Safety aspects of hypergolic propellants with hydrogen peroxide
Aspekty bezpieczeństwa materiałów pędnych hipergolicznych z nadtlenkiem wodoru

Grzegorz Rarata, Wojciech Florczuk

Zakład Technologii Kosmicznych, Instytut Lotnictwa, Al. Krakowska 110/114, 02-256 Warszawa, PL

Abstract: The hazards and risks associated with the handling, transportation and storage of hypergolic propellants based on highly concentrated hydrogen peroxide as an oxidiser, are discussed in the paper. The main focus has been placed on the assessment of possible hazards and preventative methods for the protection of technical staff and hardware associated with 98% hydrogen peroxide and the fast developing new “green” hypergolic propellants. The basic risks connected with the use of incompatible materials, human error and propellant properties have been described. The dangerous incidents and catastrophic accidents hitherto known with hypergolic propellants are related mainly to the toxic compounds based on hydrazine derivatives and dinitrogen tetroxide. The conclusions and remarks from available literature have been discussed and transferred into a form of handling procedures for “green” hypergols. As a result, the data, comparison with existing literature and the authors’ experience presented in this paper, try to illustrate what steps need to be taken during various research operations in a laboratory environment, when working with hypergolic rocket propellants. There are many ways of preventing unwanted events with the implementation of some being necessary to avoid or mitigate possible technical problems, incidents or even accidents. Some of the most important factors in risk minimization, when working with 98% hydrogen peroxide and hypergolic fuels, are presented.

Streszczenie: W artykule omówione zostały zagrożenia oraz ryzyka związane ze stosowaniem, transportem oraz przechowywaniem hipergolicznych materiałów pędnym, bazujących na wysoko stężonym nadtlenku wodoru, jako utleniacz rakietowy. W tym celu określone zostały potencjalne zagrożenia i metody ich zapobiegania w odniesieniu do ochrony fizycznej personelu technicznego oraz aparatury, która może mieć bezpośredni kontakt z 98% nadtlenkiem wodoru oraz paliwami hiperglicznymi klasy „green”, tj. „ekologicznymi” i niskotoksycznymi. Przedstawiono podstawowe ryzyka wynikające ze stosowania materiałów konstrukcyjnych, niekompatybilnych z wybranymi cieczami, ludzkich błędów oraz właściwości wybranych paliw i 98% nadtlenku wodoru. Znane są groźne zdarzenia oraz katastroficzne w skutku wypadki związane z wykorzystaniem samozapłonowych, toksycznych rakietowych materiałów pędnym, bazujących na hydrazynie i jej pochodnych, w kontakcie z czterotlenkiem diazotu. Zdobyt doświadczenia oraz uwagi zawarte w dostępnej literaturze, a związane z toksycznymi, hiperglicznymi materiałami pędnym, zostały przedstawione i zasugerowane jako procedury do zastosowania przy stosowaniu nowych, „ekologicznych” związku samozapłonowych. Na tej podstawie dokonano próby opisania środków zapobiegawczych przeciw potencjalnym zagrożeniom, występującym w praktyce badań laboratoryjnych z tego typu związkami. Opisane zostały również scenariusze zdarzeń i związane z nimi zagrożenia, a także wskazano procedury i metody, które je minimalizują lub całkowicie eliminują.

Keywords: hydrogen peroxide, HTP, hypergolicity, ignition, propulsion, oxidiser
Słowa kluczowe: nadtlenek wodoru, HTP, hipergliczność, zapłon, napęd, utleniacz
1. Introduction

Solutions of highly concentrated hydrogen peroxide have been widely used as an efficient mono-propellant or oxidiser for bipropellant rocket systems in the aerospace industry, especially in the two decades following World War II [1]. When used as a rocket oxidiser for previously developed propulsion systems, hydrogen peroxide needed to be decomposed by a suitable catalytic bed leading to the liberation of energy in the form of active oxygen and steam at high temperature. Such mixtures of decomposition products could be used to obtain combustion with a chosen fuel [2]. Recent research activities [3-12], have shown that high performance hypergolic propellants in the form of compositions of highly concentrated hydrogen peroxide with some fuels can be developed and successfully applied in laboratory scale bipropellant rocket engines.

