

# ADN and HAN-based Monopropellants – A Minireview on Compatibility and Chemical Stability in Aqueous Media

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**Abstract:** This article gives a short review on compatibility and chemical stability of selected aqueous ADN and HAN-based energetic formulations. A brief introduction will outline Energetic Ionic Liquids (EILs) as a new class of energetic materials with beneficial physical-chemical properties which make them valuable for application in propulsion

technologies. EILs combine the advantages of e.g. low toxicity, showing equal or superior propulsion power compared to the state-of-the-art monopropellant hydrazine. Focus is set on open access ADN and HAN-based monopropellant formulations that are e.g. realized in the advanced blends LMP-103S, FLP-106 or LGP 1845.

**Keywords:** Energetic ionic liquids · Ammonium dinitramide · Hydroxylammonium nitrate · aqueous monopropellants · space technology · metal compatibility

## 1 Introduction

*Ionic liquids* (ILs) are salts that consist of inorganic or organic cations and large weakly-coordinating anions. Typical anions are for example triflates ( $\text{CF}_3\text{SO}_3^-$ ), hexafluorophosphates ( $\text{PF}_6^-$ ), perchlorates ( $\text{ClO}_4^-$ ) or species with tremendous bulky groups (e.g. BARF: Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) [1].

Cationic species are mostly consisting of carbon or nitrogen-based frameworks (e.g. quaternary ammonium) or more complex building units (e.g. alkylated C, N-heteroatomic cations).

Ionic Liquids are defined as salts with melting points below 100 °C. *Room Temperature ILs (RTILs)* build up a sub-group of ILs: They are molten salts forming liquid phases at room temperature making them usable as liquid electrolytes or as solvents in inorganic chemistry [2].

Ionic Liquids combine the advantages of both, solid and liquid phases. Regarding homogeneity, solvent characteristics and viscosity ranges, ILs behaves like classical liquids. In contrast, low vapour pressures and high thermal stabilities are mainly typical characteristics for solid phases [2].

*Energetic Ionic Liquids (EILs)* are defined as ionic liquids with high internal nitrogen- and oxygen contents realized by e.g. numerous N–N or N–O bonds which make them valuable in propulsion or high-energy material (HEM) technology.

Due to initiated efforts to substitute highly toxic and corrosive propellants at European level, the need for technological compatible *green propellants* started years ago and is still ongoing. As a new sub-group of green propellants, *green energetic ionic liquids* moved into the focus of interest. They are characterized by a missing of halogen atoms in their structures. Due to this distinctiveness, they feature less gaseous toxic combustion products when

burned. In propulsion technology the definition of ionic liquids is further expanded to liquid aqueous solutions or melts of these salts which are explicitly used in combustors. In combination with their physical-chemical properties, they open a way to safer handling procedures with reduced toxicity hazards and costs.

Within this approach, two green EILs have raised from low TRL to final technical applications: *Ammonium dinitramide* (ADN) and *Hydroxylammonium nitrate* (HAN).

## 2 Ammonium Dinitramide and Hydroxylammonium Nitrate

*Ammonium dinitramide* (ADN,  $[\text{NH}_4^+\text{N}(\text{NO}_2)_2^-]$ ) is a colorless to yellowish salt. Like many ILs with hydrophilic groups, ADN provides a very high solubility in polar solvents like water and is not soluble in non-polar organic solvents. Density of the solid at 25 °C is given to 1.81 g/cm<sup>-3</sup> [3]. Due to its high hygroscopicity, dried ADN samples tend to liquefy themselves under high humidity. Moreover, the photosensitive dinitramide anion makes it necessary to protect ADN directly from light. In literature, the melting point is given to 93 °C, depending on incorporated impurities or in-

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teral water content [4]. Decomposition of ammonium dinitramide is completed at a temperature of 200 °C [5]. ADN is classified as a 1.1 explosive [5].

*Hydroxylammonium nitrate* (HAN,  $[NH_3OH^+ (NO_3^-)]$ ) is a salt of the non-stable base hydroxylamine and nitric acid. In its pure form, HAN is also a colorless solid with a high tendency to hygroscopicity. HAN melts at a temperature of 48 °C. Depending on its purity, hydroxylammonium nitrate remains thermally stable up to 140 °C [6].

