow/white needles. The density of the crystals is 1.885 g/cm³, lower than 1.950 g/cm³ of AP (ammonium perchlorate). Hygroscopicity and friction/impact sensitivities are higher than in AP. Unlike most oxidizers, ADN melts before decomposing. The melting point is around 93° C. ADN is chemically incompatible with isocyanate-based cure agents. The oxygen balance of ADN is 25.8 per cent, lower than the 34.0 per cent of AP. The apparent disadvantage is compensated by higher energy of formation (-125.3 kJ/mol) when compared to (-283.1 kJ/mol) of AP. In addition, the specific impulse of ADN-based propellants is higher than of AP-based one. Table 1 provides some properties.
Table 1: ADN Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology of crystal</td>
<td>needles</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>high</td>
</tr>
<tr>
<td>Color of crystal</td>
<td>yellow/white</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.81</td>
</tr>
<tr>
<td>Melting point (ºC)</td>
<td>92 – 95</td>
</tr>
<tr>
<td>Friction sensitivity (N)</td>
<td>64 - 72</td>
</tr>
<tr>
<td>Impact sensitivity (N.m)</td>
<td>3 – 5</td>
</tr>
<tr>
<td>Oxygen excess (%)</td>
<td>25.8</td>
</tr>
<tr>
<td>Formation energy (kJ/mol)</td>
<td>-125.3</td>
</tr>
</tbody>
</table>

ADN DEVELOPMENTS

Synthesis

Schmitt et al. (1993) originally proposed a route for synthesizing ADN from ammonia. This is a straightforward way to perform it since the two compounds have similar structures (1). However, this nitration requires expensive nitronium salts or nitryl compounds, which makes this reaction only justifiable for scientific or academic purposes. These routes are often not proper for large-scale production or commercial ends due to the high cost of the nitrating agents. Some examples of the nitrating agents unveiled in this patent are:

\[
\begin{align*}
\text{(5a)} & : \quad \text{Nitronium tetrafluoroborate} \\
\text{(5b)} & : \quad \text{Nitronium hydrogen pyrosulfate} \\
\text{(5c)} & : \quad \text{Dinitrogen pentoxide}
\end{align*}
\]

Nitronium cation \(\text{NO}_2^+\) is always an intermediate in nitration reactions. This cation is rare and cannot be confused with the nitrite anion \(\text{NO}_2^-\). Nitronium salts are efficient, but very costly (thousands of dollars per gram). On the other hand, Langlet et al. (1997) have reported the use of the nitrating acid for this purpose. Nitrating acid is a combination of fuming nitric acid and sulfuric acid, commonly used in the explosives industry. Nitrating acid is less expensive, which makes the production of ADN economically viable. The sulfuric acid catalyzes the nitronium formation, according to the reaction:

\[
\text{H}_2\text{SO}_4 + \text{HNO}_3 \leftrightarrow \text{HSO}_4^- + \text{NO}_2^+ + \text{H}_2\text{O}
\]

However, nitrating acid is not effective in nitrating directly from ammonia. In this sense, the breakthrough came with Langlet et al. (1997) They reported a method to synthesize ADN from sulfamic acid or sulfamate salts instead of ammonia. This route was first utilized by the Soviets in the former USSR. The structure of the sulfamate anion is:

\[
\text{(7)} \quad \text{Sulfamate anion}
\]

The two hydrogen groups in the sulfamate anion are more liable to react than the ones in the ammonia molecule. This route has been called "the one-step reaction". The reaction is carried out in a severe acidic medium, which results predominantly in dinitramidic acid.

\[
\text{(8)} \quad \text{Dinitramidic acid}
\]

The dinitramidic acid in this medium is not as stable as the dinitramide anion, since it is more likely to decompose to AN (ammonium nitrate). For this reason, Vörde et al. (2005) proposed a method to convert dinitramidic acid into ADN. The reaction is represented by:
Recrystallization

ADN crystals grow as long needles, which makes their re-shaping crucial. The shape can affect the end-of-mix viscosity as well as the mechanical properties of propellants. The shape also helps to increase the loading (% weight) of oxidizer in propellants. ADN melts down at about 93ºC, much lower than its decomposition temperature at about 124ºC. This feature has been used to re-shape its crystals. The high level of purity is an important condition when applying the following re-shaping techniques.

