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Green Propellants Based on Ammonium Dinitramide (ADN)

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1. Introduction

Ammonium perchlorate (AP) and hydrazine are today widely used as propellants. AP as oxidizer in solid propellants and hydrazine as liquid monopropellant (Brown, 1995; Sutton and Biblarz, 2001). These propellants are well known for their good performance characteristics, but their limitations and liabilities regarding toxicity, operational handling and environmental impact are also well documented.

Perchlorate contamination is becoming a more widespread concern in the United States (EPA, 2005). In 2009, a workshop organised by the US Department of Defence identified AP as one of the key environmental, safety and occupational health issues (DoD, 2009). Perchlorate anions (ClO_4^-) has been found in drinking water supplies throughout the south-western United States, and perchlorate may be a problem for water supplies in some regions of the USA (Urbansky, 2002). At high concentrations, perchlorate can affect thyroid gland functions, where it is mistakenly taken up in place of iodide. Apart from impacting the thyroid activity in humans, AP forms vast amount of hydrochloric acid on combustion. For instance the space shuttle and the Ariane 5, generates 580 and 270 tons of concentrated hydrochloric acid, respectively, per launch (Wingborg et al., 2008).

Hydrazine is highly toxic and carcinogenic (ATSDR, 1997; Ritz et al., 2006), and handling it requires costly safety measures. A less toxic monopropellant is expected to offer substantial cost savings (Bombelli et al., 2003; Palaszewski et al., 1998; Hurlbert et al., 1998). These economic benefits were analysed and quantified in a study funded by the European Space Agency (ESA) and were considered sufficiently large to support interest in the development of hydrazine substitutes and related propulsion hardware (Bombelli et al., 2004).

Propellants of the future must not present major hazards to the crew or ground handling personnel. The use of green propellants would greatly reduce the risks associated with toxicity, operational handling complexity, spacecraft contamination, and hazardous contamination of the environment. Green propellants have also shown promise from a system performance and total life cycle cost perspective. One material that has the potential to replace AP as well as hydrazine is ammonium dinitramide (ADN), $NH_4N(NO_2)_2$.

2. Ammonium dinitramide, ADN

ADN is a high-energy inorganic salt, mainly intended as oxidizer in solid rocket propellants (Bottaro et al., 1997; Christe et al., 1996; Östmark et al., 2000). ADN was first synthesized in

1971 at the Zelinsky Institute of Organic Chemistry in Moscow, USSR, and is one of the most significant discoveries in the field of energetic materials (Agrawal and Hodgson, 2006). It is claimed that ADN-based solid propellants are in operational use in Russian Topol intercontinental ballistic missiles (Talawar et al., 2007) and that ADN previously was produced in ton-size quantities in the former USSR (Teipel, 2004). The USSR's dinitramide technology was strictly classified and unknown to the rest of the world until 1988 when it was "re-invented" at SRI (Bottaro et al., 1997) in the USA. In the beginning of the 1990s, FOI in Sweden started research on ADN in order to develop high performance solid propellants. During this development work, it was found that ADN was highly soluble in polar solvents, which led to the realization that it also could be used as an oxidizer in liquid propellants.

2.1 Basic properties of ADN

ADN (cas nr. 140456-78-6) is a solid white salt of the ammonia cation (NH_4^+) and the dinitramide anion ($N(NO_2)_2^-$), Fig. 1. It has a high oxygen balance, +25.79 %, melts at 93 °C and starts to decompose at approximately 150 °C at a heating rate of 10 K per minute, as seen in Fig. 2. Similarly to ammonium nitrate, ADN is hygroscopic and readily soluble in water and other polar solvents but scarcely soluble in non-polar solvents. The solubility of ADN in different solvents is shown in Table 1 (Wingborg et al., 2008), and the phase diagram for the system ADN-water is shown in Fig. 3 (Wingborg, 2006). The critical relative humidity for ADN is 55.2 % at 25.0 °C (Wingborg, 2006). This means that the relative humidity must be below 55.2 % to prevent ADN from absorbing moisture from the atmosphere. The density of ADN in the solid state is 1.81 g/cm^3 (Östmark et al., 2000). Its molar volume and corresponding density in the liquid state at 25.0 °C is 74.08 g/mol and 1.675 g/cm^3 respectively (Wingborg, 2006). Some of the physical properties of ADN are summarized in Table 2, and information concerning its toxicological properties are shown in Table 3.

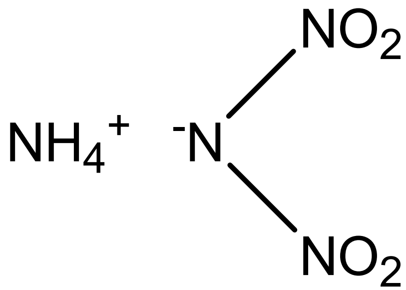

Fig. 1. The structure of ADN.

