

# Eco-Oxidizers for Composite Propellants: Ammonium Nitrate and Ammonium Dinitramide

Florin-Marian DÎRLOMAN, Tudor-Viorel ȚIGĂNESCU, Traian ROTARIU,  
Mihai-Ionuț UNGUREANU, Teodora ZECHERU, and Alin-Constantin SAVA

**Abstract**—The current paper is aimed at providing an overview of the existing literature in the field of composite solid propellants to highlight some environmentally-friendly oxidizers that could successfully substitute ammonium perchlorate. In this regard, two oxidizers, ammonium nitrate and ammonium dinitramide, are considered in terms of performances and safety parameters.

**Index Terms**—Ammonium salts, solid propellant, eco-friendly oxidizer, specific impulse

## I. ENVIRONMENTAL CONSIDERATIONS

Eco-friendly oxidizers are generally defined as oxidizers that exhibit less environmental impact, without affecting the propellant's performances and safety features.

Current composite propellant formulae use ammonium perchlorate (AP) as oxidizer, due to its overwhelming chemical and physical properties (high thermal stability, low shock sensitivity, good compatibility and long shelf-life), presented in Table I [1, 14].

TABLE I. AP CHEMICAL PROPERTIES

<b>Chemical formula</b>	$\text{NH}_4\text{ClO}_4$
<b>Appearance</b>	white crystalline solid
<b>Oxygen balance [%]</b>	+34.00
<b>Molar mass [<math>\text{g}\cdot\text{mole}^{-1}</math>]</b>	117.50
<b>Density [<math>\text{g}\cdot\text{cm}^{-3}</math>]</b>	1.95
<b>*<math>\Delta H_f</math> [<math>\text{kJ}\cdot\text{mol}^{-1}</math>]</b>	- 295.8
<b>**<math>Q_{\text{EX}}</math> (water in gaseous state) [J/g]</b>	1396
<b><math>Q_{\text{EX}}</math> (water in liquid state at 20°C) [J/g]</b>	1972
<b>Melting point [°C]</b>	130
<b>Eco-impact</b>	negative
<b>Solubility</b>	- soluble in methanol - partially soluble in acetone - insoluble in ether - soluble in water (11.56 g/100 ml (0°C); 20.85 g/100 ml (20°C); 57.01 g/100 ml (100°C))

\* Enthalpy of formation

\*\*Heat of explosion

This study has been supported by a grant of Romanian Ministry of Education and Scientific Research – UEFISCDI, under Complex Projects Conducted in Consortium Program, project no. 70PCCDI/2018.

F. M. DÎRLOMAN is with Military Technical Academy “Ferdinand I”, Doctoral School, Bucharest, Romania (e-mail: florin.dirloman@mta.ro).

T. V. ȚIGĂNESCU is with the Military Equipment and Technologies Research Agency, Ilfov, Romania (e-mail: viorel.tiganescu@mta.ro).

T. ROTARIU is with the Military Technical Academy “Ferdinand I”, Bucharest, Romania (e-mail: traian.rotariu@mta.ro).

M. I. UNGUREANU is with the Military Technical Academy “Ferdinand I”, Doctoral School, Bucharest, Romania (e-mail: mihai.ungureanu@mta.ro).

T. ZECHERU is with the Armaments Department, Ministry of National Defence, Bucharest, Romania (e-mail: teodora.zecheru@yahoo.com).

A. C. SAVA is with the Military Technical Academy “Ferdinand I”, Bucharest, Romania (e-mail: alin.sava@mta.ro).

However, its consecrate disadvantages, such as harmful combustion agents (chlorinated compounds and perchlorates residues) [2-6], pose a great risk to ecosystems. For instance, a volume of approximately 270 metric tons of hydrochloric acid is released into atmosphere during the combustion of the solid boosters from European launch system, Ariane 5 [7]. Elimination of the acid-burning agent present during the AP decomposition, highlighted in Fig. 1, is considered to be the first step in environmental improvement act.

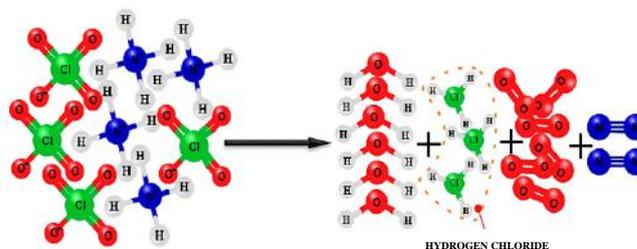


Figure 1. AP decomposition reaction

In addition to this drawback, from a tactical viewpoint, it is also important, since the large exhaust gas volume eases the enemy's task to detect and track the firing point. Also, when it comes to safety terms, the safety of personnel operating the launch system must be taken into consideration. The health of military users and surrounding population is assumed to be subject to diseases of chemical nature (thyroid-linked diseases) due to perchlorate compounds [8]. These chemical agents are known to be very stable in the environment, highly mobile, and present a high risk to groundwater and surface ecosystems [9].

Intense work has been devoted, by specialists, in the field of rocketry, in order to avoid public concern and environmental directives violation. Therefore, due to their environmentally-friendly characteristics and low toxicity of exhaust products, ammonium nitrate (AN) and ammonium dinitramide (ADN)-based propellants are highly desirable.

The purpose of the present paper is to compile all the existing data on the two energetic eco-friendly oxidizers mentioned above, AN and ADN, which appear to be the best alternatives in the substitution of AP in the near future. The two eco-oxidizers will be compared to state-of-the-art solid propellants from safety, performance and cost requirements viewpoint, to determine whether replacing AP is a feasible option.