• **Prilling tower**

In this method, melted ADN is sprinkled at the top of the prilling tower, as shown in the Fig. 1. ADN droplets come into contact with the cooling nitrogen flowing upward in counter-current as these droplets come down through the tower. This was the pioneering method to obtain ADN prills. Highsmith et al. have described this technique for ADN.

• **Spray crystallization**

This technique has been widely applied to obtain rounded particles of AN (ammonium nitrate). Heintz and Fuhr (2005) originally devised the application of this technique for ADN in 2005. Johansson et al. (2006) et al. developed this technique for ADN with further modifications. Melted ADN is sprayed through an atomizer in a liquid nitrogen vessel. This method is still under development for ADN, and the benefits reside in the compactness of the equipment when compared to the prilling tower.

• **Microencapsulation**

Encapsulation is a technique aimed at protecting ADN grains from wetting and reacting with the cure agent. The method consists of coating the surface of each particle with a thin layer of polymer. ADN is hygroscopic and chemically incompatible since it can react with isocyanate-based cure agents normally employed in binders. It is usual for suppliers to coat ADN with a thin layer of wax to give protection for shipment and storage. However, such a material is not suitable for use in propellants, and therefore it needs to be washed out before the surface receives a polymer coating. This technique is called microencapsulation.

• **Coacervation**

Initially ADN particles are poured and dispersed in an emulsion consisting of ethylcellulose in cyclohexane. The dispersion is stirred until the droplets of ethylcellulose gather around each particle and merge to form a continuous layer on its surface. The process is induced by pH, temperature and the addition of a third component. The dispersion is cooled down and the layer is left to harden. The coated ADN is separated and dried. Heintz and Teipel (2000) have described this method.

• **Fluidized bed**

In this method, ADN particles are kept floating in a chamber by air flowing upwards as shown in Fig. 2. The polymer is sprayed from either the bottom (Wurster) or top of the fluidized bed chamber. The particles are kept this way until the coating gets stiff. Heintz et al. (2008) have reported some results obtained by employing this method with different polymers normally used as binders in propellants.
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Supercritical fluidized bed

Nauflett and Farncomb (2002) introduced a modification for the fluidized bed method. Air is replaced by carbon dioxide due to the supercritical properties that this gas can exhibit at moderate temperatures and high pressure. Supercritical fluids exhibit low viscosity, similar to gases, and high densities, comparable to liquids. These properties make supercritical gases more suitable for this process. However, the chamber walls must be reinforced to withstand high-pressure operations.

Spray dryer

Spray dryer is usually applied to smaller particles (< 50 micron) in which the fluidized bed method is not applicable. In this technique, the resin and ADN grains are dispersed and sprayed into a vessel by means of an atomizer. A thin layer of coating forms around the surface of each particle. The coated particles become solid as the solvents vaporize. Fig. 3 shows schematically this technique.

Solid Propellant

ADN is compatible with single C-C, double C=C or even C-H bonds as pointed out by Teipel (2005). Nonetheless, ADN is incompatible with isocyanates, normally employed as cure agent for binders in solid propellants. In this sense, Keicher et al. (2008) reported a new method for curing GAP with an isocyanate-free curing agent. Pontius et al. (2008) also proposed another approach in this direction. However, a remarkable step forward in overcoming this obstacle was taken by microencapsulating ADN grains. Although microencapsulation is an elegant technique for this purpose, the search for an ideal coating material continues.