Solvent	Solubility in 100 g solvent (g)
Water	357
Methanol	86.9
Butyl acetate	0.18
N-heptane	0.005
Dichloromethane	0.003

Table 1. ADN solubility at 20.0 °C (Wingborg et al., 2008).

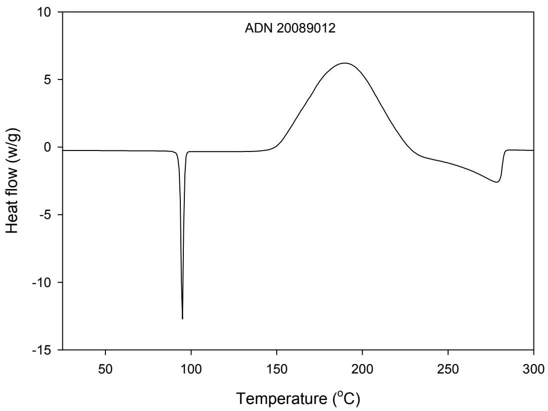

Fig. 2. Differential Scanning Calorimetry (DSC) thermogram of ADN. Heating rat 10 K/min.

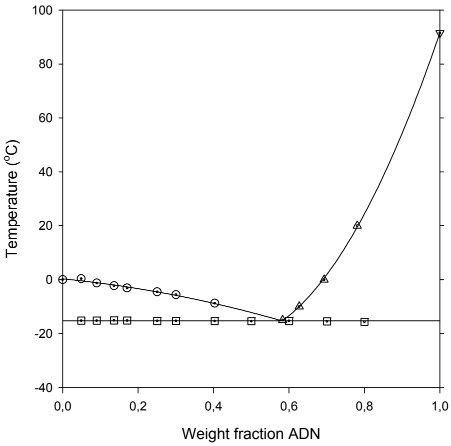

Fig. 3. Solid-liquid phase diagram for the system ADN-water (Wingborg, 2006).

Property	Value	Reference
Molecular weight	124.07 g/mol	
Mass density (solid)	1.81 g/cm^3	(Östmark et al., 2000)
Mass density (liquid)	1.675 g/cm^3	(Wingborg, 2006)
Melting point	93 °C	
Heat of melting	142 J/g	
Heat of formation	-148 kJ/mol	(Östmark et al., 2000)
Heat of combustion	424 kJ/mol	(Wingborg, 2006)
Heat of solution	35.7 kJ/mol	(Wingborg and de Flon, 2010)
Oxygen balance	+25.79 %	(Wingborg, 2006)
Molar volume (liquid)	74.08 g/mol	(Wingborg, 2006)
Critical relative humidity	55.2 %	(Wingborg, 2006)

Table 2. Properties of ADN at 25.0 °C unless otherwise stated.

Acute inhalation toxicity	Inhalation of dust may cause irritation to mucous membrane of the respiratory organ. Long-time exposure may cause problems as feeling of weakness, dizziness, indisposition and sleeping problems
Ingestion	Can cause the same symptoms as inhalation. Risk also for blood damage (anaemia), epileptic convulsion and to become unconscious
Sensitisation	Non-sensitizing
Irritant effect on skin	Rabbit test: non-irritant
Irritant effect on eyes	Rabbit test: non-irritant
LD_{50} (oral rat)	823 mg/kg (Kinkead et al., 1994)
LD_{50} (dermal rabbit)	>2000 mg/kg (Kinkead et al., 1994)
LC_{50}	Not applicable[b]
Cancer/mutation/unborn child damage/reproduction	Toxicity study: Salmonella typhimurium: positive In vitro mammalian cell gene mutation test: negative

Table 3. ADN toxicological information[a].

a) Data from Pettersson (Pettersson, 2007) unless otherwise stated.

b) ADN is a salt and is thus not present in the gas phase.

2.2 Production of ADN

ADN can be synthesized by different methods and an overview of these has been described by Venkatachalam, et. al. (Venkatachalam et al., 2004). One viable method is based on direct nitration of salts of sulfamic acid by ordinary mixed acids (sulfuric and nitric), followed by neutralization and separation of the ADN formed, Fig. 4. This method was developed and patented by FOI in the mid 1990s (Langlet et al., 1997). The method was then scaled up and the technology was transferred to EURENCO Bofors in Sweden, which has been producing dinitramides in a pilot plant scale since 1996, on license from FOI. All chemicals involved in the method are standard industrial chemicals and thus no strategic materials are needed. Sulfamic acid is, for instance, used to produce sweeteners and as an ingredient in cleaning agents. Through the years, EURENCO Bofors has delivered samples to more than fifty research establishments and companies worldwide. By providing samples to a large community, a broader range of potential applications has emerged. Dinitramides are currently used in gas generators for automotive airbags, which is their first full scale application. For this application guanylurea dinitramide, GUDN (FOX-12) (Östmark et al., 2002), is used and EURENCO Bofors has produced GUDN in industrial scale since 2000.