Currently utilised hypergolic propellants are very toxic fluids which react spontaneously and vigorously by direct contact with each other. Therefore, alternative, less or even non-toxic hypergolic propellants for use with 98% hydrogen peroxide, are under intense development at the Institute of Aviation and at other research centres in Europe. Although new hypergolic propellants are intended to be storable and stable at normal conditions, as currently used toxic liquids, they still may be hazardous, taking into account their chemical nature (98% hydrogen peroxide is a form of high energy material) and physical properties, including their limited but still important ATE index (Acute Toxicity Estimation). The ATE index is classified as 4 categories of toxicity, by parameters such as LD50 for dermal and oral doses, and by LC50 for gaseous concentration of fuel vapours in air. The lower the category for ATE, the greater the risks and hazards, including death or serious health damages in categories 1 and 2. For example, MMH is classified in 1 category of ATE by LC50 with a limit of up to 34 ppm in air. From this reason the MMH (monomethyl hydrazine), UDMH (unsymmetrical dimethylhydrazine) and hydrazine are fuels that will be replaced in the near future.

Unlike currently used toxic, volatile hypergols, the new combinations of hypergolic fuels with highly concentrated hydrogen peroxide can seriously reduce the costs and hazards that are related to the safety and service procedures during ground operations with satellite and rocket propulsion systems. Generally, the greatest operational risk to technical staff is connected to human error due to routine, hardware and/or material failures.

2. Hydrogen peroxide as an oxidizer for hypergolic compositions

Hydrogen peroxide of propulsion grade has a significant heritage of long term safe production and successful use for power and various propulsive purposes [2]. The medium, often denoted as HTP – High Test Peroxide (in the USA also known as Rocket Grade Hydrogen Peroxide – RGHP), still offers some excellent and unique opportunities [13]. First of all it is an environmentally and personnel friendly, non-cryogenic and almost non-volatile strong, liquid rocket oxidiser that is only second to liquid oxygen (LOX). Besides, the substance is characterised by greatly reduced toxicity, low storage and handling costs and relatively simple thruster and engine designs [10].

Hydrogen peroxide was discovered nearly two hundred years ago but its special properties - especially those exhibited by its concentrated states - started to be utilised just before World War II by German researchers [14]. At that time it was also reported as the first monopropellant – utilised for air-independent propulsion systems in Germany since the middle of the 1930’s [14]. During World War II the compound gained even more significant applications, especially in the form of more concentrated and relatively pure solutions, which would now be known as HTP grade. The Germans were able to obtain fairly pure solutions of up to 85% by weight using vacuum fractional distillation techniques. The solutions were used as working fluids for steam generators and turbo-pump driving systems in such famous applications as the first rocket ballistic missile V-2 (A4). In 1935 Hellmuth Walter was the first to set up his own company (named as Walterwerke) in Kiel to produce 80% hydrogen peroxide stabilised solutions and sell them mostly for propulsive applications [15]. The solutions were known at that time in Germany as T-Stoff or T-substance. One of the first applications was its use in the Heinkel aircraft He176 - the first aircraft to be propelled solely by a liquid rocket engine [16]. The first successful experiments with hypergolic propellants were also performed by Germany during World War II [17]. The most
successful propellants at that time were used in the world’s first rocket-powered aircraft fighter, the famous Messerschmitt Me-163 [18]. The post-World War II period was the most prolific for concentrated hydrogen peroxide production as its intensive development as a main rocket propellant began. In fact, the large scale utilisation of hydrogen peroxide of rocket class as a propellant in the US had begun in the mid-1940s, with the seizure of German hydrogen peroxide propulsion technology [19]. After the Second World War, new concepts for hydrogen peroxide utilization were invented and developed. The medium was the first propellant used in the monopropellant thrusters for attitude control systems not only on satellite platforms but also on experimental aircraft and furthermore, for launchers. HTP was then used in many US military projects, such as X-1, X-15, Mercury, Redstone, Centaur, Scout, SATAR, COMSAT, SynCom, and a few more – mostly as a monopropellant for attitude controls. The hypersonic rocket-powered aircraft X-15, Scout missile, Centaur missile and Mercury capsule spacecraft utilised 90% hydrogen peroxide decomposed by a heterogeneous catalyst - usually a pack of silver plated 20 mesh brass or nickel screens [18, 20].

A significant amount of work with hydrogen peroxide was also done in England during the years after World War II, with improvements in its stability, through the use of appropriate stabilising agents and improved purification methods during production. For this reason hydrogen peroxide became the primary monopropellant and rocket oxidiser in the UK and was used for underwater propulsion, aerospace propulsion, space launchers and auxiliary power units [16, 18].

