EUREN CO
GROUPE SNPE

DINITRAMIDE NEWS

OCTOBER 2004

GENERAL

The main purpose of this newsletter is to briefly update the readers on the research on dinitramide and the development of new applications. It is also an opportunity for us to inform you on our plans and ideas for dinitramides. Today it is produced in a pilot scale with a capacity of several metric tons annually. The plan is now to build a plant for industrial scale at EURENCO Bofors in Sweden. Ammonium Dinitramide, ADN, is a strong oxidizer and an explosive. It is an ionic compound with the formula. $NH_4{}^+N(NO_2)_2{}^-$. The existence of stable dinitramides was first published in 1991 in two patent applications filed by the US Research stablishment, SRI. The anion, $N(NO_2)_2{}^-$, was then named dinitramide for the first time. However, it is indisputable that a large effort on synthesizing and using ADN was done in the Soviet Union. Due to its high strategic military impact it was never published until SRI published the patents and Soviet Union was no longer. It was not until FOI in 1996 invented a new one-step process for making ADN that things started to happen. With this efficient method EURENCO Bofors could start a pilot production the year after. One of many potential applications is as a replacement of ammonium or potassium perchlorate in composite propellants. Substituting perchlorate would give increased impulse but more important no secondary smoke that is formed when a perchlorate composite burns due to the formation of hydrogen chloride. This will be an important tactical advantage making launched rockets less visible. Since ADN and other dinitramide salts became available they have been tested for several other applications not even thought of when we started to produce in 1997. Some of them are described in this publication. The need for a replacement of perchlorate has been accentuated after last year's reports that it could inhibit the function of the thyroid. High levels of contamination of drinking water have been reported in some parts of the US. The contamination is likely originating from rocket fuel. On March 11, California set a standard for perchlorate that could lead to expensive cleanups at military bases.

In this issue

Dinitramide Users Meeting in 2005, Call for Papers

We believe that the first Dinitramide Users Meeting that was held in Karlskoga in March last year was successful. Logically, we plan a new meeting on April 11-12, 2005 at the same location. These meetings are unique opportunities to meet a large group of people, all working or interested in dinitramides. Fifty people from 9 different countries and 22 affiliations attended the meeting last year. Twelve presentations where given and lively discussed during two days. This type of meetings concentrating on one topic is also a learning forum for the specialists. Please, mail your abstract to: **per.sjoberg@eurenco.com**.

Dinitramide Users Meeting in March 2003. Second from right stands Jeffrey Bottaro, who invented and named the anion.

High Energy Minimum Signature Propellants

Since ADN does not contain Chlorine it does not like AP form hydrogen chloride when it is consumed in composite propellant. Consequently, no tail of condensed water forms behind a missile or a rocket. This is of great tactical importance on the battlefield. A composite propellant with ADN will also outperform one with AP. Theoretical calculations tells that replacing AP with ADN increases the specific impulse. Calculations also show that an ADN propellant has nearly the same performance as a propellant with CL 20 and HNF. Due to the more favourable oxygen balance is the maximum performance for an ADN propellant shifted to a lower solid content (approx. 80%). This is an important advantage for the cost of production since the ability to cast is better when the amount of solids is low. ADN is synthesized in a one-step process from readably available raw materials. It is therefore likely that the price for industrially produced ADN will be significantly lower than that for CL 20 and HNF. Several propellant composition studies were discussed and presented at the Dinitramide Users Meeting that was held in 2003 at EURENCO Bofors. Besides burn rate studies, studies on sensitivity and stability were presented as well as compatibility relevant to propellant formulations. Undoubtedly, these issues were in the focus at the meeting. It was obvious that a lot of work on AND had been done in the military research establishment.

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ADN IN DEPTH CHARGES

ADN is a high explosive with a detonation velocity around 7000 m/s. Therefore it serves both as oxidizer and as high explosive in depth charges where Aluminium is used as fuel. Therefore, ADN replaces both the conventional oxidizer, which is perchlorate, and the high explosive, which most often is RDX. Since RDX has a negative oxygen balance this means more Aluminium burns per weight unit of charge. The effect is that more and hotter gas forms increasing the bubble energy.

Metallic salts

Most alkali metal salts of dinitramide are presented in the literature. An application would be as a strong oxidant in pyrotechnical compositions. A salt of metal (M) is easily synthesized from an aqueous solution of ADN in the laboratory scale.