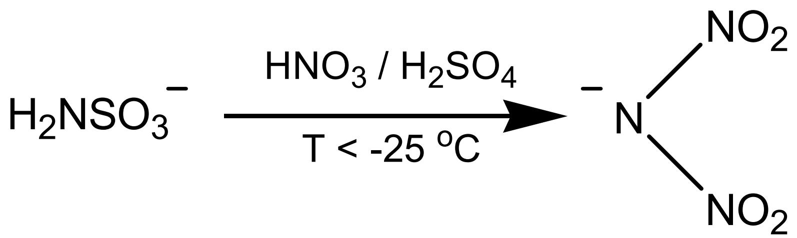

Fig. 4. Synthesis of dinitramide from sulfamic acid.

3. Solid propellants based on ADN

Solid propellants for space applications are today widely used in large boosters for launchers and, to some extent, for in-space propulsion. Propellants for these applications are based on the oxidizer ammonium perchlorate (AP), NH_4ClO_4, and aluminium powder embedded in a polymer binder matrix. AP is in many ways an excellent oxidizer due to its relative low hazardness and the possibility to tailor its ballistic properties. However, AP has negative impacts on the environment and on personal health. By substituting AP with ADN there will be no hydrochloric emission since ADN only contains hydrogen, nitrogen and oxygen. Calculations show that ADN-based solid propellants can achieve performance equal to or higher than that of the conventional AP-based propellants (Wingborg et al., 2008).
Due to their large size, launcher boosters may not be the first application for a newly developed propellant. Smaller and less cost-sensitive applications seem to be a better choice. ADN-based solid propellants are thus more likely to initially be used for in-space propulsion applications. Today the majority of spacecrafts use liquid propulsion systems. Liquid rockets provide high performance and adjustable thrust, but they are complex, costly and use toxic propellants such as hydrazine, mono-methyl hydrazine (MMH) and nitrogen tetroxide (NTO).
When adjustable thrust is not required, solid propellants possess benefits such as storability, compactness and simplicity. No propellant delivery system is required which enables a huge improvement in reliability and cost. One disadvantage is however their relatively low specific impulse. Despite this, solid propellant rocket motors have been used to propel spacecrafts in numerous missions since first used in the upper stage of the first U.S. Satellite Explorer I in 1958. More recently solid propellant rocket motors are considered to be used for the ascend module in the Mars sample return mission (Stephenson and Willenberg, 2006). Replacing the AP-based propellants with ADN will provide higher performance and lower environmental impact.

3.1 Specific impulse

To perform a correct performance comparison between different propellants the complete propulsion system must be taken into account. This is a complex task and requires a specific spacecraft to be studied. In this case only the theoretical vacuum specific impulses were calculated for different ADN-based solid propellants and for the liquid bi-propellant combination NTO/MMH. The calculations were performed using the NASA CEA 600 computer program (Gordon and McBride, 1994; McBride and Gordon, 1996). An infinite area combustor and shifted equilibrium during expansion were assumed. Typical combustion chamber pressure for solid rocket motors (7 MPa) and liquid rocket engines (1 MPa) were used and the nozzle area expansion ratio were in all cases equal to 50.
The binder considered in combination with ADN was polyglycidylazide (GAP). GAP was chosen because it:

- is compatible with ADN
- improves performance
- provides good ballistic properties in combination with ADN.

The thermochemical inputs used in the calculations are shown in Tabela 4. The maximum solid loading in a propellant is generally limited by the viscosity of the uncured propellant slurry and must be low enough to allow casting. To obtain realistic results the maximum solid loading was in this case limited to 80 %. The mixing ratio for the liquid bi-propellant combination NTO/MMH was two to one, similarly as used in the AESTUS rocket engine (ASTRIUM, 2007). The results from the thermochemical calculations are shown in Table 5. The results show that the theoretical specific impulse for ADN/Al/GAP with 20 % Al approaches that of NTO/MMH. At a solid loading of 80 %, the ADN-based propellants have densities 40 to 50 % higher compared to NTO/MMH. This implies that the density specific impulses ($\rho \cdot I_{sp}$) are about 30 to almost 50 % higher for the ADN-based propellants compared to NTO/MMH. Propellants with high Al-content is known to have lower performance than predicted due to Al particle agglomeration and two phase flow. Taking this into account ADN-based propellants still seems competitive due to their high densities.

Material	Formula	ρ (g/cm³)	ΔH_f (kJ/mol)
ADN[b]	$NH_4N(NO_2)_2$	1.81	-148
Al	Al	2.70	0
GAP	$C_3H_5N_3O$	1.29	+114
MMH	CH_6N_2	0.87	+54
NTO	N_2O_4	1.45	-20

Table 4. Input for the thermochemical calculations[a].
a) all data from the ICT – Database (Bathelt et al., 2004) unless otherwise stated.
b) data from Östmark et al. (Östmark et al., 2000).