Research activity in the recent decade has shown that hydrogen peroxide concentrated up to 98% is still an attractive oxidizer for rocket propulsion systems. A lot of laboratory scale thrusters have been tested, also in self-igniting mode. Due to the nature of HTP, its acidity, the potential fuels should be strong bases. Moreover, hypergolic fuels with HTP are classified in two groups, catalytically promoted or energetically. The special additives, such as hydrides or metal salts, mixed with chosen fuels, such as amines or alcohols, can cause hypergolic ignition with IDT (ignition delay time) even below 3 ms, with an Isp greater than 320 sec. For example, the IDT for MMH-NTO is about 2 ms. This shows that the new investigated compositions of propellants based on HTP have great potential to be replacements for toxic and dangerous hydrazine derivatives. For this reason the potential hazardous incidents or catastrophic accidents when using low toxic hypergolic propellants based on HTP, should be assessed using methods and procedures to prevent them.

3. Key findings from the literature review

Hydrogen peroxide, as a rocket oxidiser, is still not typically recognised as a hypergol, and is mostly utilised via its catalytic decomposition. Therefore, early studies with peroxide as a hypergol still require some kind of hazard assessment. Moreover, hydrogen peroxide as a hypergol is still in the research phase than in real applications, and it is necessary to make definitive statements about some safety procedures. Therefore, the paper presents some basic examples and guidelines for determining if a particular hazard may exist and when.

Specific hazards related to hydrogen peroxide as a hypergol are presented only in general terms in the form of corresponding accidents and their effects. Some findings, e.g. concerning personnel and the environmental toxicity hazards of hydrogen peroxide have been omitted. Based upon the review of the available literature of the last two decades, the authors noticed that accidents with hypergolic propellants based on hydrogen peroxide were not registered or at least not publicly revealed. Probably this is mainly due to the long experience gained, with the prior application of hydrazine and its derivatives in space propulsion systems. The only accidents that are described in the reports concern leakages, spills and errors made with construction materials used for tanks, seals and valves [21]. Nonetheless, all these accidents led to serious damage of test sites and personnel injuries [21]. Due to the lack of literature information of any confirmed accidents involving the handling of “green” hypergolic propellants, the review includes events concerning toxic hypergols. The long-term legacy of handling hypergolic liquids in the form of safety procedures, hardware requirements, monitoring systems or rescue and decontamination methods, can be transferred to the newly developed hypergolic fuels with 98% HTP. The literature review shows that available and reliable sources describing dangerous events with hypergolic
propellants come mainly from relevant U.S. reports. However, toxic hypergols have also been widely used in Europe, Russia, Ukraine and China since the 1960s [17]. Nevertheless, any detailed information or reports related to accidents with hypergolic liquids from some of these countries is, realistically, not available in open literature sources.

Typical incidents and accidents involving the use of traditional hypergolic propellants (fuels and oxidisers) are mainly connected to leakages and spills during storage (can cause fires or poisonings) and transportation or more commonly during testing campaigns (transfer operations) [22]. This is mostly due to the fact that typical hypergolic propellants (especially oxidisers) are very volatile and corrosive fluids. Moreover, the oxides of nitrogen exhibit additional and unique properties which may cause extra potential hazards. For example, the vapours of nitrogen tetroxide (which is in a liquid in equilibrium with nitrogen dioxide vapour) are approximately three times heavier than air and immediately fill out any available volume (shown on Fig. 1). Besides, liquid nitrogen tetroxide evaporates about five times faster than water at ambient conditions which means that the medium is very volatile [23].

Figure 1. Nitrogen tetroxide in equilibrium with nitrogen dioxide vapour at room temperature

As was noted earlier, currently utilised hypergolic propellants were introduced at the beginning of the 1950s by both the United States and the Soviet Union. Therefore, it can be said that state-of-the-art bi-propellant rocket hypergolic technology has been in existence for nearly sixty years. This is quite unusual in the aeronautical industry, especially taking into account the nature of the propellants being considered here. The toxicity and corrosivity may be what generates much of the costs associated with handling and transportation, another may be the potential explosivity of these fluids. The U.S. Bureau of Mines, during the Apollo program, examined the explosivity of residues of MMH and NTO (nitrogen tetroxide) using ballistic mortar and other tests [24]. They also performed some tests in low-thrust engines prior to ignition. They found that frozen hydrazine, monomethyl hydrazine, (UDMH), and Aerozine-50 (a 50/50 mix by weight of hydrazine and UDMH) mixed with NTO at liquid nitrogen temperature, exhibited a violent exothermic reaction upon warming between -50°C and 70°C, depending on the fuel used. The Aerozine-50 and NTO mixtures always yielded a detonative reaction; the other mixtures exhibiting less violent reactions. Hydrazine exhibited an explosive reaction having a TNT equivalence of about 130% when explosively fired in atmospheres of air, oxygen, or NTO. Stoichiometric mixtures of the various liquid fuels and liquid NTO indicated TNT equivalences of about 160% in all cases [24].