MOH + NH4N(NO2)2 = MN(NO2)2 + NH3(g) + H2O

The ammonium ion fumes off as gaseous ammonia. The salt precipitates when the water evaporates. We have produced and tested KDN. A mixture of KDN and cellulose acetyl butyrate (CAB) burns significantly faster than corresponding mixture of potassium perchlorate.

ADN REPLACES TOXIC HYDRAZINE AS PROPELLANT

Hydrazine has since the 1960s been the standard liquid monopropellant for commercial and military use. Personnel safety and increased environmental awareness have become important issues in the context of propulsion system handling and operation. The cost of fuelling a spacecraft with hydrazine has therefore increased significantly along with the repeated lowering of the limit value of exposure, as hydrazine is not only toxic but also more seriously carcinogenic.

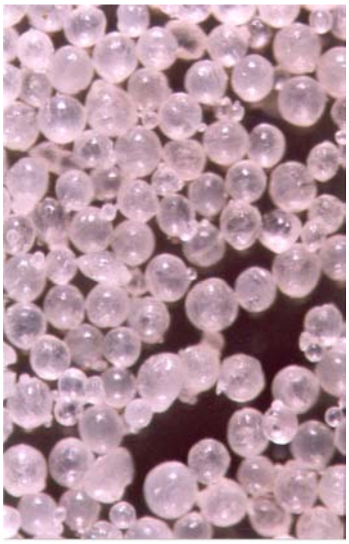
Reducing risks and costs associated with handling and operation of hydrazine systems is an important issue for the Aerospace industry.

A new non-toxic liquid monopropellant with ADN has higher impulse than hydrazine. The composition is a solution of ADN in an alcohol and small amounts of water. Below is a table of performance and toxicity compared with hydrazine and HAN (hydroxyl ammonium nitrate). The specific weight for the ADN composition is 1.3 compared to 1.0 for hydrazine. The impulse per volume is therefore even more advantageous. Swedish Space Corporation and Volvo Aero have through their joint venture ECAPS developed a prototype motor, see picture, that will use the ADN based monopropellant for spacecraft propulsion.

In these applications, where large volumes of propellant burns in a small burning chamber the requirement for deposits from the burning reaction is very strict. We are, for this application, producing an ultra-pure grade of ADN.

	I_{sp} (Ns/kg)	LD50 rat, orally (mg/kg)
ADN/glycerol/water	2420	1360
HAN/glycine/water	2001	325 (pure HAN)
Hydrazine	2325	59

IMPROVING ADN



".. it is important that composite rocket formulators get access to prilled and stabilized ADN as soon as possible since the good quality composites with sufficient loading of ADN cannot be made with the ill-shaped crystals of neat product."

Even though ADN has been known for over 30 years in Russia and for over 10 years in what was used to be called the free world, it still needs to be improved before it will be procured for a military program. The main three problems are the ill-shaped crystals which makes it difficult to use as a filler in cast formulations, the thermal stability which is not bad but could and therefore should be improved and finally the hygroscopicity as a raw material.

The ease and the cost of casting of composite propellants is very much dependent on the shape and the size distribution for the ingoing solids. Uniformly shaped particles with a good balance between coarse and fine particles is most important to a low viscosity which drastically simplifies the casting. Spherically shaped particles also improve the mechanical integrity for the cured propellant.

The crystals that come out from the synthesis process are irregularly shaped and the particle size distribution cannot be controlled. It is therefore necessarily that methods are developed for industrial production of uniformly shaped particles with tailored size distributions. Logically many laboratories do today develop methods to produce controlled particles of ADN. FOI in Sweden, ICT in Germany, Qinetiqs in UK and Pratt Whitney and ATK Thiokol both in US, have published and patented methods. The methods with which these institutions are working can all be described as prilling processes or emulsion crystallization. The ADN is melted in a liquid and emulsified to droplets. When the temperature is lowered below the melting point solid particles whit the shape of the droplets are formed. In the method described by ATK, the crystals are melted and droplets formed when falling down inside a tower with a heating zone.