As an additional feature, the HAN molecule contains an anionic oxygen source combined with a combustible cation with a highly redox sensitive H–N–O-group.

Due to the polar character of the HAN molecule, which is also a feature in ADN-based formulations, the solubility in water or other solvents is sufficient enough to form e.g. liquid propellants. This feature makes technical handling (e.g. pumping) of solutions more feasible [7]. Comparable to ADN-based blends, the addition of fuels (e.g. alcohols, amines) and the amount of water gives the opportunity of changing the propellants' energy content, adiabatic combustion temperature and physical-chemical properties [8].

## 2.1 Binary ADN and HAN-Water Mixtures

The HAN molecule is very sensitive towards catalytic decomposition. Binary HAN-water and HAN containing propellant mixtures with a high content of EIL are extremely sensitive to metals of the platinum group which act as catalytic active material [9]. This circumstance in particular made it possible to realize ignition temperatures lower than the self-decomposition temperature of the HAN molecule [10]. Like in the case of thermal decomposition, products of catalytic induced degradation are oxides of nitrogen, nitric acid or nitrogen [11].

Products of thermal degradation of binary, aqueous HAN solutions highly depend on the concentration of HAN and its water content: Nitrous oxide (N<sub>2</sub>O) was found as the only product of the thermal decomposition of low concentrated HAN mixtures. For higher concentrations up to 81 wt.-%, reaction pathways are not unique, leading to the release of various nitrogen-containing gases like NO<sub>2</sub>, NO or gaseous nitrogen [7].

Experimental work on catalytic decomposition of binary ADN-water mixtures have been performed, among others, by e.g. *Hori* and co-workers: They used La<sub>2</sub>O<sub>3</sub> doped alumina supported with CuO. Catalytic decomposition experiments were performed with high concentrated ADN-water solutions (75 wt.-% ADN). Results revealed that catalytic induced ADN decomposition is possible in aqueous solution at temperatures below the decomposition temperature of the pure solid. As gaseous products, oxygen, nitrogen and water were detected by mass spectroscopy [12].

## 3 ADN and HAN-Based Monopropellants

### 3.1 General Aspects

Use of ADN in rocketry was originally focused as oxidizer in solid rocket motors [13]. It was first synthesized in 1971 at the Zelinsky Institute of Organic Chemistry in Moscow. Due to the Iron Curtain and prior to the break-up of the Soviet Union, ADN was not known to the Western hemisphere and thus fell into oblivion. At the beginning of the 1990s, ammonium dinitramide was then rediscovered in the United States.

Early on, people recognized ADN as a new green oxidizer in monopropellant formulations and revolutionary replacement for AP in solid rocket propellants. Later, FOI and EURENCO developed synthetic routes for technical production of ADN and advanced aqueous monopropellant formulations named LMP-103S and FLP-106. In subsequent periods, an ADN-based monopropellant was successfully tested during the PRISMA satellite mission [14].

Intensive examinations of HAN-based monopropellant formulations started in the 1980s for military application: The best-known and familiar HAN formulations named LGP 1845 and LGP 1846. They were used as advanced *Liquid Gun Propellants* (LGP) with improved storability properties, reduced chemical aggressiveness and toxicity compared to earlier tested, encapsulated hypergolic bipropellant combinations on basis of e.g. hydrogen peroxide-hydrazine combinations [15,16]. Due to unexpected explosions in feeding lines and tanks which were difficult to explain at that time, HAN-based LGP programs were put on hold [17]. Nevertheless, work on HAN was continued: In the following time, intensive research activities all over the world contributed to a better understanding of occurring decomposition steps in HAN-based monopropellant formulations. In detail, degradation reactions that were induced by catalytic reactions or fluctuations in temperature were identified as limiting factors in propellants' lifetime.

As a result, the high complexity and diversity of HAN decomposition chemistry depending on external conditions became increasingly obvious [18].

In Table 1, typical compositions of selected literature known LGP formulations and ADN-based blends are listed [19,20].

### 3.2 Compatibility and Chemical Behaviour of EIL-based Monopropellants Towards Metallic Impurities

#### 3.2.1 ADN-based Monopropellants

The two commonly used monopropellant formulations are named LMP-103S and FLP-106. In general, the blends constitute of an aqueous ADN solution, fuel additives and stabilising agents on the basis of amines. In the case of FLP-106, the stabilizing agent is also used as fuel.

