ADN: PRODUCTION, PROPERTIES AND FUTURE PERSPECTIVES

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ABSTRACT

This paper presents the ongoing work to improve the production method of ADN in order to improve the capacity and to reduce the cost. Matters such as toxicity, REACH, patents and future industrial perspectives related to ADN are also discussed.

1. INTRODUCTION

Research on the use of the oxidiser ammonium dinitramide (ADN) in solid and liquid propellants are ongoing at different institutes in many countries.

ADN is used in the development of green solid propellants in the Horizon 2020 project GRAIL.[1] ADN is also the main ingredient in the liquid monopropellant LMP-103S which is currently the most mature propellant option in Europe to serve as a REACH compliant hydrazine substitute.[2] The development of liquid ADN based propellants and thrusters are currently studied in the Horizon 2020 project RHEFORM.[3]

Today ADN is produced by EURENCO Bofors (EuB) in Sweden and available in larger amounts for evaluation and research. The purity of the material produced is above 99 % and it has a high thermal stability. Although its thermal stability has been debated, the current conclusion at FOI is that ADN produced by EuB does not require any stabilizer.

The current, small-scale production of ADN at EuB is performed in a plant initially built for the production of other energetic materials and is thus not optimized for the production ADN. As a consequence, ADN is today very expensive. In order to reduce the cost, ways to improve the synthesis of ADN are of interest.

In collaboration with EuB, a new synthesis improvement has recently been developed.[4] The new method has the potential to substantially decrease the cost of ADN, increase the purity and decrease the amounts of waste.

2. PROPERTIES

ADN is a solid white salt of the ammonium cation (NH_4^+) and the dinitramide anion ($N(NO_2)_2^-$), see Figure 1.

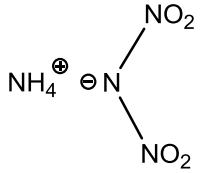

Figure 1. Structure of ADN.

Just as ammonium nitrate, ADN is hygroscopic and readily soluble in water and other polar solvents, but scarcely soluble in non-polar solvents. Its properties are compiled in Table 1.

Table 1. Properties of ADN at 25.0 °C

Property	Value
CAS no.	140456-78-6
Molecular weight	124.07 g/mol
Oxygen balance	+25.79 %
Melting point	93.2°C [5]
Heat of formation	-134.6 kJ/mol [6]
Heat of solution	+36.4 kJ/mol [6]
Heat of combustion	437.0 kJ/mol
Density (solid)	1.81 g/cm^3 [7]
Density (liquid)	1.675 g/cm^3 [8]
Molar volume (liquid)	74.08 cm^3/mol [8]
Critical relative humidity	55.2 % [8]

3. TOXICITY AND REACH

Table 2. Toxicity and environmental testing of ADN[a]

Test	Results
Toxicity	LD_{50} (oral rat) 823 mg/l [9] LD_{50} (dermal rat) >2000 mg/kg [9]
Toxicity to aquatic organisms	EC_{50} >10000 mg/l (15 min)
Acute inhalation	May cause irritation
Sensitizing	Not sensitizing
Effect on skin	Not irritating
Effect on eyes	Not irritating
Lipophilicity	Log $P_{o/w}$ < -2.8
Mutagenicity	Mammalian cell, negative
Biodegradability	0.2 g/g BOD_7/COD 0.5

a) data from reference [10] unless otherwise stated.

Table 2 shows information concerning toxicological and environmental properties of ADN. It is considered as non-carcinogenic and non-allergenic. ADN may cause irritation if inhaled and it is harmful if swallowed, but not irritating in contact with eyes or skin. However, ADN is categorised as a 1.1D explosive and should be handled with care.

ADN is registered according to REACH and has the ELINCS number 453-090-2. All chemicals used in the production are registered and none of these are toxic.

4. SYNTHESIS

There are different approaches to synthesise ADN.[11] In the early methods the most powerful nitration agents, such as nitronium tetraflouroborate or dinitrogen pentoxide, was used to nitrate urethanes.[12] Other methods included direct nitration of ammonia with dinitrogen pentoxide. Drawbacks with these methods are the high costs of the rare chemicals in large scale production.