The various variations of the prilling process involves a stage where ADN is in melted form. This is a good opportunity to add and distribute a stabilizer to the product. Many compounds have shown to stabilize ADN from thermal decomposition. Most of them have not been published, but ICT has shown that some of them have a remarkable effect on the mass loss at 80 Celsius compared to neat crystallized ADN. This is a very important work and from a ADN producers perspective it is important that composite rocket formulators get access to prilled and stabilized ADN as soon as possible since the good quality composites with sufficient loading of ADN cannot be made with the ill-shaped crystals of neat product.
EURENCO Bofors has therefore started to prill ADN in 5 litres equipment. We use paraffin as the liquid media. Earlier we used DOS as the media but we changed to paraffin when we realized that the small solubility of ADN in DOS could influence the shape stability of the prills. By using different ways of controlling the size of the melted droplets, we can control the size distribution from 20 to 300 microns. As an option for our customer, we send the prilled product coated with a small percentage of paraffin. This will protect the prills from agglomerate due to the high hygroscopicity of ADN (the hygroscopicity is in the same magnitude as for ammonium nitrate). The paraffin is removed before use by washing the product in heptane. We add hexamine as a stabilizer. This decreases the gassing at 85 Celsius down to about 30% compared to neat product. A problem is that the melting point is somewhat decreased for the prills compared to neat ADN. The melting point could be around 90 Celsius compared to 92 C for neat product. We believe this results from small amounts of the medium (paraffin) that is used the prilling process is encapsulated in the product.

Availability

EURENCO Bofors AB produces ADN and other dinitramides since 1996. We have sold samples to more than 50 different research establishments and companies' worldwide. By providing samples to a large community, a broader range of potential applications for dinitramides has emerged since1996. Today, it is a fact that the first application in full scale will be as a gas generating substance in air bags. For this application is the dinitramide salt of guanylurea used, GUDN. Subsequently we will produce ton quantities of dinitramide this year with the intention to continue increasing the capacity over the next few years. Since ADN is a down stream product from GUDN, this will also result in an increased capacity of ADN.

Dinitramide is synthesized with a mixed acid nitration of a sulphamic acids salt. The dinitramide is then precipitated as GUDN from a water solution by adding guanylurea. The spent nitration acids are regenerated by using standard procedures. In a following step GUDN is transformed to ADN in two separate ion exchange reaction. First, GUDN is changed to potassium dinitramide (KDN) using potassium hydroxide. Finally, KDN is transformed to ADN in an ion exchange reaction with ammonium sulphate.
ADN is crystallized from the solution and potassium sulphate is generated as a waste. The solvents used in all steps are recycled.

"The use of GUDN for making ADN is a breakthrough for an environmentally sound process"

The use of GUDN for making ADN is a breakthrough for an environmentally sound process. Earlier, when we produced ADN directly, we could not recover the nitric acid since it was too diluted in the process to separate the dinitramide from the nitrate in an ion exchange colon. The nitrates were then considered as an environmental problem. With this new process, we are convinced that we will not be hampered by waste problems when the production is scaled up.

Insensitive Gun Propellants

GUDN is a very stable salt of dinitramide. The formula is $C_2N_4OH_7(N(NO_2)_2$ In contrast to ADN it does not melt. The DSC onset is above 205^0C. The cat ion is formed when the strong base guanylurea is protonated. The development of gun propellants at our company took a new turn in 1999 when FOX-7 (DADNE) and GUDN became available for extensive testing in gun propellants.

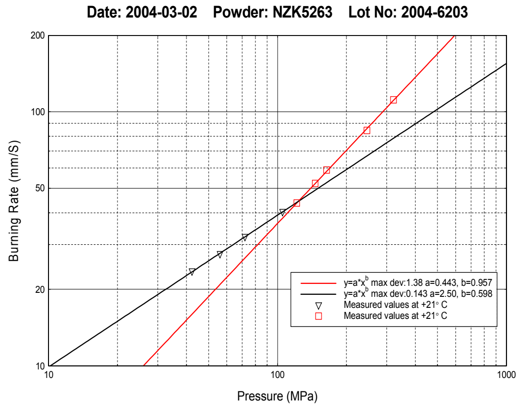
The research on gun propellants based on new ingredients was initially included in a government funded research program. In 2002, preliminary tests with the new propellants led to a new research program aiming towards a more detailed study of insensitive gun propellants. The program was funded by both government and industry and led to a production scale capability allowing for large scale testing.

The propellants that are under development at EURENCO Bofors are mainly based on combinations of FOX-7, GUDN and RDX together with a binder system consisting of NENA and nitrocellulose. For comparative testing, a carrier composition was developed in which RDX, FOX-7 and GUDN could be interchanged to screen possible performances. The most promising combinations where then further optimised.

