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Approaches Towards Improving the Safety of Dinitramides as Energetic Materials

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***Abstract*— In recent years, there has been a resurgence of scientific interest in polynitrogen energetic materials. The considerable number of nitrogen bonds contributes to a high formation heat, and their low carbon and hydrogen content results in a good oxygen balance. The main decomposition product is nitrogen and that turns them into environmental-friendly energetic materials attracting research and investment. Very promising chlorine-free oxidizer is Ammonium dinitramide (ADN). In addition to its excellent performance and low ecological impact, this innovative oxidizer provides tactical advantages by eliminating primary metal oxide smoke and secondary aerosol smoke from condensed water vapor and exhaust products. Mitigating the risk of detection, reduction in corrosive combustion products and low flame temperature define Ammonium dinitramide as high energy eco-propellant and pyrotechnic igniter for rocket fuels. The minimized smoke output and reliable combustion characteristics make it well-suited for high-acceleration tactical missiles and underwater propulsion systems. Nevertheless, the high hygroscopicity of Ammonium dinitramide is a property severely influencing the hazards and safety of this promising energetic. To prevent ADN from absorbing moisture during handling, storage and processing the relative humidity of the environment should be below 55% [1]. Beyond its hygroscopic nature, ADN is also known to be incompatible with isocyanates, leading to spontaneous reactions and decomposition. To address the challenges associated with ADN and facilitate its production and application, the research community employs innovative methods. There are ongoing studies investigating the most efficient ADN particle form. The research discovers the utilisation of different polymers to lay uniform ADN particle coating thus improve the absorption of ambient humidity. This paper presents a summary of recent advancements in ADN improvement methods aimed at enhancing stability. Successful solutions for anti-hygroscopicity method are essential for the future application. Tests are being conducted to enhance the conditions of the ADN synthesis for scalable production.**

Keywords*— *Ammonium dinitramide, Hygroscopicity, Synthesis, Sensitivity.

I. Introduction

Numerous studies with promising results are being published from various geographical regions, competing with the hope of breakthroughs. The advantages of the polynitrogen salts over their atomic-like non-ionic analogues include lower vapor pressure, higher density, and higher thermal stability.

It is extremely important that polynitrogen salts are ecological, "green materials," as the primary product of decomposition is molecular nitrogen. Although it is expected that purely polynitrogen compounds will reach ten times higher detonation pressure and a detonation velocity of 30 km/s, their synthesis and regeneration under atmospheric conditions are problematic. The properties of polynitrogen salts are improved when combined with various cations and anions or because of independent modification of the ionic parts. Progress is being observed in the creation of high-performance polynitrogen salts with improved sensitivity.

II. Materials And Methods

A. Ammonium dinitramide

In 1971, a triazole, called dinitramide $N(NO_2)_2^-$, was created, characterized as an ammonium salt with potential use in rocket fuels. This molecule can be used as a partially oxidizing product of the azide ion, where an oxygen molecule is added to each nitrogen atom. Ammonium nitrate (AN) and ammonium perchlorate (AP) are the most utilized propellant oxidizers. AP has excellent performance characteristics but during the decomposition process releases large amounts of chlorine containing gas with negative influence on ozone layer, formation of acid rain and toxic pollution of soil and water. The aammonium

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dinitramide (ADN) excelled in performance, reaching explosive heat 3.92 kJ/g and detonation velocity 6000 m/s with charge diameter of 100 mm [2]. Thanks to the low characteristic signal, enthalpy of formation – 1207.4 kJ/kg and high gas yield its application spread from solid propellants to explosives [3]. The mechanical properties, stabilities and detonation performance of hexogen (RDX) and octogen (HMX) are not satisfactory. Another nitramine explosive hexanitrohexaazaisowurtzitane (Cl-20) expresses high mechanical sensitivity that increases its hazard and safety handling. Cl-20 is reporting with impact sensitivity 4 N and friction sensitivity 94 N [4]. Compared with these nitramine explosives ADN is an excellent chlorine-free inorganic oxidizer with high performance and detonation velocity and can be quickly introduced as their replacement.