Propellant	Mixture	I_{sp}(s)	ρ (g/cm³)	$\rho \cdot I_{sp}$ (gs/cm³)
ADN/GAP	70/30	301	1.61	485
ADN/GAP	80/20	313	1.67	523
ADN/Al/GAP	70/10/20	327	1.73	566
ADN/Al/GAP	65/15/20	332	1.76	584
ADN/Al/GAP	60/20/20	335	1.78	596
NTO/MMH	2/1	340	1.19	405

Table 5. Results from the thermochemical calculations.

3.2 ADN prilling

A high solid loading is required to obtain high specific impulse. However, high solid loading increases the viscosity of the uncured propellant slurry. Thus, the maximum solid loading and impulse is limited by processing constraints. To obtain a castable propellant formulation with reasonable viscosity and high solid loading, particles with minimum spatial extension are required. For this reason the particles should have a low aspect ratio or more preferably spherical shape. The particle shape of ADN received from EURENCO is needle shaped and thus not suitable for formulation. Controlling the shape and size of ADN crystals is one of the most critical problems that have hampered the development of ADN-based propellants until now. At FOI, a method to produce spherical ADN particles, prills, have been developed (Johansson et al., 2006). The prills are produced by spraying molten ADN through a nozzle. In the nozzle the molten ADN is atomized to form droplets which then solidify to the desired prills seen in Fig. 5. The particle size can be controlled to some extent by varying spray nozzle size and pressure. Typical particle size distributions for the fine and coarse prills produced are shown in Table 6 and Fig. 6.

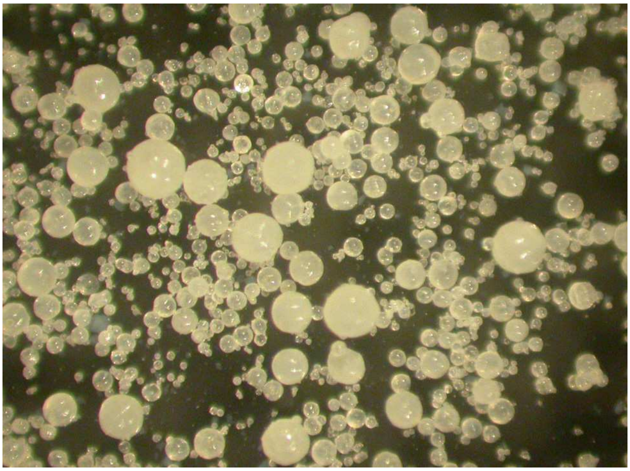

Fig. 5. Spray-prilled ADN.

Currently the prills are produced using up to 250 g ADN per batch. However, with modifications the method can be run continuously making the technology suitable for industrial production. Fumed silica (Cab-O-Sil) is added to the prilled material as an anti-caking agent. Without any anti-caking agent, the prilled ADN cakes after a short time of storage, even at dry conditions. The prills were characterized with respect to particle density, tap density, melting point and purity. The results are shown in Table 7. Properties of as-received ADN are shown for comparison. From the results in Table 7 it can be seen that the particle density decreases by 1 %, but the tap density of the prilled material increases by 30 %, which is important to obtain high solid loading. The decrease in particle density might be due to inclusions formed during the spraying. The somewhat higher nitrate content in the prilled material is due to degradation of ADN during the prilling and is probably responsible for the change in melting point.

Grade	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
Fine	30	60	120
Coarse	30	200	400

Table 6. Typical particle size distributions of prilled ADN.

	As received	Prilled
Amount Cab-O-Sil (%)	-	0.5
Particle density (g/cm3)	1.81	1.79
Tap density (g/cm3)	0.86	1.11
Volumetric loading (%)	47.5	62.0
Melting point (°C)	93.2	92.5
Nitrate content (%)	0.03	0.08

Table 7. Typical properties of as-received ADN and coarse prills (Eldsäter et al., 2009).

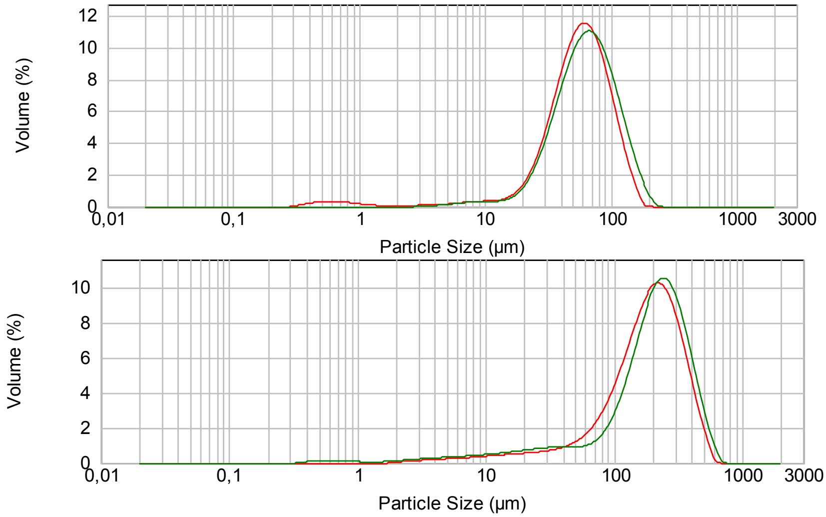

Fig. 6. Particle size distribution of fine (upper graph) and coarse (lower graph) ADN prills. Two measurements on each grade.