## II. DATA ON OXIDIZERS

### 2.1 Structure

AN and ADN are two inorganic salts of ammonia cation ( $\text{NH}_4^+$ ) with nitrate anion ( $\text{NO}_3^-$ ), respectively with dinitramide anion ( $\text{N}(\text{NO}_2)_2^-$ ) [10]. Some of the most

significant data on AN and ADN are summarized in Table II [10-14], and their ionic structure is given in Fig. 2.

TABLE II. PHYSICO-CHEMICAL PERFORMANCE OF AN AND ADN

Properties	AN	ADN
Chemical formula	$\text{NH}_4\text{NO}_3$	$\text{NH}_4\text{N}(\text{NO}_2)_2$
Appearance	white solid crystal	white solid crystal
Oxygen balance (%)	+ 20	+ 25.8
Molar mass ( $\text{g}\cdot\text{mole}^{-1}$ )	80.04	124.07
Density ( $\text{g}\cdot\text{cm}^{-3}$ )	1.72	1.81
$\Delta H_f$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	- 365.22	- 148
$Q_{\text{ex}}$ (water in gas state) [J/g]	1441	2668
$Q_{\text{ex}}$ (water in liquid state at 20°C) [J/g]	2479	3337
Melting point (°C)	169.6	92–95
Environment impact	positive	positive
Solubility	very soluble in water (190 g/100 mL (20°C)) and other polar solvents	very soluble in water (357 g/100 mL (20°C)) and other polar solvents
Critical relative humidity (%) at 25 °C	55.2	61.9

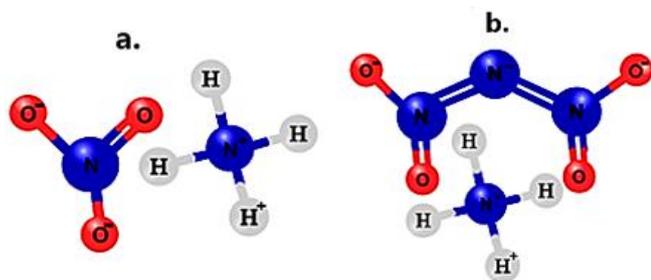


Figure 2. Chemical structures of (a) AN and (b) ADN

Similar to AP, AN and ADN are readily soluble in water and other polar solvents. The solubility of ADN in water is higher than that of AP and AN (ADN 350% > AN 200% > AP 10.7% at 20°C). However, compared to AN, the solubility of ADN is an opportunity, as it can be easily used as oxidizer, due to its energetic character, in liquid monopropellants dissolved in a fuel / water mixture [15]. Also, the low oxygen balance of ADN, compared to AP, is compensated by its superior enthalpy of formation. AN and ADN possess clearly a much lower thermal stability than AP, together with the relatively low melting point, 92–94°C, in case of ADN [14]. But the lower stability must not exclude its application in some types of rocketry systems. AN and ADN heats of explosion are higher than that of AP. ADN possesses lower critical relative humidity (RH) than AN and to prevent from absorbing moisture during handling, storage and processing, RH in the atmosphere must be kept below this level or to coat its surface with a polymer (hydroxyl terminated polybutadiene, polystyrene, or polyacrylate) [16].

## 2.2 “Green” character

The first step in classification of a “green” level can be obtained only by analyzing the decomposition products.

Nevertheless, when it comes to the decomposition process, things get more and more complex, due to its temperature and pressure dependence. Thus, it can be

concluded that a compound can present several modes of decomposition. Part of the reported AN and ADN decomposition reactions are presented in Fig. 3 [17], respectively in Fig. 5 [18].

In the case of AN, reaction a, endothermic decomposition, occurs when heated from 200 to 230°C; after decomposition, reaction a is succeeded by b, above 230°C, and then the path continues with reaction c during detonation [17]. The final decomposition of AN occurs between 280–320°C related to the final endothermic peak in a thermogram representation, obtained during DTA tests, as shown in Fig. 4.

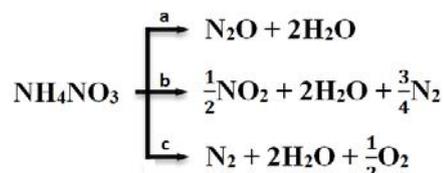


Figure 3. Chemical reactions of AN thermal decomposition

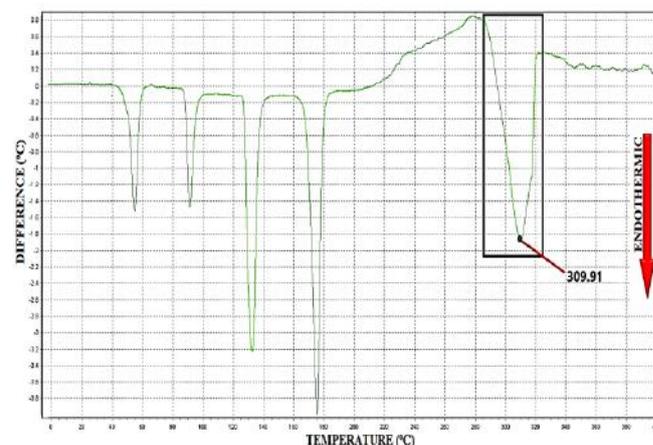


Figure 4. DTA thermogram of AN

Theoretical and experimental studies reported that ADN decomposition proceeds by reactions b and c, in condensed phase, while in the gas phase, reactions a and b prevail [19]. AND decomposition temperature obtained from differential scanning calorimetry (DSC) analysis is reported to be around 180–190°C [20-23].