Any binder normally employed in solid propellants could be used, provided that the cure agent is chemically compatible with ADN. However, most of the curing process takes place through urethane links, which demand the use of isocyanate-based cure agents. Asthana and Mukundan (2002) have reported a new generation of energetic binders that holds azide groups (-N₃) in their backbone viz. GAP (glycidyl azide polymer), PBAMMO (poly bis azido methyl oxetane), PNIMMO (poly nitrato methyl oxetane), PGN (poly glycidyl nitrate), PAMMO (poly azido methyl methyl oxetane). On the one hand, PBAMO exhibits the best performance among them. On the other hand, it is solid and has to be combined with energetic copolymers or plasticizers to turn it into liquid. GAP was the first polymer to be successfully applied in propellants. In contrast to what occurs with AP (ammonium perchlorate), GAP exhibits better results with ADN than HTPB (hydroxyl terminated poly butadiene). GAP has higher enthalpy of formation than HTPB. In addition, it exhibits higher specific impulse as shown in the Fig. 4.
Stability

Stabilizers are intended to prevent ADN from decomposing under increasing temperatures or through time. The decomposition mechanism is not completely understood, but it is largely accepted to occur through a chain reaction process. The decomposition occurs at lower temperatures (<100°C) in a gradual and continuous way, mainly evolving ammonia NH₃ and nitrous oxide N₂O. The decomposition becomes prominent even at temperatures as low as 60°C. At higher temperatures (>100°C), nitrogen N₂, nitrous dioxide NO₂ and nitrous oxide N₂O are common gases evolved in one or more steps as discussed by Andreev et al. (2000). The first step necessarily involves rearrangement of ADN. At moderate temperatures, ADN is converted to the less stable dinitramidic acid, usually catalyzed by acids. This reaction is believed to occur early on, regardless of the temperature to which ADN is subjected.

\[
\begin{align*}
\text{NH}_2\text{N} & \rightarrow \text{NH}_3 + \text{H} - \text{N} - \text{N} \rightarrow \text{NH}_2\text{NO}_2 \\
\text{ADN} & \rightarrow \text{ammonia} \quad \text{dinitramidic acid}
\end{align*}
\] (10)

The dinitramidic acid formed in the first step continues to decompose since it is more labile. In the next step, dinitramidic acid decomposes and evolves nitrous oxide N₂O. Russel et al. monitored the evolution of N₂O during degradation tests with ADN. Nitrous oxide N₂O and ammonia NH₃ are typical gases evolved during ADN decomposition. However, the proportion between the two gases can vary remarkably, depending on the temperature, as pointed out by Yang et al. (2005). Nitric acid is also formed in this step.

\[
\begin{align*}
\text{H} - \text{N} - \text{NO}_2 & \rightarrow \text{HNO}_3 + \text{N}_2 \rightarrow \text{nitric} \quad \text{nitrous oxide}
\end{align*}
\] (11)

dinitramidic acid \quad \text{nitric acid} \quad \text{nitrous oxide}

At low temperatures (<100°C), nitric acid and ammonia combine to produce ammonium nitrate AN.

\[
\begin{align*}
\text{NH}_3 + \text{HNO}_3 & \rightarrow \text{NH}_4\text{NO}_3 \\
\text{ammonia} & \quad \text{nitric acid} \quad \text{ammonium nitrate}
\end{align*}
\] (12)

AN (ammonium nitrate) and HNO₃ (nitric acid) are the common impurities capable of speeding up the rate of ADN decomposition. Santhosh and Ghee (2008) have proposed two additional steps for the decomposition at higher temperatures

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \\
\text{ammonium nitrate} & \quad \text{nitrous oxide} \quad \text{water}
\end{align*}
\] (13a)

The lack of a consistent theory has hampered the development of stabilizers. Attempts have been made based on the backgrounds in explosives or by trial and error. Organic bases are believed to play an important role in stabilizing ADN. Lobbecke et al. (1997) tested five compounds as shown in the Table 2.

Table 2: Comparison of stabilizers

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Time (hours) at 10% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>58</td>
</tr>
<tr>
<td>MgO</td>
<td>55</td>
</tr>
<tr>
<td>NaBO₂</td>
<td>97</td>
</tr>
<tr>
<td>hexamethylenetetramine</td>
<td>149</td>
</tr>
<tr>
<td>nitrodiphenulamine</td>
<td>157</td>
</tr>
<tr>
<td>Arkadit II</td>
<td>248</td>
</tr>
</tbody>
</table>

Inorganic and organic bases have been tested; metal oxides are less effective when compared to organic amines. Arkadit II, usually employed as a stabilizer in explosives, turned out to be the most effective in this evaluation. Evidence points to organic bases as being overall the most effective among them. According to Teipel (2005), stabilizers should be incorporated directly into the raw material, or during the recrystallization process.

