



LOW TOXICITY ROCKET PROPELLANTS

Hydrazine (N_2H_4) and its hypergolic mate nitrogen tetroxide (N_2O_4) are used on virtually all spacecraft and on a large number of launch vehicles. In recent years however, there has been an effort in identifying and developing alternatives to replace hydrazine as a rocket propellant.

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HYDRAZINE AND ITS DERIVATIVES

Hydrazine (N_2H_4) is the most widespread rocket propellant. Since its development in the late fifties and early sixties, variations like Monomethyl Hydrazine (MMH) and Unsymmetrical dimethyl Hydrazine (UDMH) have been the standard propellant for nearly all spacecraft. On a technical level, hydrazine derivatives combine long-term storability with relatively good performance. Hydrazine is easily decomposed using a catalyst, simplifying monopropellant thruster designs. On top of that, hydrazine is hypergolic (ignites on contact) with a large range of storable oxidizers like Nitrogen Tetroxide and Nitric Acid variations, greatly simplifying the bipropellant thruster design.

TOXICITY AND REACH REGULATION

These merits come at a price. Hydrazine derivatives, including hypergolic rocket propellant, are highly flammable, toxic and carcinogenic. Furthermore, most variations have a vapor pressure higher than ambient air, which means that if a leak occurs during ground operations, the hydrazine will quickly evaporate and mix in the air, increasing the risk of inhalation by ground personnel. These adverse properties induce the need of strict safety precautions and regulations while handling

the propellants. Any operation involving hydrazine requires all personnel to wear so-called S.C.A.P.E. (Self Contained Atmospheric Protective Ensemble) suits, which greatly reduces mobility of the personnel. The environmental impact is also severe, resulting in strict regulations for the design and operations of ground equipment. These factors induce great risk and complexity in the development and operation of hydrazine-based systems, which in turn results in a high cost.

Apart from the operational aspects, future legislation might complicate matters even more. The European Union's REACH (Regulation conserving the Registration, Evaluation, Authorization and Restriction of Chemicals) regulation puts hydrazine on a list of substances that are candidates for complete abolishment in the near future. If this is implemented, no European country can allow its industries to work with hydrazine anymore. This will render further development of hydrazine-based spacecraft propulsion in Europe practically impossible.

These factors have led to a recent interest in low toxicity (or "green") rocket propellants. Multiple ESA and EU projects are trying to identify and increase the tech-

nology readiness level of different potential hydrazine replacements.

ENERGETIC SALTS: ADN, HAN AND HNF

In Europe, most focus has been on a group of energetic, which include Ammonium Dinitramide (ADN), Hydroxylammonium nitrate (HAN) and Hydrazinium Nitroformate (HNF). These energetic salts form solid crystals and can be used as a low toxicity oxidizer in solid rocket motors. However, the crystals can also be dissolved in water for monopropellant applications acting as a hydrazine replacement. The combustion products of the propellants have relatively large molecules, but the high operating temperatures compensate this.

ADN is the ammonium salt of dinitramic acid and decomposes into nitrogen, oxygen and water. It was originally developed in the Soviet Union. In the early 1990s, the Swedish Defense Research Institute (FOI) started development on ADN as a non-toxic and smokeless solid rocket oxidizer for missile applications. Currently, multiple parties including ESA, NASA, Nammo Raufoss and Swedish Space Company are further developing ADN based liquid rocket applications. Dissolved in water,



Figure 1. Crew wearing S.C.A.P.E suits for fueling NASA spacecraft



Figure 2. Proton Launch, toxic yellow fumes originating from the UDMH and NTO propellants

ADN has a slightly lower performance but higher specific impulse density as hydrazine. In 2010, the Swedish Prisma mission was the first spacecraft to feature ADN based thrusters.

Hydroxylamine Nitrate (HAN) was originally invented as a reducing agent for plutonium ions for nuclear energy applications. It also attracted great interest as green rocket oxidizer. Much like ADN, HAN is being developed as a smokeless propellant for tactical missiles by Raytheon. Dissolved in water, it potentially has a slightly higher performance compared to ADN. NASA is planning a demonstration mission (GPIM or Green Propellant Infusion Mission) by the end of 2015.

Hydrazinium nitroformate (HNF) was developed in the late 1990s in cooperation between the TU Delft, TNO and APP. Like ADN and HAN, its initial application was to replace Ammonium Perchlorate as solid oxidizer. However most solid propellant combinations of HNF were plagued by a high-pressure exponent (which is unwanted in solid rocket motors). However in theory it has the same merits as ADN and HAN when dissolved in water. Additionally, it is the most energetic of the described salts, which might offer a performance increase compared to HAN and ADN. However, currently no spacecraft mission is planned to fly HNF based systems in the near future.

HYDROGEN PEROXIDE AND NITROUS OXIDE

The ionic liquids described above feature large combustion product molecules and

high operating temperatures. This imposes significant challenges for the development of durable catalytic reactors and often requires the combustion chamber and nozzle to be regenerative cooled. Liquids like Hydrogen Peroxide and Nitrous Oxide do not have these problems.

Hydrogen peroxide is a wide spread substance, mostly used as a bleaching agent. For rocket applications purity between 85 and 95 percent is needed. The development of this so-called High Test Peroxide (HTP) took place in Germany in the late 1930s and 1940s. After the Second World War, the technology spread across the globe. It gained some popularity in the 1960s as oxidizer and featured on the British Black Arrow missile. It was also used to power the main engines of NASA's X-15 spaceplane. Furthermore, it is used in the gas generators of the Russian Soyuz rockets. It delivers relatively good performance while featuring storability; high density and non-toxic exhaust products. It does however have its challenges. In its high purity form, HTP can spontaneously decompose if subjected to pollution. Moreover, its viscosity is very low, making feed systems very prone to leakage problems. Numerous accidents have occurred throughout history due to these factors, making further development difficult

Nitrous oxide, also known as laughing gas is considered to be the most safe of the propellants described in this review. It is being used as an anesthetic agent as well as an aerosol propellant in whipped cream canisters. It is also used to enhance car performance when injected

into the engine. Its wide spread nature and low toxicity makes it an attractive rocket propellant. It can be used both in monopropellant as in bi-propellant applications. It has a very high vapor pressure, which gives it self-pressurizing capabilities. This can greatly simplify the propulsion system. However, it also has by far the lowest performance of the described propellants. Dissolving hydrocarbons in the Nitrous oxide will increase the performance but also increase its explosive risks. The US Company Firestar has patented a number of nitrous oxide fuel blends dubbed NOFBX, where Nitrous oxide is mixed with fuels like ethane, ethene and acetylene as well as with a number of stabilizing agents to get a high performance monopropellant. An additional complication of nitrous oxide based systems is the fact that nitrous oxide is a very effective dissolving agent. This makes the development of durable catalyst a challenge. Furthermore, it makes development of composite tanks difficult since it will dissolve the epoxy of the composite.

CONCLUSION

The replacement of hydrazine by low toxicity alternatives will continue to be a challenge in the near future. Each alternative has its own specific drawbacks and since virtually all spacecraft used hydrazine derivatives, it will require a lot of effort of the space industry to gain similar experience and confidence with any alternative. On the other side, the development of green rocket propellants will have the potential to significantly reduce the environmental impact and cost of spaceflight. ✓