3.3 Formulation

An ADN-based solid propellant with a GAP-based binder has been formulated containing 70 % bimodal prilled ADN. The GAP used was obtained from EURENCO France (Lot: 76S04 (Perez, 2007)). The relatively low solid loading was chosen to ensure low viscosity and hence good quality of the casted propellant. Based on our experience, it is now clear that the solid loading can be increased. Batches up to 3.75 kg have been mixed using an IKA HKV 5 high performance kneader and samples for characterization and motor testing have successfully been cast and cured. The thermal stability of the propellants was measured using a heat flow calorimeter. According to STANAG 4582 (STANAG, 2002), the heat flow should not exceed 63.1 µW/g at 75 °C during 19 days. Fig. 7 shows that the propellant has an excellent thermal stability with a heat flow well below the acceptance limit.

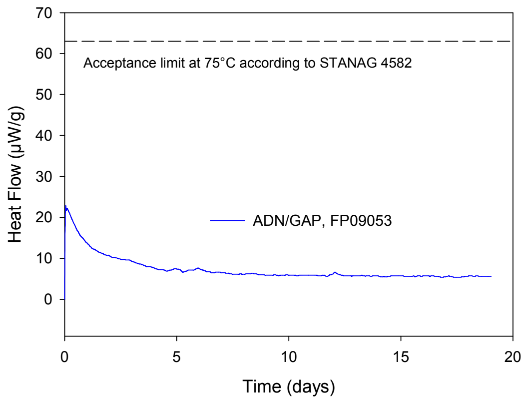

Fig. 7. Thermal stability at 75 °C of ADN/GAP propellant containing 70 % ADN.

3.4 Burning rate measurements

The burning rate was determined using a strand burner. The results were evaluated using the interpolation formula $r = ap^n$, where p is the combustion pressure, in MPa, and r is the measured burning rate in mm/s. The pressure exponent, n, and the burning rate constant, a, where determined by linear regression analysis of the data in a log-log diagram. The results from testing of four propellant batches are shown in Fig. 8 and Table 8. The data correlates well with the interpolation formula, as shown with a linear correlations coefficient, R, close to unity. The propellant has a high burning rate, 24 mm/s at 7 MPa, and a pressure exponent below 0.5 in the pressure interval examined.

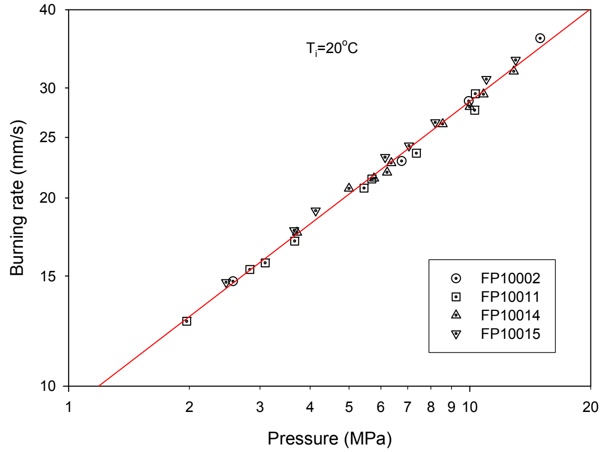

Fig. 8. Burning rate for ADN/GAP 70/30 for four different batches.

a	n	$R^{2\,a}$	r_7 (mm/s)
9.2	0.49	0.993	24

Table 8. Coefficients in the interpolation formula $r = ap^n$ and burning rate at 7 MPa.
a) R^2 is the linear correlations coefficient.

3.5 Motor testing

Rocket motor firings were performed to verify the calculated specific impulse. Three 3 kg case bonded grains were cast in steel cartridges as shown in Fig. 9. A liner based on HTPB was used. Some minor machining was needed after casting. The propellant was easy to machine yielding a smooth surface. Figure 10 shows the motor during firing. The red curve in Fig. 11 shows the recorded pressure as a function of time, and the black is the calculated pressure using the strand burner data in Fig. 8. Some characteristics of the grain and the test motor, as well as some evaluated parameters from the motor firing, are shown in Table 9. The results from the test show that the burning rate was 14 % higher in the rocket motor compared to the strand burner data and the shape of the pressure curve reasonably agreed with the calculations. The measured specific impulse was a few percents lower than predicted, as is usually the case, confirming the high performance potential of ADN/GAP.

Fig. 9. Case bonded 3 kg ADN/GAP (70/30) grain cartridges for motor testing.

Fig. 10. Test firing of ADN/GAP rocket motor.