The use of dinitramide salts in composite solid fuels prevents the formation of chlorine waste products during combustion. These salts have high heat of formation and density. They are promising candidates for high-energy materials with extensive military and civilian applications. Key advantages of these salts include high specific impulse, high combustion speeds, low gas emissions, and attractive prices.
ADN is the best-known dinitramide salt due to its good performance in composite solid fuels. As a natural alternative to AP, ADN is characterized by a lower oxygen balance and lower formation heat than perchlorate, but with better specific impulse and combustion gases that do not contain hydrogen chloride. The drawback is that like other ammonium salts, this salt is hygroscopic, which challenges its use in fuels. Unlike nitramines, ADN burns near the surface with a strong exothermic reaction, contributing to higher heat efficiency by returning it to the deflagrating surface, hence increasing the burning rate.

Various methods are known for obtaining ADN, but it is mainly produced in large quantities from sulfamate salts and nitrating acid. The production process is known as the "one-step reaction" (1) and occurs in a strongly acidic environment, leading primarily to dinitramide acid $HN(NO_2)_2$ [5].

$$[H_2NO_3S]^- + 2NO_2 + H_2O \rightarrow HN(NO_2)_2 + [SO_3\,OH]^- + 2H^+ \quad (1)$$

Dinitramide acid in this acidic environment is unstable and prone to decomposition into AN. For this reason, in 2005, Carin Voerde and Henrik Skifs patented a method for converting dinitramide acid into ADN [6]. The reaction is shown in (2).

$$HN(NO_2)_2 + NH_4{}^+ \rightarrow NH_4 + [N(NO_2)_2]^- + H^+ \quad (2)$$

The resulting ADN has properties that can be compared with AP, as shown in Table 1.

TABLE 1. COMPARISON OF PROPERTIES OF AP AND ADN

Compound	Formula	Density (g/cm^3)	Formation Heat (MJ/kg)	Detonation Velocity (km/s)	Oxygen Balance (%)
AP	NH_4ClO_4	1.90	-2.52	160	34.00
ADN	$NH_4[N(NO_2)_2]$	1.80	-1.22	206	-4.40

ADN is registered under REACH with the number 453-090-2. Assessment tests were conducted by an independent and accredited institute in Switzerland with results determine ammonium dinitramide as non-carcinogenic and non-allergenic. It is not irritating when in contact with skin and eyes but may cause irritation if inhaled. ADN is harmful if ingested. Toxicological studies with 90-day follow-up on the reproductive system of female rats indicate embryotoxicity of ammonium dinitramide. Studies show that it can decompose and form reactive nitrogen metabolites that could be harmful to biological systems. Hepatocyte studies suggest that the compound affects cellular DNA in vitro. Further traditional gene-toxicity tests indicate that it is potentially mutagenic [4].

The form of the synthesized ADN crystals, produced in the standard manner without solvent or cooling, is rod-like or needle-like. These forms are unsuitable as they increase the viciousness of the product. This has led to research for a more suitable crystal form. The preferred form is spherical. This plays an important role in solid fuels since round crystals contribute to higher density of ADN. In 2011, Muskatei proposed a method for shaping the initial crystals by applying a chemical modifier during the crystallization process. This method results in obtaining crystals with a specific size ranging from a few microns to several hundred microns, with a spherical shape. Key parameters to be determined include: the type of solvent, primarily its viscosity to control the crystallization rate and atom integration; temperature cycles affecting solubility; impurity presence; stirring speed, and others [7].

B. Silver Dinitramide

In 2016, a group of scientists synthesized and characterized the structure of silver dinitramide ($AgN(NO_2)_2$) [8]. The aim was to investigate its potential use as an ecological alternative to AP. The thermal decomposition mechanism was studied to track the toxicity of the products and the conditions for activating the process. The thermal decomposition of $AgN(NO_2)_2$ occurs in two stages: the first stage (408-483 K) results in a 21.86% weight loss, and the second stage (483-800 K) results in a 28.24% mass loss. The products of the decomposition include N_2O , $AgNO_3$, NO_2 , O_2 , and Ag. The activation energy was found to be Ea = 66.59 kJ/mol,

with a linear correlation coefficient of $r = 0.9913$, calculated using the Kissinger method. The silver dinitramide shows promise as a high-energy material with potential industrial or military applications. Its advantage over current materials is the elimination of pollution from chlorinated combustion products.