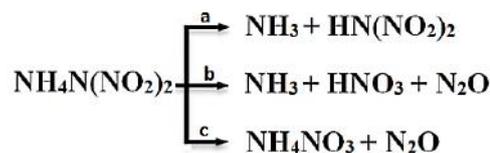


Figure 5. Chemical equations of ADN thermal decomposition

The decomposition products of both oxidizers are chlorine-free and generally include combinations of NO (nitric oxide),  $\text{N}_2$  (nitrogen),  $\text{H}_2\text{O}$  (water),  $\text{O}_2$  (oxygen),  $\text{N}_2\text{O}$  (dinitrogen oxide),  $\text{NH}_3$  (ammonia),  $\text{HNO}_3$  (nitric acid),  $\text{HN}(\text{NO}_2)_2$  (dinitramide acid). It should be noted that, in case of ADN, among those chemicals, AN is also obtained as decomposition product.

AN and ADN are considered non-carcinogenic and non-allergenic, even reported as conducting to the irritation of the respiratory tract, eyes and skin. Table III outlines data on toxicological and environmental properties of both oxidizers.

TABLE III. PHYSICO-CHEMICAL PROPERTIES OF AN AND ADN [24-26]

Test	AN	ADN
Toxicity	*LD <sub>50</sub> (oral rat) = 2217 mg/kg [1,3] LD <sub>50</sub> (inhalation rat) > 88.8 mg/kg (4h)	LD <sub>50</sub> (oral rat) = 823 mg/kg [2] LD <sub>50</sub> (dermal rat) > 823 mg/kg
Toxicity against aquatic organisms	555 mg/L	**EC <sub>50</sub> > 10000 mg/L (15 min)
Acute inhalation	May cause irritation	May cause irritation
Effect on skin	May cause some irritation	Not irritating
Effect on eyes	May cause irritation	Not irritating

\* 50% lethal dose; \*\*the concentration of substance in vitro that damages 50% of the exposed cells

### 2.3 Polymorphism

Polymorphism is a phenomenon present in crystalline materials and represents their ability to exist in two or more crystalline phases that have different arrangements of molecules in solid state, but identical in terms of chemical content [27]. Polymorphic transition of propellant elements is a crucial factor when it comes to propellant grain structure. Polymorphic studies are important as a particular polymorph is responsible of the structural integrity of propellant grain. Thus, the mechanical features are influenced by the polymorphic transition, which directly affects the safety properties and internal ballistic performances of the rocket system.

Analyzing the solid mass percentage of a solid composite propellant, it can be concluded that the oxidizer is the ingredient capable of undergoing a phase transition phenomenon. The main stimulus that influences polymorphic transformations is the temperature [29].

AN is a white crystalline salt with five crystal forms and four phase transitions, as follows [28]:



The crystalline forms are depicted in Fig. 6.

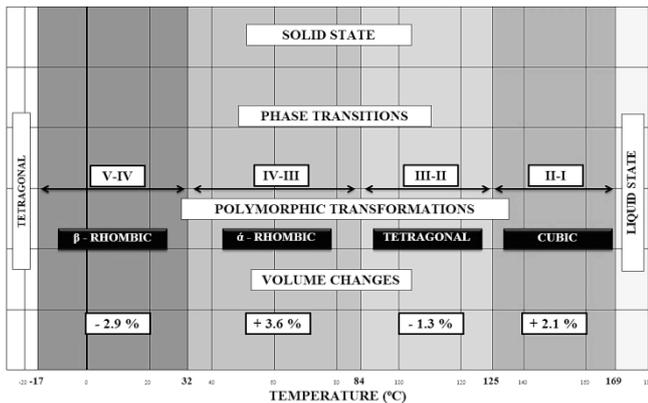


Figure 6. AN crystallography transitions

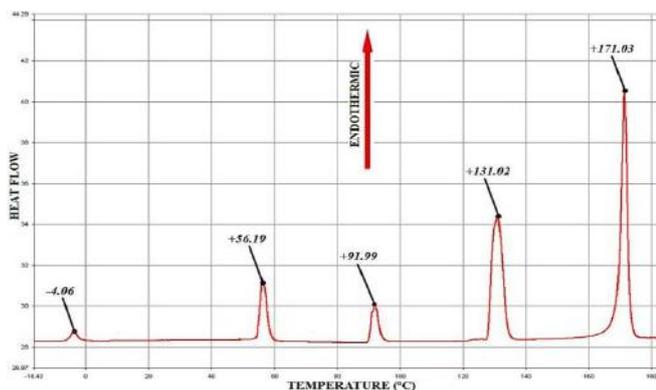


Figure 7. Ammonium nitrate DSC thermogram

The thermal analysis by DSC of 2.5 mg AN, at a heating rate of 5°C/min, showed that the four-phase transitions can be associated with the first four endothermic peaks. The last endothermic peak may be associated with the solid-to-liquid transition. DSC trace is represented in Fig. 7. Among the phase transition studies, it was discovered that this phenomenon is accompanied by volumetric changes, presented in Fig. 6. These changes can lead to cracks in the propellant grain, affecting its capability to burn evenly.

It is already known that the most intriguing phase transition of AN is that at room temperature (IV-III). The expansion of volume with approx. + 3.8%, during this phase transition, concludes in storable and practical problems [29].

To overcome this drawback, specialists engaged extensive research in finding materials to achieve the phase stabilized ammonium nitrate (PSAN) desideratum. AN phase transformation can be disrupted by using organic (polyvinyl pyrrolidone, polyethylene oxide, and polyacrylamide) or inorganic compounds (alkali metal salts, potassium salts) [29, 30]. Multigraph representation of PSAN and AN obtained by thermal analysis with a DTA apparatus (differential thermal analysis) of stabilized compound, obtained by mixing AN and potassium nitrate in aqueous solution (distilled water) followed by recrystallization in a ventilated drying oven, shows that the transition which normally occurs around 44°C, in case of AN, has disappeared (as shown Fig. 8). Since the crystalline transition depends on the sample purity, the AN and PSAN analysed were characterized using the same experimental conditions.