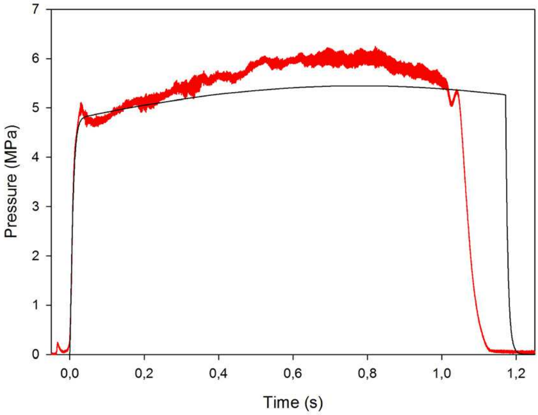

Fig. 11. Combustion pressure as a function of time. Red curve experimental, black curve calculated.

Propellant	ADN/GAP 70/30 batch no FP10015
Grain internal diameter	73.0 mm
Grain external diameter	123.2 mm
Propellant weight	3025 g
Mean pressure	5.55 MPa
Burning rate	24 mm/s (calc. 21 mm/s)
Nozzle throat diameter	31 mm
Nozzle area expansion ratio	5.0 (under-expanded)
Specific impulse	233 s

Table 9. Grain and nozzle characteristics and evaluated parameters.

3.6 Sensitivity and mechanical properties

The propellant used in this work did not contain any plasticizer or bonding agent and its mechanical properties needs to be improved to obtain the desired elasticity. The sensitivity is one of the most important issues to consider when developing new propellants. ADN/GAP-propellants with high solid loading are expected to be hazard class 1.1 materials. However, at low solid loading the sensitivity is expected to be reduced. The calculations presented in Section 3.1 show that the highest specific impulse is obtained using an aluminized formulation containing only 60 % ADN. Due to the low amount ADN needed it is feasible that future high performance solid propellants based on ADN will have an acceptable sensitivity.

4. Liquid Monopropellants based on ADN

One of the most promising alternatives to monopropellant hydrazine is blends based on an oxidizer salt dissolved in a fuel/water mixture. Hydroxylammonium nitrates (HAN) has been studied for this purpose (Meinhardt et al., 1998; Meinhardt et al., 1999; Mittendorf et al., 1997; Wucherer and Christofferson, 2000; Zube et al., 2003). Due to its high solubility, ADN can be used in the same way as HAN. The development of ADN-based monopropellants started at FOI in 1997 on a contract from the Swedish Space Corporation, SSC, and several different propellant formulations have been developed and tested.

4.1 Formulation

When formulating an ADN-based liquid monopropellant, the minimum service temperature allowed for the monopropellant when used in a spacecraft must be considered. In order to use the same thermal management system as for hydrazine (freezing point +2 °C (Schmidt, 2001)), a new monopropellant should have a similar minimum temperature limit. The solubility of the oxidizer salt must therefore be taken into account to determine which formulation that actually can be prepared at this minimum temperature. A reasonable and convenient minimum temperature limit is 0 °C, since this is close to the freezing point of hydrazine and it is easy to obtain in the laboratory by the use of ice water.

The first fuels considered in the development of ADN/fuel/water mixtures were acetone, ethanol and methanol respectively. Figure 12 shows how to optimize the composition with respect to specific impulse. The solubility curve defines the maximum amount of ADN that can be dissolved in a methanol/water mixture at 0 °C. By performance calculations, the optimum formulation is found for a methanol/water mixture containing 30.6 % methanol. The final composition is 63.4 % ADN, 25.4 % water and 11.2 % methanol.

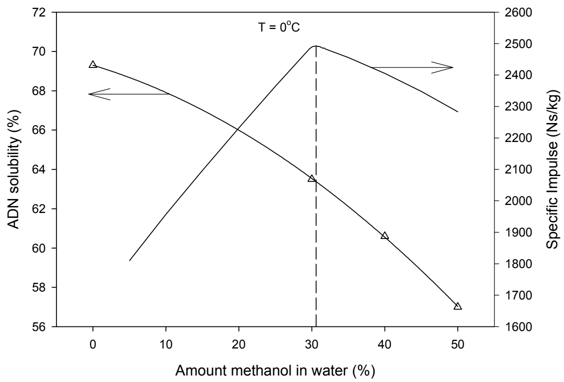

Fig. 12. Specific impulse and ADN solubility in water/methanol mixtures at 0°C. p_c = 2.0 MPa, ε = 50.

Low volatile fuels such as 1,4-butanediol, glycerol, ethylene glycol and trimethylol propane where studied to minimize the amount of ignitable and/or toxic fumes. First glycerol was chosen due to the superior thermal ignition properties of the ADN/glycerol/water-blend. This monopropellant formulation was called LMP-101 (Anflo et al., 2000). However, it was discovered that LMP-101 suffered from poor thermal stability, and as a consequence it was rejected from further development. During the years, several different ADN-based monopropellants have been developed (Wingborg et al., 2004; Wingborg and Tryman, 2003). Two formulations, LMP-103S and FLP-106 have received particular attention. LMP-103S has been selected by SSC and FLP-106 has been selected by FOI as the main monopropellant candidate for further development efforts.