**Table 1.** ADN and HAN-based monopropellant formulations with typical ingredients.

Propellant name	Ingredients (wt.-%)		
LGP1845	HAN (63.2)	TEAN (19.9)	H <sub>2</sub> O (16.9)
LGP1846	HAN (60.8)	TEAN (19.2)	H <sub>2</sub> O (20)
HAN269MEO	HAN (69.1)	MeOH (15.4)	AN (0.5) H <sub>2</sub> O (15)
LMP-103S	ADN (63)	MeOH (18.4)	NH <sub>3, aq</sub> (18.6)
FLP-106	ADN (64.6)	MMF (11.5)	H <sub>2</sub> O (23.9)

The LMP-103S and FLP-106 formulations provide a higher density and energy content compared to hydrazine without its sensitivity towards water and oxygen [5]. Decomposition reactions and adiabatic combustion temperatures of ADN-based formulations strongly depend on the purity of the used ingredients and their water content [21].

Published project results (e.g. Rheform, GRASP) and intensive ground tests (e.g. compatibility, storability) were performed, showing that these amine-containing propellant formulations are not compatible with copper and copper alloys, forming blue and green solutions. The effect strongly corresponds with the basicity of the used amine. In Figure 1, a freshly prepared FLP-106 propellant sample with the typical yellowish colour is shown. Figure 2 shows prepared LMP-103S propellant samples that are contaminated with metallic impurities after testing procedures. Chemical analysis revealed that copper ions are responsible for the colouring of the liquids.

Grönland *et al.* patented catalysts that work with aqueous ADN-MeOH monopropellant blends. Improved combustion characteristics were obtained by adding base stabilisers (e.g. urea, hexamine) into the liquid propellant formulation. The catalysts beds were La<sub>2</sub>O<sub>3</sub> doped alumina, supported with metals of the platinum group and of high thermal stability [22].

**Figure 1.** Prepared ADN-based monopropellant FLP-106.**Figure 2.** Prepared LMP-103S samples contaminated with metal ions.

### 3.2.2 HAN-based Monopropellants

As already mentioned, HAN-based formulations were extensively studied in the 1980s. In these formulations, amines were used as fuel components. Triethylammonium nitrate (TEAN) was incorporated in the LGP 1845, LGP 1846 and XM46 formulations, while diethylhydroxylamine (DEAN) was implemented as additive in the LGP 1898 blend. Both additives were used as nitrate-based energizers. Like in ADN-based formulations, adiabatic combustion temperatures of these propellants based on the amount of incorporated water and amine fuel [23]. Further investigations revealed a stabilising effect of ternary amines towards occurring decomposition reactions of the HAN molecule preventing uncontrolled gas phase reactions or micro-explosions [24]. Further research activities showed a pressure dependency of the HAN decomposition [25].

Besides thermal ignition, the first advanced HAN formulations with other fuels components that ignitable by catalytic decomposition contained glycine or methanol as fuel. Glycine-based HAN formulations (HANGLY26) are sensitive to the commonly used Shell-405 catalyst, providing sufficient thermal catalyst stability and compatibility [20]. Methanol-based formulations burned with higher temperatures compared to glycine containing fuels and thus limiting the lifetime of solid catalysts.

Concerning storability and durability, HAN-based monopropellants are in general highly sensitive to impurities, changes of temperature or pH value: Binary HAN-water mixtures are not long-term stable due to autocatalytic reactions that are accelerated in acid conditions. Besides ammonium nitrate, dihydroxylamine and nitric acid are formed as by-products. The intermediately formed dihydroxylamine is not stable under acidic conditions and decomposed into nitrous oxide and water [26].

Apart from the above mentioned sensitivity towards certain pH regimes, metallic impurities originating from e.g. HAN production processes or storage tanks have a tremendous influence on HAN decomposition reactions: The [NH<sub>3</sub>OH]<sup>+</sup> cation is sensitive towards metallic ions of e.g. iron or copper. On long-time scales, the hereof formed ni-

tric acid is corrosive towards tanks or feeding lines. In combination with higher temperatures, storability is further limited [27].