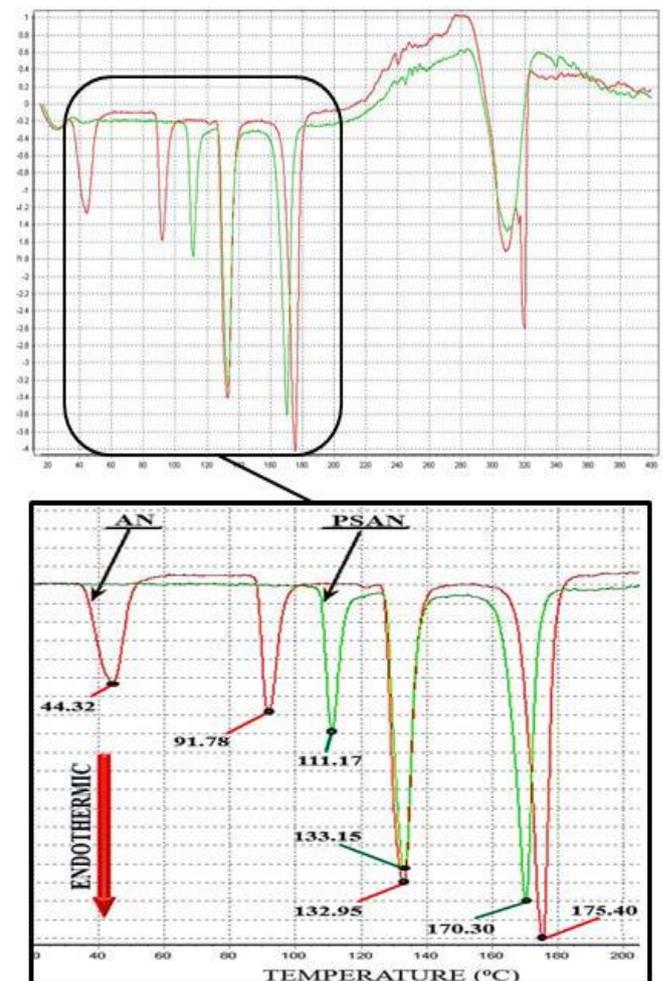


Figure 8. DTA multigraph representation of PSAN-AN

ADN is a colorless salt that becomes yellowish when wet. It has been reported that ADN presents two crystalline structures. First structure,  $\alpha$ -ADN, is a monoclinic system group, P21/c, with four molecules per unit cell. There is strong hydrogen bonding involving all four ammonium hydrogen atoms with the oxygen atoms of the surrounding dinitramide ions (see Fig. 2b) [31,32]. The second monoclinic,  $\beta$ -ADN, occurs at high pressure phase, over 2 MPa [33]. Due to its structure there is no phase transition and volume change, unlike AN. Similar to all dinitramide salts ADN is photosensitive, and should not be subjected to excessive UV light. Thus, it seems likely that a long exposure at solar light affects the stability of ADN during storage.

#### 2.4 Sensitivity parameters

The sensitivity data on AP, AN and ADN reported are presented in Table IV.

TABLE IV. AP, AN AND ADN MECHANICAL SENSITIVITY DATA [34-37]

Test	AP	ADN	AN
Friction sensitivity	> 363 N	72 N	> 363 N
Impact sensitivity	5 N	5 N	> 50 N
Sensitivity against electrostatic discharge (ESD)	0.41 J	0.45 J	0.58 J

AN and AP are relatively insensitive to friction versus ADN. The impact sensitivity values indicate that AP and ADN are close to the threshold value of sensitiveness for transport than AN. AN shows some sensitivity to ESD versus AP and ADN. Obviously, the sensitivity data are related to the oxidative state. The needle-like crystal and aggregations are more sensitive to impact than powder and column-like crystal [36,37].

#### 2.5 Performances

The substitution of AP with AN and ADN for high-performance systems must take into consideration two major parameters: burning rate and specific impulse ( $I_{SP}$ ). They are considered to be the most important characteristics in relation with solid composite propellants performances, and understanding the performances of rocket motors.

Generally, combustion mechanism of propellants varies with their grain geometry, as shown in Fig. 9 [38].

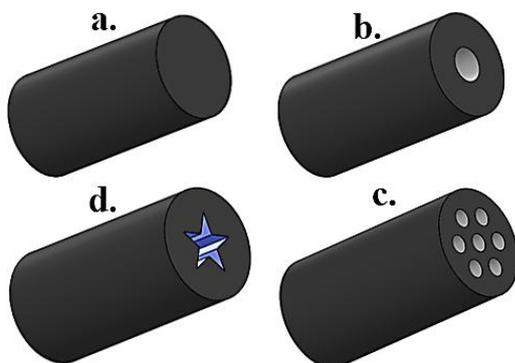


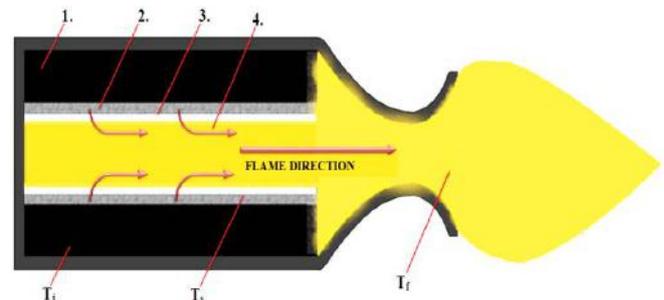
Figure 9. Grain geometry configurations: a) end burner; b) internal burning tube; c) multiperforated; d) star

Based on the grain geometry, there are three types of burning mechanisms:

- neutral burning: *burn time during which thrust, pressure, and burning surface area remain approximately constant, typically within  $\pm 15\%$ .* (Fig. 9 a,d);

- progressive burning: *burn time during which thrust, pressure, and burning surface area increase* (Fig. 9b);
- regressive burning: *burn time during which thrust, pressure, and burning surface area decrease* (Fig. 9c).