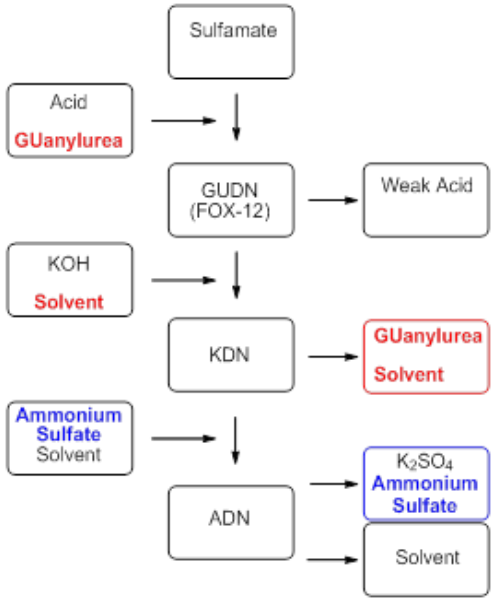

Figure 2. ADN production process at EuB

4.1 CURRENT METHOD USED AT EURENCO

Production of ADN is today normally performed by nitration of salts of sulphamic in mixed acids to form *guanylurea dinitramide* (FOX-12, GUDN), which then is converted by the use of potassium hydroxide to yield *potassium dinitramide* (KDN).[13, 14] In a final reaction step, KDN is further reacted with ammonium sulphate to yield ADN, see Figure 2.

4.2 PRODUCTION IMPROVMENTS IN EARLIER PROJECTS

The intermediate in the three-step synthesis of ADN is FOX-12. Although the succeeding two steps are ion-exchange reactions with high yields, some reaction losses were observed. In the EU-project HISP,[15] processes to minimise these losses were studied. It was shown that a large part of the losses could be recovered, thus rendering the overall process more attractive. For the common solvents used in the process, there are already industrial techniques available. Considering the properties of ADN crystals: explosive, acicular habit (needle shaped) and hygroscopic, a good large scale industrial drying process is a challenge.

One drawback of the current production method is the two-step ion exchange reaction with the intermediate KDN. Apart from being more complex, the presence of potassium impurities in the final product might increase the radar signature, which is of interest in military applications.[16] For liquid ADN based propellants potassium might also cause problems such as thruster catalyst poisoning. [17]

As FOX-12 is converted first into KDN and finally ADN in two ion exchange reactions, it should theoretically be possible to convert FOX-12 into ADN in one reaction step, see Scheme 1.

$$NH_2C(NH)_2CONH_3N(NO_2)_2 + (NH_4)_2SO_4 \rightarrow$$

$$NH_2C(NH)_2CONH_3SO_4(s)\downarrow + NH_4N(NO_2)_2$$

Scheme 1.Potassium-free synthesis of ADN from FOX-12

An ion exchange between a source of ammonium – for example ammonium sulphate – should, under the right conditions, yield ADN from FOX-12 and the by-product guanylurea sulphate in a one-step reaction. This would eliminate presence of potassium and reduce the number of reactions steps.

FOX-12 could indeed undergo ion exchange reaction with ammonium sulphate in a water and/or water/alcohol solution. Precipitation of guanylurea sulphate in the reaction mixture drives the reaction to favour the desired product, ADN. This method was patented by Ek *et al.* in 2015.[4]

4.3 CURRENT WORK IN THE GRAIL PROJECT

The work on the optimisation of the one-step synthesis of ADN from FOX-12, reducing the total number of steps from three to two, continues at FOI with the aim to develop a procedure sufficiently efficient to be transferred to EuB for industrialisation. The main focus of this work is to reduce the volumes of solvents required to obtain reproducible results in an economically viable way. Such a reduction is important, as large volumes of solvents increase the production costs, both for the energy and working time required in the evaporation to remove said solvents. This method should also decrease the risk of presence of potassium in the final product, as the intermediate KDN no longer is involved in the process. The elimination of one step and one intermediate will also reduce the production of waste, especially so as the guanylurea sulphate produced can be recycled into the production of FOX-12. This should also favour lower production costs. Recent work in kilogram scale has shown this method to be very successful and it seems suitable for industrial scale up.

5. FUTURE PERSPECTIVES

EuB has been producing ADN since 1997 and is today the only commercial producer. Due to the extensive know-how gained through all these years and the close cooperation with FOI, EuB expect to be the dominating ADN producer for decades to come, ensuring long term European supply.