III. Results And Discussion

In 2013, research was published where the viscosity of ADN was lowered using an alcohol solvent such as glycerol or a mixture of alcohols, such as glycerol and 1,4-butanediol. The experiment used a solvent with a viscosity equal to or higher than 0.25 Pa/s, at which spontaneous nucleation occurs. Under these conditions, the crystallization process results in ADN with a high charge level [9].

Other methods for controlling the shaping of ADN crystals are also being explored. Important conditions include product purity and viscosity, considering its melting point of 93°C, which is lower than its decomposition temperature of 124°C.

A. Prilling Tower

In this method, molten AND is sprinkled at the top of a prilling tower. The droplets, moving downward in the cooling tower, meet a counterflow of cooling nitrogen, resulting in granules of AND as depicted in Fig. 1 [10].

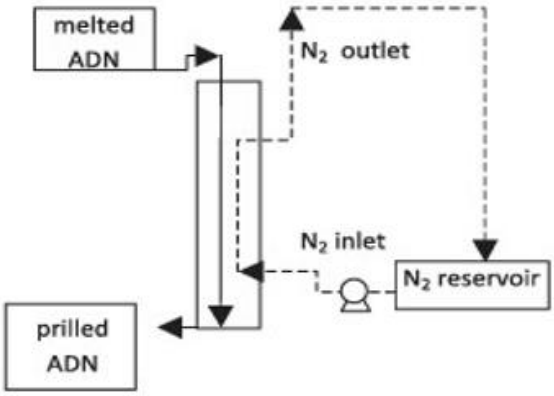

Fig. 1. The schematics of Prilling Tower technique for production of ammonium dinitramide granules.

B. Emulsion Crystallization

High-purity ADN is poured into a reactor with a non-polar liquid. The mixture is stirred constantly to form a homogeneous dispersion. The liquid is heated until the crystals melt, forming an emulsion. Stirring continues until the desired droplet size is achieved. The emulsion is cooled, and the droplets solidify into spherical shapes [11] [12].

C. Spray Crystallization

In this method, molten ADN is sprayed through a nozzle into a container filled with liquid nitrogen. This technique was introduced for ammonium dinitramide in 2005 and further modified in 2006. Its advantage lies in the compactness of the equipment used [5].

D. Microencapsulation

The surface of each particle is coated with a thin polymer layer, typically wax, to protect it from moisture and reaction with hardening agents during transport and storage. However, wax is not suitable for use in rocket propellants, and it must be washed off the surface before further polymer processing.

E. Coacervation

ADN particles are dispersed in an emulsion of ethyl cellulose in cyclohexane. The dispersion continues until the ethyl cellulose particles surround each ADN particle, forming a thin, continuous layer on its surface. The process is induced by pH, temperature, and the addition of a third component. The dispersion is then cooled, and the layer hardens. The processed ADN is separated and dried.

F. Fluidized Bed

In this method, ADN particles are suspended in a chamber with an upward flow of air. The polymer is sprayed into the chamber, either from the bottom or the top. The particles remain suspended until the coating hardens. The process is outlined in Fig. 2 [5]. In 2009 Heintz successfully tests different polymers used as binders in propellants.

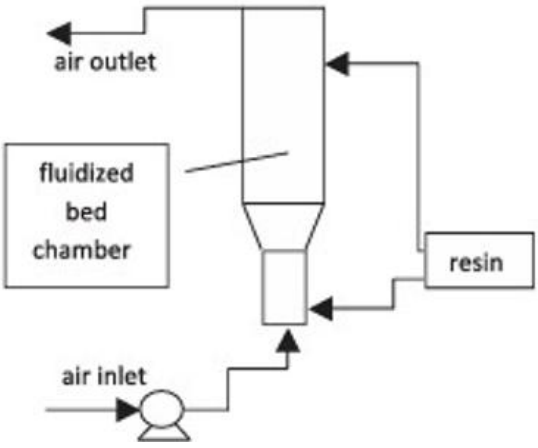

Fig. 2. The schematic of Fluidized Bed process.

G. Supercritical Fluidized Bed

This is a modification of the fluidized bed method, where air is replaced with carbon dioxide, taking advantage of its supercritical properties at moderate temperatures and high pressure. Supercritical fluids exhibit low viscosity (like gases) and high density (like liquids), making them more suitable for this process. However, the chamber walls must be reinforced to withstand the high pressure.