The most tragic and also the largest catastrophe in the history of rocketry, occurred in the former Soviet Union in October of 1960 and is connected to the explosive properties of the traditional hypergolic mixtures [25]. It was the R-16 ballistic missile disaster in which dozens of people were killed as a result of a vast explosion of hypergolic propellant - unsymmetrical dimethyl hydrazine as the fuel and inhibited red fuming nitric acid
(IFRNA) as the oxidiser. The immediate cause of the catastrophe was a failure in the electrical system of the engine. However, the underlying issues also included the number of unauthorised people close to the launch pad during final technical operations. Other safety procedures were also ignored or did not exist at the time. Other factors behind the catastrophic event were: poor documentation and design, as well as rushed development and design-verification test flight. Moreover, the most common sense safety practices were ignored, such as soldering on a fully fuelled rocket.

Hydrazine and its derivatives are classified as possible carcinogens [11]. Additionally, these are very flammable liquids – hydrazine may even ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as rust, wood or soil [22]. It will explode when in contact with concentrated hydrogen peroxide or nitric acid. One of the best known accidents involving hydrazine derivative and hydrogen peroxide is a case when a chemist was killed when he inadvertently poured concentrated hydrogen peroxide into a laboratory sink [26]. The hydrogen peroxide reacted violently with some UDMH remaining in the trap and the trap exploded. However, no other details were reported on this case.

The period when hypergolic propellants were introduced (1950s and the beginning of 1960s) is characterised by a relatively large number of various incidents and accidents. One reason is the fact that the technology of hypergolic propellants was quite immature at that time. Experience was gained through mishaps, unlike in the case of monopropellant where the general safety practices were created with hydrogen peroxide, beginning in the 1940s.

4. Main hazards and risks

The main hazards and risks which have been considered by the authors are derived from the literature review of toxic propellants and the authors’ experience in preparation, handling and storage of novel “green” hypergolic liquids. The potential hazards related to the handling and utilization of hypergolic propellants with 98% HTP as an oxidizer are the sum of hazards derived from handling, storage and transportation of hydrogen peroxide and chosen fuel compositions. Moreover, hazards and risks of the overall combination of the liquids ie oxidiser and fuel should be assessed, taking into account possible phase changes.

The typical and most frequent risks are spills and leakages. According to NASA [22], such incidents are due to human error and through the use of incompatible materials for storage of hydrazine and its derivatives and dinitrogen tetroxide. It was observed that leakages have occurred due to long term material corrosion at changing temperature conditions, often accelerating this process. Likewise, such accidents are very possible when using 98% hydrogen peroxide. Spills or leakages can be catastrophic, especially if HTP has contact with strong catalysts such as manganese oxides, silver, cooper, iron, cobalt and other metal salts, or reducing agents like hydrides or metal hydrides. Moreover, HTP in contact with organic materials like leather can also be decomposed, liberating high temperature gases which can ignite fuels or other materials, for example clothing (Fig. 2).

![Figure 2. Ignition of leather exposed to direct contact with 98% hydrogen peroxide](image)
Other risks are related to human injuries by direct contact with HTP due to the spills on skin, eyes or due to the mistakenly drinking it. Nonetheless, using special protective equipment such as gloves, glasses or overalls can significantly decrease such risk.

In the case of fuels, the main hazards and risks are related predominantly to the acute toxicity described by LD50 oral or dermal and by LC50 indicators. It is important to develop fuels with higher values of these indicators. Unlike spills or leakages which can be rapidly detected, the vapours of highly volatile fuels are rather difficult or impossible to detect by observation. For these reasons new hypergolic fuels should be storable as toxic hypergols. Fuels that are known to be hypergolic with HTP usually belong to hydrocarbons, amines, alcohols, aldehydes, ethers or glycol ethers. Most of them, at least those presented in literature [2-12], are amines such as ethanolamine (MEA), diethylhydroxylamine (DETA), diethylenetriamine (DETA), pyridine or triethylamine (TEA). Although less toxic than hydrazine and its derivatives, they still have a toxicological effect on humans in the event of direct contact with them in their liquid phase or with their vapours. Although some of them are 4 category in LD50 oral and dermal, they can be deadly through inhalation. For this reason it is important to analyse, in detail, their MSDS (material safety data sheet) applying it to the safety documentation. The typical hazards and risks related to utilization of both HTP and new compositions of hypergolic fuels, with a description of preventative measures are detailed in Table 1.