Liquid Monopropellant

Over the years, scientists have also been looking for a suitable substitute for hydrazine, one of the most hazardous and harmful liquid propellants. In this regard, HAN (hydroxylammonium nitrate) has been on trial since as early as the 1970s. Large amounts of HAN can be dissolved in water, which is the primary requirement for use as a liquid monopropellant. This monopropellant is more stable and storable than its hydrazine-based counterparts as reported by Schmidt and Gavin (1996). The solubility achieved in this case is as high as 96 per cent. Nonetheless, Morgan and Meinhardt (1999) pointed out recurring lower specific impulse for HAN-based...
monopropellants when compared to hydrazine, even with the addition of a third part of glycerol as a fuel.

In 1999, Van den Berg et al. (1999) et al. revealed the specific impulse of monopropellants consisted of ADN dissolved in water and alcohols. The specific impulses in both cases are higher than the ones achieved by either HAN-based monopropellants or hydrazine. Anflo et al. (2002) added a third part of fuel to the solution of water/ADN achieving monopropellants with higher specific impulse. Wingborg et al. (2005) have reported specific/density impulse of ADN/water/fuel as being 10 per cent and 60 per cent higher than for hydrazine, respectively. In 2009, Sjöberg and Skif (2009) disclosed LMP-103S, the ADN-based monopropellant with four components developed by Eurenco-AB Bofors. The formulation is shown in Table 3.

Table 3: Formulation of ADN-base monopropellant

<table>
<thead>
<tr>
<th>Component</th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN</td>
<td>60-65 %</td>
</tr>
<tr>
<td>methanol</td>
<td>15-20 %</td>
</tr>
<tr>
<td>ammonia</td>
<td>3-6 %</td>
</tr>
<tr>
<td>water</td>
<td></td>
</tr>
</tbody>
</table>

LMP-103S delivers 6 per cent more specific impulse and 30 per cent more density impulse than hydrazine. The recent developments in ADN-based liquid monopropellants render ADN also eligible as the potential substitute for hydrazine.

CONCLUSION

Half a century ago, ammonium perchlorate AP began to emerge as the potential component for strategic smokeless propellants in the middle of the Cold War. At that time, it sparked great interest due to its high performance, even though the resulting propellant never met requirements to be regarded as smokeless. In the 1980s, scientists started looking for a new generation of green propellants in response to rising environmental concerns. In this sense, HAN (hydroxyl ammonium nitrate) and HNF (hydrazine nitro-formate) were on trial in terms of examining their potential to replace hydrazine and ammonium perchlorate, respectively. HAN was ruled out for not achieving the performance of hydrazine. On the other hand, HNF had already been under development in the 1980s by ESA (European Space Agency) and Thiokol by the time ADN appeared. Even though HNF achieves higher performance compared to ADN with similar drawbacks, its application never came about due to its high cost.

The outcome of the developments over the last two decades indicates that ADN will have an important role in the solid rocket industry, a function that HNF never achieved. The one-step reaction for ADN synthesis has made its large-scale production viable as well as its application in rocket motors. The new oxidizer is meant to comply with upcoming tighter environmental legislation, in addition to being smokeless from a strategic point of view. The low melting point of ADN has led to the development of efficient processes to make round particles, which resulted in propellants with high density. On the other hand, microencapsulation made ADN less hygroscopic, more compatible, less sensitive, and, to some extent, more stable. Nevertheless, development is far from over as the search continues for an ideal stabilizer. In addition, ADN trials have shown its potential to replace hydrazine as a more storable and less hazardous and less harmful monopropellant. This text could go further in presenting more benefits of the application of ADN and its achievements. However, the intention of this report is to provide a snapshot of one of the most promising components for solid and liquid propellants in this century and its development to date.

REFERENCES