The degradation of the HAN molecule in the presence of iron and copper ions originates from the reductive character of these metal ions and their ability to form corresponding redox pairs easily. This situation was validated by material compatibility tests and chemical analysis of high concentrated binary HAN-water mixtures. Tests were performed with the propellant blend XM46: Herein, steel and other metallic samples were stored at higher temperatures (up to 65 °C) over periods of years. As a result, bluish colours of the aqueous fuels were obtained with samples that were in contact with nickel (e.g. Ni200) or copper alloys. Propellant samples treated with pure titanium, tantalum metals show no incidence of decomposition and are used as storage materials. Moreover, an increase of temperature will negatively influence the rate of HAN decomposition [28,18]. Although the HAN-based formulation XM46 was object of numerous experimental investigations, the described limitations concerning long-term stability, contamination and degradation vulnerability of the HAN molecule prevent the further use of these monopropellants in technical applications. As a result, the search for possible stabilizing agents started [29].

As a standard method in chemical processing, catching of metallic impurities is realized by the addition of so called chelating agents. During the time, numerous possible candidates for HAN were identified and tested: Salts of EDTA as well as polyphosphonates were in the focus of work [30]. But results were not satisfactory. Internal chemical changes of the propellant composition due to chemical reactions led to significant changes of the propellants' parameter and thus gradually reduced effectiveness of the stabiliser [18].

AF-M315E presents a newer monopropellant formulation that was developed by the Air Force Research Laboratory at the end of the 1990s. It is used and tested as hydrazine substitute in the *Green Propellant Infusion Mission* (GPIM) [31]. AF-M315E has an approximately 50% higher density-specific impulse ( $\rho I_{sp}$ ) than hydrazine [32]. Concerning handling and storage, AF-M315E provides superior safety characteristics due to its low-volatile compounds. AF-M315E is a liquid blend of the EILs HEHN, HAN and water [33].

In Table 2, literature data of this HAN based compared to hydrazine is listed [34]. It is considered to have low-toxicity characteristics and provides compatibility with the state-of-the-art material 6Al-4V titanium. Due to the as-mentioned negligible vapour pressure of all used compounds, handling at open environment is no safety issue [34]. An advanced HAN-based monopropellant formulation named SHP163 was also developed by Japanese researchers. Besides HAN, the liquid monopropellant formulation consists of AN, methanol and water [35]. The pro-

**Table 2.** Comparison of some performance and propellant data of AF-M315E and SHP163 [32,35].

Properties	Hydrazine monopropellant	AF-M315E	SHP163
Density (kg/m <sup>3</sup> )	1000	1470	1400
Theoretical $I_{sp}$ (s) ( $p_{ch} = 0.7$ MPa)	240	250	276

pellant is considered as a green substitute for the *Innovative Satellite Technology* project [36].

## 4 Conclusion

Up to date, ADN and HAN-based monopropellants are the most advanced EILs that managed the leap from laboratory into practical application. They both belong to the raising group of EILs facing similar benefits and challenges:

- Reduced toxicity due to non-volatile characteristics
- High solubility in aqueous media offers tuning properties regarding energy content and other propellant parameters (e.g. adiabatic combustion temperature, density, freezing point)
- Decomposition and final combustion of these EILs is preferably initiated by absence of water
- Both EILs are sensitive to internal and external parameters. In particular, metallic impurities, temperature and pH changes will decrease lifetime of the monopropellants dramatically
- In the case of early HAN formulations, stabilizing agents showed no significant effect on the long-term stability of these blends

Although detailed knowledge and numerous data are available of experimental approaches, the results have to be interpreted carefully. Concerning HAN, the accident in the Akiruno Research Center in 2012 shows, that besides all knowledge and data, handling of all EILs has to be carefully managed [36,18].

## Symbols and Abbreviations

ADN	Ammonium dinitramide
AN	Ammonium nitrate
AP	Ammonium perchlorate
DEAN	Diethylhydroxylamine
EDTA	Ethylenediaminetetraacetic acid
EIL	Energetic Ionic Liquid
FOI	Totalförsvarets forskningsinstitut
HAN	Hydroxylammonium nitrate
HEHN	Hydroxyethylhydrazinium nitrate
HEM	High Energetic Material
IL	Ionic Liquid

LGP	Liquid Gun Propellant
MeOH	Methanol
MMF	Monomethylformamide
RTIL	Room Temperature Ionic Liquid
TEAN	Triethylammonium nitrate
TRL	Technology Readiness Level

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## REVIEW

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