Due to the different performance of FOX-7 and GUDN as energetic fillers in gun propellants, new compositions can be tailored for a specific application without loosing the sensitivity aspect. FOX-7 is more energetic and delivers more gun performance to the propellant than GUDN. GUDN on the other hand, contributes with a very low flame temperature and enough gun performance for artillery or machine gun applications where low barrel ware is important. At present FOX-7, propellants are tested in the kinetic round for BOFORS 40 mm gun, where as the GUDN propellants are tested in the modular charge system for BOFORS 155 mm gun.
From the stability, testing it was found that some of the GUDN combinations tested in the long-term storage test were unstable with standard stabilizer systems. A new stabilizer is therefore under development to broaden the range of possible compositions. Preliminary testing shows good results.

A typical composition with 60% GUDN generates a burning-rate of approximately 40 mm/s at 100 MPa with two different burning exponents over the pressure regime. Compared to a reference composition containing RDX as a replacement for GUDN, the ignition start-up time is significantly reduced for the propellant containing GUDN. The gun performance equals that of a single-base propellant but the flame temperatures are as low as 2200 K. The temperature dependence is somewhat higher than for a singlebase propellant in the 155 mm gun.

GUDN propellants are now manufactured in production scale for the BOFORS 155 mm howitzer modular charge system. The standard solvent-less manufacturing process for double base propellants is used for the GUDN propellants, this means that no adaptation of the production facility is needed. The sensitivity of a propellant containing 60% GUDN is in general low in terms of the standard drop-weight and friction test. Initiation tests also shows that no sustained detonation could be achieved axially along a 135 mm 19-perf propellant stick using a standard blasting cap and a 6 gram C-4 booster-charge. For some applications it is however interesting to improve the performance further by replacing a smaller percentage of GUDN with RDX. Preliminary testing shows that this can be done up to a percentage of about 10% with the same result in the initiation test. Impact sensitivity testing will be done with modular charges in autumn/winter 2004.



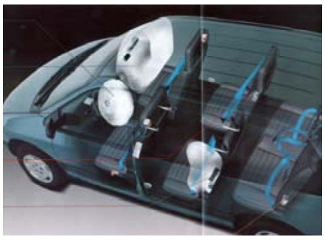
19-perf, slotted, rosette of GUDN propellant NZK5263

Modular charge for BOFORS 155 mm system

The most useful dinitramide

The burning characteristic of GUDN and its high gas yield makes it excellent as a gas-generant for automotive safety devices. The use in air bags has shown to be the first commercial application for dinitramides. The high oxygen balance in GUDN is to a great advantage since only small amounts of inorganic oxidizer are needed to achieve an emission free from the poisonous carbon monoxide. In the end, only small amounts of propellants are needed to blow up a bag to a certain volume. This is extra important in utility cars where the passenger bags are large.
GUDN burns with a moderate rate at a pressure coefficient approximately 0.5 – 0.7. However, when mixed with inorganic oxidizers, such as perchlorates or nitrates, they burn with a rate of 22 mm/second at 20 MPa with a pressure coefficient of 0.3 – 0.4.

People have suggested GUDN as a burning modifier in ADN-based rocket propellants. This application has not yet been investigated or at least not published. However, we assume that it will be investigated when continuing with ADN-based rocket formulations.



Another characteristic, which makes GUDN interesting, is the extremely low sensitivity. The substance did not react when we tested it for impact and friction. Today GUDN is classified as 1.3C. The picture shows a transport paperboard drum after its content of 110 kg of GUDN has burnt. As can be seen it is quite intact due to the very low intensity with which GUDN burns at atmospheric conditions.

Due to its extreme insensitivity, we hope to find interests to use GUDN as an energetic material in ammunition when the user accentuates low vulnerability. Even though it is extremely insensitive, it can be detonated if confined and boosted. It has a potential as energetic filler in warheads with very high safety towards any form of unintentional explosions. The calculated performance places GUDN between RDX and TNT. Below is a two-dimensional property plot showing safety versus performance, defined as impact threshold energy and detonation pressure. The large dot for GUDN represents the uncertainty for the performance, which so far only is calculated.

For the same reason, we also foresee a use of GUDN for propellants. Besides the advantage with low sensitivity, GUDN burns with at an extremely low temperature, which is important in automatic guns where barrel erosion often is a problem. Also for Howitzer-ammunition, there is a potential to GUDN since we have made tests that show that the performance is the same as for a conventional gun propellant.

GUDN is already readily available at a cost that is very competitive compared to almost any other currently used energetic compound. The process for making GUDN is environmentally friendly with essentially no waste streams.

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