Fig. 10 illustrates the change of the grain geometry by highlighting the reaction zones [29]. Combustion of grain surface occurs layer by layer with a constant time interval between adjacent surface contours. Fig. 10 shows this phenomenon for a two-dimensional grain with an internal central cylindrical cavity.



1. grain; 2. condensed phase; 3. gas phase; 4. luminous flame zone.

$T_i$  - initial temperature;  $T_s$  - burning surface temperature;  $T_f$  - flame temperature

Figure 10. Combustion pattern of a grain with internal central cylindrical cavity

Studies on burning behavior have concluded that ADN burns without any luminous emission at low pressure, forming copious white vapors [39-41]. As the pressure increases, small framesets emanate from the local reaction. Above 1–2 MPa, gases become almost transparent, a luminous flame appears, and the condensed products of combustion are not observed. At atmospheric pressure, ADN combustion is unable to self-sustain, while raising the temperature up to 80°C, it becomes incapable of complete combustion. The AN will not burn instantly by itself, but will if in contact with another combustible chemical [42].

State-of-the-art propellant formulations, at their most basic level, are composed of an oxidizer and a fuel, usually metallic (aluminum, magnesium, beryllium, or lithium). Combustion reaction undergone by these two elements provides the energy necessary to propel the rocket. Since the oxidizer-fuel combination must withstand the stresses of handling, aging, storage and use, it is necessary to provide enhancement elements, such as binders (HTPB (hydroxyl-terminated polybutadiene), CTPB (carboxyl-terminated polybutadiene), GAP (glycidylazide polymer)), plasticizers (DEP (diethyl phthalate), DBP (dibutyl phthalate), TEGDN (Triethylene glycol dinitrate), TMETN (trimethylolethanetrinitrate)) and various other solid or liquid ingredients in the formula [38]. Ideally, all the components in the grain formulation act either as oxidizers or fuels, contributing to the necessary energy for maximum propulsion performance, although in practice, certain necessary ingredients such as stabilizers and burn rate catalyst/modifiers (ferric oxide, copper chromite) [38], possess low or no energy to improve the reaction.

Compared to AP and ADN, AN is a low energy oxidizer, which results in low  $I_{SP}$  of AN in propellants. Thus, the addition of metallic fuel in the form of aluminum or magnesium powder may be the common solution to increase grain performance ( $I_{SP}$  and burning rate). The binder enhances the fuel performances, next to its role to provide

good mechanical properties to the grain propellant. The metallic fuel-binder combination seems to be essential in propellant design process.

Some of the most significant results reported in the literature related to the use of AN and ADN as oxidizers are summarized in Table V.

TABLE V. PROPELLANTS SPECIFIC IMPULSE VERSUS CHEMICAL COMPOSITION [43-47]

COMPOSITION [%]									
AP	68	60	69.6	10					
AN				59	59	60			
ADN							70	55	60
Al	18		16	15		12			
Mg					26	12			
GAP		28.4					30	19	28.4
HTPB	14		14	12					
HTPB <sup>a</sup>					15	16			
HMX		10						11	10
TMETN								13.4	
Stab.		1.6						1.6	1.6
Br.md.			0.4	4					
$I_{SP}$ (s)	256	247	262	246	259	260	253	254	250

where: HMX (octogen); Stab. (stabilizer); Br.md. (burning rate modifier)

Despite the fact that AP propellants possess a higher  $I_{SP}$ , when it comes to reagents, it occupies a leading place on the board of harmful oxidizers. For instance, when using only AP, HCl exhaust is reported to be 20.9%, while using a dual AN-AP oxidizer combination the harmful exhaust amount decreases at ca. 3% [45]. Mg-Al metallic fuel formula seems to work very well in terms of performances for the AN propellants, while the AND-based ones have characteristics close to those based on AP, even without metallic fuel in their formulations [43-47]. Other studies [48-52] reported that the AN-ADN dual oxidizer formula represents the next step in the design of "clean" performance propellants. The increase in  $I_{SP}$  will serve as important input for decision-makers when considering the development of future rocket systems.

### III. SYNTHESIS PROCESS

Significant advances have been made in the synthesis, production, characterization and development of AN and ADN for their employment in solid propellant formulations. ADN is reported [53] that it can be synthesized by different methods. The most viable method was developed and patented by FOI-Swedish Defence Research Agency [54]. The method consisted in direct nitration of sulfamic acid salts ( $\text{NH}_2\text{SO}_3\text{NH}_4$ ) by ordinary mixture of acids ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ), followed by neutralization and separation of the ADN formed (presented in Fig. 11). The European company EUROCON (Sweden) is considered to be the main manufacturer of ADN since 1997, under FOI patent license [55].

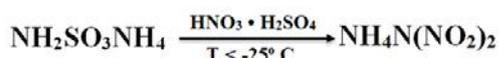


Figure 11. ADN synthesis

Due to its applicability in agriculture, as fertilizer, AN is one of the most commercially available and important ammonium compounds, both in terms of production volume and usage. According to the World Data Atlas [56], Russian Federation is the top country by AN production in the world.

As of 2017, AN production in Russian Federation was 9.86 million tons that accounts for 45.69% of the world's AN production. The top 5 is complemented by Egypt, Uzbekistan, the United States of America, and Poland, which account for 84.59% of it. The world's total AN production was estimated at 21.6 million tons in 2017 [56]. AN synthesis is quite simple, consisting of the neutralization reaction of nitric acid with ammonia [57] (Fig. 12).