H. Spray Dryer

This method is typically used for smaller particles (<50 microns), where the fluidized bed method is not

applicable. The resin and ADN are dispersed and sprayed into a container, where solvents evaporate, leaving a polymer coating on the surface of each particle. The coated particles harden and are separated from the solvents as shown in Fig. 3.

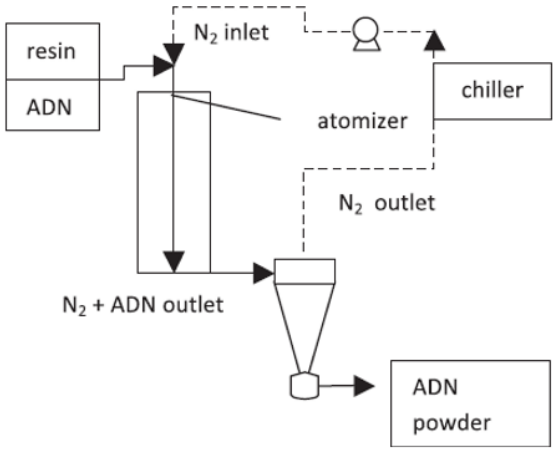

Fig. 3. The spray dryer technique.

I. Prilling and Coating with Ultrasound

This method, researched in 2018, involves forming spherical ADN granules and coating them with a polymer using ultrasound [13]. The polymer mixture includes toluene, graphene, citryl ammonium butyl, Cab-o-sil, and a coating polymer (polystyrene or polybutadiene). The method reduces the working temperature and eliminates melting during the shape transformation process. The resulting product has particle sizes and thermal stability close to those obtained through conventional melting methods. This innovative method could provide an alternative route for producing ADN particles for use in rocket propulsion systems.

Other research published in 2021 combines utilization of ultrasound with power of 70 W, volume ratio of solvent to antisolvent is 1:50 and the antisolvent temperature 20℃ [14]. The conclusion based on the test results is that the volume ratio of solvent to antisolvent is the most important factor in controlling the morphology and particle size of ADN crystals. There is a correlation between the antisolvent temperature and crystal size. The increase in antisolvent temperature leads to gradual increase in crystal size.

J. Co-crystalization technology

Co-crystallization is a supra-molecular method that two or more diverse types of molecules could be placed in one cell with a pre-defined molar ratio and interactions like hydrogen bonds, electrostatic interactions, π-π stacking, van der Waals forces etc. would occur among these molecules initiating co-crystallization. The main driver for co-crystallization mechanism are the interactions. This technology is utilized to amend the oxygen balance, molecular structure, density, improve mechanical properties, decrease sensitivity, increase detonation performance, and enhance thermal stability of energetic materials. Co-crystallization has been used to improve the hygroscopicity of ADN. In 2019, Bellas and Matzger developed an ADN/ PDO (pyrazine-1,4-dioxide) composite using stoichiometric ratio of 2:1. This compound reached excellent physical and energy characteristics, zero oxygen balance, enhanced specific impulse and improved hygroscopicity. The relative humidity at 25°C elevated from 53.5% to 79.5%. However, the melting point of ADN/PDO cocrystal was low of 113℃ [15]. Co-crystallization can improve the hygroscopicity and density of ADN, but attention should be paid to the ligand content since higher values can negatively impact the energy characteristics of the composite. Co-crystallization technology succeeded to improve ADN hygroscopicity, but results lead to a conclusion that the method will not be able to complete the target by its own.

All above methods illustrate various approaches to improving the physical and chemical properties of ADN, as part of ongoing efforts to reduce its hygroscopicity and expand its potential use in rocket propellant systems and explosives.

IV. Conclusions

The replacement of AP with the environmentally friendly and economical ADN results in an increase of the specific impulse of a rocket by 20%, with a 40% decrease in rocket motor weight. In other applications like low characteristic signal propellants, the total specific impulse can be increased by 7%. ADN unveils excellent characteristics paving the road to successful utilization if the obstacles as high hygroscopicity and sensitivity to mechanical stimulation are eliminated. Methods like prilling, surface coating, and co-crystallization prove to be to some degree successful but not enough or not well developed yet to deliver the desired goals. A combination of different technologies might be the future direction for further development in the research field.

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