4.2 Properties of ADN liquid monopropellant formulation FLP-106

FLP-106 is a low-viscous yellowish liquid, as seen in Fig. 13, with high performance, low vapour pressure and low sensitivity. It is based on a low volatile fuel, water and 64.6 % ADN. The development, characterization and selection of FLP-106 are reported elsewhere (Wingborg and de Flon, 2010; Wingborg et al., 2004; Wingborg et al., 2006; Wingborg et al., 2005). Some of the properties of FLP-106 are shown in Tables 10 and 11, and its mass density as function of temperature is shown in Fig. 14.

Fig. 13. Monopropellant FLP-106.

	Hydrazine	FLP-106
Specific impulse[b] (s)	230 (Brown, 1995)	259
Density (g/cm^3)	1.0037	1.357
Temp. in chamber (°C)	1120	1880
T_{min} [c] (°C)	2.01	0.0
Viscosity (cP, mPas)	0.913	3.7
Thermal expansion coefficient (1/K)	$9.538 \cdot 10^{-4}$	$6.04 \cdot 10^{-4}$
Heat capacity (J/gK)	3.0778	2.41

Table 10. Properties of hydrazine and FLP-106[a].

a) All properties at 25 °C. Hydrazine data from Schmidt (Schmidt, 2001) and FLP-106 data from Wingborg et al. (Wingborg and de Flon, 2010; Wingborg et al., 2004; Wingborg et al., 2006; Wingborg et al., 2005).

b) Calculated Isp. Pc = 2.0 MPa, Pa = 0.0 MPa, ε = 50.

c) Minimum storage temperature determined by freezing (hydrazine) or precipitation (FLP-106).

A_e/A_t	50	100	150	200
I_{sp} (s) [a]	259	264	266	268

Table 11. Vaccum specific impulse at different nozzle area expansion ratios.

a) Pc = 2.0 MPa

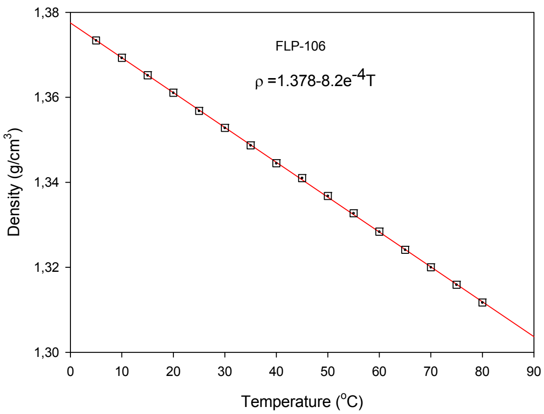

Fig. 14. Mass density of FLP-106 as a function of temperature.

4.3 FLP-106 manufacturing and batch control

FLP-106 is manufactured in two steps; first the fuel is dissolved in water and secondly ADN is mixed in the fuel/water blend. The temperature drops substantially during the dissolution of ADN and thus it takes some time before all ADN has dissolved. To speed up the dissolution, the mixture can be heated using a warm water bath. The ADN used was procured from EURENCO Bofors in Sweden. The purity of the material is above 99 %. However, small amounts of insoluble impurities are present, which is clearly seen when dissolving ADN. The purity can be improved by recrystallization. In this way insoluble

impurities are removed, but the content of ammonium nitrate increases due to ADN degradation. To prevent this, the prepared propellant is instead purified *in-situ* by filtration using a 0.45 µm PTFE filter, and a completely clear liquid propellant of high purity is formed.
When manufacturing batches of FLP-106 it is important to verify it has been prepared correctly and conforms to the specification. Apart from visual examination, each batch of propellant is analysed with respect to density using a Mettler Toledo DE40 density meter. It is estimated that the ADN content in this way can be determined within ±0.05 %. The high precision is possible due to the low volatility of FLP-106.

4.3 FLP-106 material compatibility

The compatibility between the propellant and different construction materials used in propulsion systems have been assessed (Wingborg and de Flon, 2010). The materials considered are shown in Table 12. The tests were performed using a Thermometric TAM 2277 heat flow calorimeter. Pieces of respective test material were immersed in approximately 0.2 g FLP-106 in 3 cm^3 glass ampoules. The measurements were performed at 75 °C for 19 days. All the tested materials were supplied by Astrium GmbH, Bremen, except sample no. 13, which was cut out from a Nalgene bottle.