Figure 12. AN synthesis

From the data presented hereby, it appears that, in terms of applicability and production, AN exceeds the performances of ADN.

### IV. CONCLUSIONS AND PERSPECTIVES

The replacement of AP with environmentally-friendly and high-performance materials continues to be a challenging focus area for energetic materials chemists. One may conclude that propellants with AN as oxidizer present lower energy, while the AP and ADN are high energy propellants. Thermodynamic properties show that the decomposition reactions of AP and ADN are more and more favorable as the temperature increases. Moreover, ADN is easier to decompose than AP.

Among the two performance characteristics, burning rate and  $I_{SP}$ , there are a number of variables that must be considered regarding the formulation of a desirable grain propellant, such as: end-of-mix viscosity, solid loading (percentage), physical properties (stress and strain), density, cost and toxicity. Partial replacement of AP with AN results in decreased performance and chlorine exhaust.

Although many green propellant formulations have been designed and tested worldwide, most of them are far from being practically usable in the near future due to a number of difficulties, including cost considerations, and consequently further effort is required to produce mature green propulsion systems. Currently, work is continuing at industrial level to overcome the existing problems and to find reasonable solutions.

### REFERENCES

- [1] D. Trache, T. M. Klapötke, L. Maiz, M. Abd-Elghany, and L. T. DeLuca, "Recent advances in new oxidizers for solid rocket propulsion", *Green Chem.*, vol. 19, no. 20, pp. 4711-4736, Aug. 2017. doi:10.1039/c7gc01928a
- [2] R. R. Sobczak, "Ammonium Perchlorate Composite Basics," *J. Pyro.*, no. 3, pp. 35-45, Jun. 1996.
- [3] S. Ramamurthy and P. G. Shrotri, "Catalytic decomposition of ammonium perchlorate a survey," *Journal of Energetic Materials*, vol. 14, no. 2, pp. 97-126, 1996, published online: Aug. 2006, doi: 10.1080/07370659608216060.
- [4] S. Chaturvedi and P. N. Dave, "Solid propellants: AP/HTPB composite propellants," *Arabian Journal of Chemistry*, vol. 12, no. 8, pp. 2061-2068, Dec. 2019. doi:10.1016/j.arabjc.2014.12.033
- [5] S. Chaturvedi and P. N. Dave, "Nano-metal oxide: potential catalyst on thermal decomposition of ammonium perchlorate," *Journal of Experimental Nanoscience*, vol. 7, no. 2, pp. 205-231, 2012. doi:10.1080/17458080.2010.517571
- [6] O. Domínguez, "Thermal decomposition of ammonium perchlorate/exfoliated-graphene and the relationship between activation energy and band gap," *Journal of Energetic Materials*, vol. 37, no.3, pp. 270-281, Apr. 2019. doi:10.1080/07370652.2019.1601793
- [7] T. Brinck, *Green Energetic Materials*, John Wiley & Sons, Sweden, 2014. doi:10.1002/9781118676448
- [8] C. M. Steinmaus, "Perchlorate in Water Supplies: Sources, Exposures, and Health Effects," *Current Environmental Health Reports*, vol. 3, no. 2, pp. 136-143, Jun 2016. doi:10.1007/s40572-016-0087-y