EuB cooperates with customers who are interested in ADN both for solid rocket motors, as well as for liquid monopropellants. The interest for the substance is constantly increasing and EuB has the impression that the demand will continue to increase. Currently, the maximum annual production capacity is 40 000 kg. In order to meet future demands, EuB works actively with production process improvements both to increase the capacity and reduce the costs.

The future cost of ADN, if produced in large scale, were estimated to be in the range of 20-60 €/kg, depending on the assumptions made.[18] In these estimates, current production improvements were not included. In the GRAIL project, a new estimate will consequently be performed taking all improvements into account, to obtain a more reliable estimate of its future cost.

6. PATENTS

The production of ADN is covered by three main patents. The production of ADN by nitration of sulphamic salts was first patented in 1996.[19] The method with FOX-12 as an intermediate was patented in 2005.[14] The potassium-free method was patented in 2015.[4] All these patents are owned by the Swedish Government represented by FOI.

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7. REFERENCES

1. Grail project website, www.grail-h2020.eu ,The 27th of April 2016
2. ESA Clean Space, http://www.esa.int/Our_Activities/Space_Engineering/Clean_Space/Considering_hydrazine-free_satellite_propulsion, The 27th of April 2016
3. Rheform project website, www.rheform-h2020.eu, The 27th of April 2016
4. S. Ek, M. Skarstind, N. Latypov, H. Skifs, J. Johansson, WO2015115962 A1, *Synthesis of ammonium dinitramide from guanylurea dinitramide for explosives*, Totalförsvarets Forskningsinstitut, Sweden, 2015.
5. C. Eldsäter, J. de Flon, E. Holmgren, M. Liljedahl, Å. Pettersson, M. Wanhatalo, N. Wingborg, *ADN Prills: Production, Characterisation and Formulation,* 40th Int. Ann. Conf. of the ICT, Karlsruhe, Germany, 2009.
6. T.S. Kon´kova, Y.N. Matyushin, E.A. Miroshnichenko, A.B. Vorob´ev, *Thermochemical properties of dinitramidic acid salts*, Russ. Chem. Bull., Int. Ed., 58 2020-2027, 2009.
7. H. Östmark, U. Bemm, A. Langlet, R. Sandén, N. Wingborg, *The Properties of Ammonium Dinitramide (ADN): Part 1, Basic Properties and Spectroscopic Data*, J. Energ. Mater., 18, 123-128, 2000.
8. N. Wingborg, *Ammonium Dinitramide-Water: Interaction and Properties*, J. Chem. Eng. Data, 51 (2006) 1582-1586.
9. E.R. Kinkead, S.A. Salins, R.E. Wolfe, G.B. Marit, *Acute and Subacute Toxicity Evaluation of Ammonium Dinitramide*, Mantech Environmental Technology, 1994.
10. H. Stenmark, S. Sjökvist, *Toxicological testing of ADN, GUDN and FOX-7*, 41st Int. Ann. Conf. of the ICT, Karlsruhe, Germany, 2010.
11. 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, 29, 178-187, 2009.
12. R. Meyer, J. Köhler, A. Homburg, *Explosives*, Wiley-VCH.
13. A. Langlet, H. Oestmark, N. Wingborg, *Manufacture of dinitramidic acid and its salts for solid propellants*, Patent WO9706099 A1, Försvarets Forskningsanstalt, Sweden, 1997
14. C. Vörde, H. Skifs, Patent WO 2005/070823, *Method of Producing Salts of Dinitramidic Acid*, Totalförsvarets forskningsinstitut, Sweden, 2004.
15. HISP project website, www.hisp-fp7.eu, the 27th of April 2017.
16. E. Miller, *The Suppression of Afterburning in Solid Rocket*, Air Force Office of Scientific Research, 1984.
17. P. Thormählen, ECAPS, 2015, Personal communications.
18. J. Zevenbergen, H. Stenmark, H. Skifs, M. Skarstind, *Large Scale Production of Ammonium Dinitramide (oral presentation)*, New Energetics Workshop, Stockholm, Sweden, 2014.
19. A. Langlet, N. Wingborg, H. Östmark, *ADN: A new high performance oxidizer for solid propellants*, in: K.K. Kuo (Ed.) Challenges in Propellants and Combustion, pp. 616-626, 1997.