Sample no.	Materials
1	Metal, AISI 304L
2	Metal, AISI 321
3	Metal, AISI 347
4	Metal, Inconel 600
5	Metal, AMS 4902
6	Metal, AMS 4906
7	Metal, Nimonic 75
8	Polymer, PTFE
9	Rubber, EPDM
10	O-ring, Kalrez 4079, Du Pont
11	O-ring, Kalrez 1050LF, Du Pont
12	O-ring, 58-00391, Parker Hannifin GmbH
13	Polymer, PETG, Nalgene

Table 12. Materials used in the compatibility assessment.

In all cases the heat flow induced by the tested materials were below 0.1 $\mu W/mm^2$ (Wingborg and de Flon, 2010). Based on the heat flow measurements all materials tested are considered to be compatible with FLP-106. However, EPDM and PETG samples both showed a slight colour shift. This might be due to thermal degradation of the materials. Since the tests were performed at substantially harsher conditions than, for instance the NASA Test 15 (test time 48 h, test temp 71 °C) (NASA, 1998), it is not clear that the colour shift detected is an issue.

4.4 Ignition of FLP-106

One important aspect in the development of a new monopropellant is the ignition. State of the art hydrazine thrusters use catalytic ignition, which is simple and reliable. To replace hydrazine, ADN-based monopropellants must be as easy to ignite. However, a disadvantage of the ADN-based monopropellants is the high combustion temperature, which is approximately 800°C higher than hydrazine, as seen in Table 10. The combustion temperature is in the same range as for HAN-based monopropellants, and it has been reported that the current state of the art hydrazine catalyst (Shell 405) cannot withstand such high temperatures (Reed, 2003; Zube et al., 2003). This and the fact that hydrazine and ADN-based liquid propellants are very different, both physically and chemically, require development of new ignition methods, or new catalysts. When dripping the FLP-106 on a hot plate, with a temperature in the range of 200 to 250°C, it ignite and burn fast. This clearly shows that thermal ignition is possible and thermal ignition might thus be a feasible ignition method. Three different methods of heating the propellant to the ignition temperature have been identified:

- Pyrotechnic (by forming hot gases using a solid energetic material which in turn will heat the propellant)
- Thermal conduction (by spraying the propellant on a hot object which in turn is heated by electric means)
- Resistive (ADN is a salt and the propellants thereby possess a relatively high electric conductivity. This means that an ADN-based monopropellant can be resistively heated)

Development of catalytic (Scharlemann, 2010), thermal (Wingborg et al., 2006), and resistive (Wingborg et al., 2005) ignition methods is ongoing.

4.5 FLP-106 compared to LMP-103S

Both FLP-106 and LMP-103S are compatible with materials currently used in propulsion systems. They both also have similar *oral* toxicity and should be considered as harmful, but not toxic. However, FLP-106 has a substantial lower vapour pressure and requires no respiratory protection during handling. They are not sensitive to shock initiation and should, from this point of view, not be considered as hazard class 1.1 materials (ECAPS, 2010; Wingborg and de Flon, 2010). The advantage using FLP-106, apart from its lower volatility, is its higher performance and higher density as shown in Table 13. The specific impulse for FLP-106 is 7 s higher compared to LMP-103S, and the density-impulse ($\rho \cdot I_{sp}$) is 13 % higher.

Propellant	FLP-106	LMP-103S
I_{sp} (s) [a]	259	252 (ECAPS, 2009)
ρ (g/cm^3) [b]	1.362	1.240 (ECAPS, 2010)
$\rho \cdot I_{sp}$ (gs/cm^3)	353	312

Table 13. Properties of ADN-based monopropellants.
a) at a nozzle area expansion ratio of 50.
b) at 20 °C.

5. Concluding remarks

Ammonium dinitramide, ADN, seems promising as a green substitute for both ammonium perchlorate, AP, and for monopropellant hydrazine. A solid ADN propellant has been formulated and test fired successfully and a high performance liquid ADN-based monopropellant has been developed.

Future work concerning solid ADN-based propellants will focus on improving the mechanical properties and to characterize the sensitivity.
Future work concerning liquid ADN-based monopropellants will focus on ignition and thruster development.

6. Acknowledgements

The authors like to acknowledge all colleagues at FOI involved in the ADN development and the Swedish Armed Forces for financial support.

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Advances in Spacecraft Technologies
Edited by Dr Jason Hall

ISBN 978-953-307-551-8
Hard cover, 596 pages
Publisher InTech
Published online 14, February, 2011
Published in print edition February, 2011

The development and launch of the first artificial satellite Sputnik more than five decades ago propelled both the scientific and engineering communities to new heights as they worked together to develop novel solutions to the challenges of spacecraft system design. This symbiotic relationship has brought significant technological advances that have enabled the design of systems that can withstand the rigors of space while providing valuable space-based services. With its 26 chapters divided into three sections, this book brings together critical contributions from renowned international researchers to provide an outstanding survey of recent advances in spacecraft technologies. The first section includes nine chapters that focus on innovative hardware technologies while the next section is comprised of seven chapters that center on cutting-edge state estimation techniques. The final section contains eleven chapters that present a series of novel control methods for spacecraft orbit and attitude control.

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