- [9] A. S. Cumming and M. S. Johnson, *Energetic Materials and Munitions: Life Cycle Management, Environmental Impact and Demilitarization*, John Wiley & Sons, 2019.
- [10] J. De Flon, S. Andreasson, M. Liljedahl, C. Oscarson, M. Wanhatal, and N. Wingborg, "Solid Propellants based on ADN and HTPB", in *47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, San Diego, California, 2011. doi:10.2514/6.2011-6136
- [11] H. Östmark, U. Bemm, A. Langlet, R. Sandén and N. Wingborg, "The properties of ammonium dinitramide (ADN): Part 1, basic properties and spectroscopic data," *Journal of Energetic Materials*, vol. 18, no. 2-3, pp. 123-138, Jun. 2000. doi:10.1080/07370650008216116
- [12] N. L. Bowen, "Properties of Ammonium Nitrate. I", *J. Phys. Chem.*, vol. 30, no. 6, pp. 721-725, Jun. 1926. doi:10.1021/j150264a001
- [13] K. D. Shah and A. G. Roberts, "Properties of ammonium nitrate," *GSA Journal*, vol. 1, no. 1, pp. 171-196, 1985.
- [14] M. Bohn, "Stabilization of the New Oxidizer Ammonium Dinitramide (ADN) in Solid Phase," in *RTO-MP-091-Advances in Rocket Performance Life and Disposal*, Aalborg, Denmark, 2002.
- [15] T. A. Gronland, B. Westerberg, G. Bergman, K. Anflo, J. Brandt, O. Lyckfeldt, J. Agrell, A. Ersson, S. Jaras, M. Boutonnet and N. Wingborg, "Reactor for decomposition of ammonium dinitramide-based liquid monopropellant and process for the decomposition", U.S. Patent 7137244B2, Nov. 21, 2006
- [16] A. Rahman, J. Chin, and K. Cheah, "Prilling and Coating of Ammonium Dinitramide (ADN) Solid Green Propellant in Toluene Mixture Using Ultrasound Sonication," *Aerospace*, vol. 5, no. 1, Mar. 2018. doi:10.3390/aerospace5010029
- [17] S. Chaturvedi and P. N. Dave, "Review on Thermal Decomposition of Ammonium Nitrate," *Journal of Energetic Materials*, vol. 31, no. 1, pp. 1-26, 2013. doi:10.1080/07370652.2011.573523
- [18] M. J. Rossi, D. F. McMillen, and D. M. Golden, "Low pressure thermal decomposition studies selected nitramine and dinitramine energetic materials," SRI Project 8999, Office of naval research, Arlington, Texas, 1992.
- [19] R. Yang, P. Thakre, and V. Yang, "Thermal Decomposition and Combustion of Ammonium Dinitramide (Review)", *Combust Explos Shock Waves*, vol. 41, no. 6, pp. 657-679, Nov. 2005. doi:10.1007/s10573-005-0079-y
- [20] J. C. Oxley, J. L. Smith, W. Zheng, E. Rogers, and M. D. Coburn, "Thermal Decomposition Studies on Ammonium Dinitramide (ADN) and <sup>15</sup>N and <sup>2</sup>H Isotopomers", *J. Phys. Chem. A*, vol. 10, no. 31, pp. 5646-5652, Jul. 1997. doi:10.1021/jp9625063
- [21] S. Vyazovkin and C. A. Wight, "Thermal Decomposition of Ammonium Dinitramide at Moderate and High Temperatures", *J. Phys. Chem. A*, vol. 101, no. 39, pp. 7217-7221, Sep. 1997. doi:10.1021/jp963116j
- [22] A. S. Tompa, R. F. Boswell, P. Skahan, and C. Gotzmer, "Low/high temperature relationships in dinitramide salts by DEA/DSC and study of oxidation of aluminum powders by DSC/TG," *Journal of Thermal Analysis*, vol. 49, no. 3, pp. 1161-1170, Aug. 1997. doi:10.1007/bf01983671
- [23] A. Langlet, N. Wingborg, and H. Ostmark, "ADN: A new high performance oxidizer for solid propellants", *International Journal of Energetic Materials and Chemical Propulsion*, vol. 4, no. 1-6, pp. 616-626, May 1996. doi:10.1615/IntJEnergeticMaterialsChemProp.v4.i1-6.580
- [24] National Center for Biotechnology Information (NCBI) (2005) PubChem database. Ammonium nitrate, CID = 22985, <https://pubchem.ncbi.nlm.nih.gov/compound/22985>. Accessed 04 APRIL 2020
- [25] Ammonium Nitrate Safety Data Sheet SDS: P-1 Version: 6 Revision Date: 03/24/2017, [https://www.austinpowder.com/wp-content/uploads/2019/01/Ammonium\\_Nitrate.pdf](https://www.austinpowder.com/wp-content/uploads/2019/01/Ammonium_Nitrate.pdf). Accessed 04 APRIL 2020
- [26] D. R. Mattie and T. R. Sterner, "Review of Ammonium Dinitramide Toxicity Studies", AFRL-RH-WP-TR-2011-0059, Interim Report for October 2009 to November 2010, 2011.
- [27] D. D. Le Pevelen and G. E. Tranter, "FT-IR and Raman Spectroscopies, Polymorphism Applications", *Encyclopedia of Spectroscopy and Spectrometry*, 3<sup>rd</sup> Edition, pp. 750-761, 2007. doi:10.1016/b978-0-12-409547-2.12161-4
- [28] S. Mathew, K. Krishnan, and K. N. Ninan, "A DSC Study on the Effect of RDX and HMX on the Thermal Decomposition of Phase Stabilized Ammonium Nitrate", *Propellants, Explosives, Pyrotechnics*, vol. 23, no. 3, pp. 150-154, Jun. 1998. doi:10.1002/(sici)1521-4087(199806)23:3<150::aid-prep150>3.0.co;2-0
- [29] J. Jisna and M. Suresh, "Ammonium Nitrate as an Eco-Friendly Oxidizer for Composite Solid Propellants: Promises and Challenges", *Critical Reviews in Solid State and Materials Sciences*, vol. 42, no. 6, pp. 470-498, Dec. 2016. doi:10.1080/10408436.2016.1244642
- [30] C. Oommen and S. R. Jain, "Ammonium nitrate: a promising rocket propellant oxidizer", *J Hazard Mater.*, vol. 67, no. 3, pp. 253-281, Jun. 1999. doi:10.1016/s0304-3894(99)00039-4
- [31] W. Zhu, T. Wei, W. Zhu, and H. Xiao, "Comparative DFT Study of Crystalline Ammonium Perchlorate and Ammonium Dinitramide", *The J. Phys. Chem. A*, vol. 112, no. 20, pp. 4688-4693, Apr. 2008. doi:10.1021/jp800693e
- [32] R. Gilardi, J. Flippen-Anderson, C. George, and R. J. Butcher, "A New Class of Flexible Energetic Salts: The Crystal Structures of the Ammonium, Lithium, Potassium, and Cesium Salts of Dinitramide", *J. Am. Chem. Soc.*, vol. 119, no. 40, pp. 9411-9416, Oct. 1997. doi:10.1021/ja9709280
- [33] T. P. Russell, G. J. Piermarini, S. Block, and P. J. Miller, "Pressure, temperature reaction phase diagram for ammonium dinitramide", *J. Phys. Chem.*, vol. 100, no. 8, pp. 3248-325, Feb. 1996. doi:10.1021/jp952144j
- [34] U. Teipel, T. Heintz and H. H. Krause, "Crystallization of Spherical Ammonium Dinitramide (ADN) Particles", *Propellants, Explosives, Pyrotechnics*, vol. 25, no. 2, pp. 81-85, Apr. 2000. doi:10.1002/(sici)1521-4087(200004)25:2<81::aid-prep81>3.0.co;2-f
- [35] M. D. Cliff, D. P. Edwards, and M. W. Smith, "Alkali Metal Dinitramides. Properties, Thermal Behavior, and Decomposition Products", in *29th Int. Annual Conference of ICT, Karlsruhe, Germany*, 1998, pp. 24:1-12.
- [36] T. A. Roberts and M. Royle, "Classification of energetic industrial chemicals for transport", in *ICHEME Symposium Series no. 124*, United Kingdom, 1991, pp. 191-208.
- [37] D. Skinner, D. Olson, and A. Block-Bolten, "Electrostatic Discharge Ignition of Energetic Materials", *Propellants, Explosives, Pyrotechnics*, vol. 23, no. 1, pp. 34-42, Dec. 1998. doi:10.1002/(sici)1521-4087(199802)23:1<34::aid-prep34>3.0.co;2-v
- [38] G. P. Sutto and O. Biblarz, "Rocket Propulsion Elements, Seventh Edition", John Wiley & Sons, 2001.
- [39] V. P. Sinditskii, V. Y. Egorshv, A. I. Levshenkov, and V. Serushkin, "Combustion of Ammonium Dinitramide, Part I: Burning Behavior", *Journal of Propulsion and Power*, vol. 22, no. 4, pp. 769-776, Jul. 2006. doi:10.2514/1.17950
- [40] V. P. Sinditskii, V. Y. Egorshv, A. I. Levshenkov, and V. Serushkin, "Combustion of Ammonium Dinitramide, Part 2: Combustion Mechanism", *Journal of Propulsion and Power*, vol. 22, no. 4, pp. 777-785, Jul. 2006. doi:10.2514/1.17955
- [41] P. Kumar, "An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants", *Defence Technology*, vol. 14, no. 6, pp. 661-673, Dec. 2018. doi:10.1016/j.dt.2018.03.009
- [42] V. P. Sinditskii, V. Y. Egorshv, A. I. Levshenkov, and V. Serushkin, "Ammonium Nitrate: Combustion Mechanism and the Role of Additives", *Propellants, Explosives, Pyrotechnics*, vol. 30, no. 4, pp. 269-280, Sep. 2005. doi:10.1002/prep.200500017
- [43] K. Menke, T. Heintz, W. Schweikert, T. Keicher, and H. Krause, "Formulation and Properties of ADN/GAP Propellants", *Propellants, Explosives, Pyrotechnics*, vol. 34, no. 3, pp. 218-230, Jun. 2009. doi:10.1002/prep.200900013
- [44] G. Cican and A. D. Mitrache, "Rocket Solid Propellant Alternative Based on Ammonium Dinitramide", *INCAS BULLETIN*, vol. 9, no. 1, pp. 17-24, Mar. 2017. doi:10.13111/2066-8201.2017.9.1.2
- [45] A. E. Oberth, "Energetic plasticizers for polybutadiene-type solid propellant binders", U.S. Patent 5578789, Nov. 26, 1996.
- [46] R. A. Frosch and F. A. Andreson, "High performance ammonium nitrate propellant", U.S. Patent 4158583, Jun.19, 1979.
- [47] A. Larsson and N. Wingborg, "Green Propellants Based on Ammonium Dinitramide (ADN)", *Advances in Spacecraft Technologies*, chapter 7, Feb. 2011. doi:10.5772/13640
- [48] L. T. De Luca, L. Galfetti, D. Signoriello, S. Levi, S. Cianfanelli, V. A. Babuk, G. F. Klyakin, V. P. Sinditskii and A. B. Vorozhtsov, "Dual-Oxidizer Metallized Solid Propellants for Low-Cost Space Access", *57th International Astronautical Congress*, Oct. 2006. doi:10.2514/6.iac-06-c4.p.3.02
- [49] N. Wingborg, M. Skarstind, M. Sjöblom, A. Lindborg, M. Brantlind, J. Johansson, S. Ek, M. Liljedahl and J. Kjellberg, "GRALL: Green Solid Propellants for Launchers", in *7th European Conference for Aeronautics and Space Sciences*, Milan, Italy, 2017.
- [50] V. Gettwert, C. Tagliabue and V. Weiser, "Burning Behavior of Aluminized ADN/PSAN Propellants", in *7th European Conference for Aeronautics and Space Sciences*, Milan, Italy, 2017.
- [51] F. Cristilli, V. Weiser, F. Maggi, A. Imiolek, C. Tagliabue, V. Gettwert & S. Dossi, "Burning Behavior of ADN-Based Propellants Loaded with Al-Mg Mechanically Activated Powders", in *7th European Conference for Aeronautics and Space Sciences*, Milan, Italy, 2017.
- [52] C. Tagliabue, V. Weiser, A. Imiolek, M. A. Bohn, T. Heintz, and V. Gettwert, "Burning Behavior of AN/ADN Propellants", in *47th International Annual Conference of the Fraunhofer ICT*, Karlsruhe, Germany, 2016.
- [53] S. Venkatachalam, G. Santhosh & K. N. Ninan, "An Overview on the Synthetic Routes and Properties of Ammonium Dinitramide (ADN) and other Dinitramide Salts", *Propellants, Explosives, Pyrotechnics*, vol. 29, no. 3, pp. 178 - 187, Jun. 2004. doi:10.1002/prep.200400043
- [54] A. Langlet, H. Östmark and N. Wingborg, "Method of Preparing Dinitramidic Acid and Salts Thereof", EP 0 843 647 B1, May, 27, 1998.
- [55] <http://www.eurenc.com/content/explosives/defencesecurity/oxidizers-energetic-polymers/adn/>
- [56] <https://knoema.com/atlas/topics/Agriculture/Fertilizers-Production-Quantity-in-Nutrients/Ammonium-nitrate-production>
- [57] A. Villard and Y. Cotonea, "Process of producing concentrated solutions of ammonium nitrate", U.S. Patent 4927617, May, 22, 1990.