![Image](image1.png)

**Figure 3.** The effect of ignition drop tests with 15% (left) and 4% propargyl alcohol-catalyst mixture

The oxidative nature of concentrated solutions of hydrogen peroxide must be taken into account when handling this substance during hypergolic ignition tests. Fires can be started easily by contacting combustible materials with peroxide solutions stronger than about 70% by weight, provided that the proper catalyst is present. However, spilled 98% hydrogen peroxide may be initially harmful to the staff or environment, but is rapidly decomposed to environmentally friendly water and oxygen, especially after diluting with excessive amounts of tap water. What is more, diluted solutions of hydrogen peroxide have been successfully used as a supplementary oxygen source in the bioremediation of hydrocarbon fuel-contaminated soils [27]. Therefore, handling 98% hydrogen peroxide requires only basic means of personal protection, as the medium is more irritating and slightly corrosive than toxic. Besides it is characterised by a low vapour pressure and a high density and boiling point. The situation changes significantly when handling typical hypergolics as hydrazine derivatives and NTO. Liquid nitrogen tetroxide and its vapours can explode on contact with hydrazine or its derivatives, as well as with amines or alcohols [23]. Besides, NTO as a chemical substance is a strong oxidiser and reacts violently with many combustible and reducing materials. It reacts with water to produce nitric acid and nitric oxide and attacks many metals in the presence of water. Therefore, staff must wear special protective equipment as it can be absorbed into the body by inhalation with harmful concentrations of the vapour in air being reached very quickly. Hydrogen peroxide has a very low vapour pressure and as such it is more safe in handling than hydrazine and its derivatives. On the other hand, its low vapour pressure makes it more demanding regarding the hypergolic ignition in a rocket engine.
Table 1. Types of possible hazards with description and possible protection methods (authors)

<table>
<thead>
<tr>
<th>Risks</th>
<th>Hazards</th>
<th>Protection and Prevention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncontrolled ignition/decomposition or detonation</td>
<td>Incidents during fuel preparation (the additives should be added to fuels, not the other way round). Spills of HTP on catalytic materials. High sensitivity on organic or inorganic contamination leading to exothermic decomposition or even ignition with air. Accumulation of fuel vapours at the top of the storage/service room. Electrostatic sparks. New fuels mixed with energetic additives can react vigorously with oxidizers, even leading to detonation (Fig. 3). Chemically unstable mixtures for long term storage.</td>
<td>Operating with small samples under fume hood. Using protective and fire extinguish equipment. Maintaining high level of cleanliness of work spaces. Using cleaned or specially passivated vessels, tanks or other laboratory equipment which are in contact with medium. Storing and handling propellants in ventilated rooms. Using special sensors for vapour detection. Using non-sparking electrical devices. Electrically grounded and antistatic floor.</td>
</tr>
<tr>
<td>Poisoning or injuring to technical staff, operators or human crew</td>
<td>Technical staff operations without personal protective equipment. Low LD50 and LC50 of chosen fuel composition. High volatility and low relative gaseous density of fuels.</td>
<td>Using personal protective equipment such as gloves, glasses, suits and masks with active absorber. Working in ventilated rooms.</td>
</tr>
<tr>
<td>Contamination of external environment</td>
<td>Long biodegraded liquids with high bioaccumulation, toxic for animals and plants. Uncontrolled spills to groundwater. Toxic clouds of high volatile liquids.</td>
<td>Using special materials for fast and safe decontamination. Operating in specially protected rooms or laboratories. Storing of special containers in protected and isolated warehouse.</td>
</tr>
<tr>
<td>Surface corrosion</td>
<td>High chemical activity with construction metals such as stainless steel, alumina alloy, cooper, Inconel, titanium, etc.</td>
<td>Using long term compatible materials, special protective layers with elastomers (PTFE, PE, PP).</td>
</tr>
</tbody>
</table>
5. Conclusions

The development of a novel class of low toxicity fuels which may be used together with 98% hydrogen peroxide has created a new class of hypergolic propellants of increased safety. This is particularly true in terms of their lowered toxicity and corrosivity compared with the currently utilised. Bi-propellant hypergolic systems, based on 98% hydrogen peroxide as oxidiser, produce more environmentally friendly exhaust products, and the propellants themselves pose a greatly reduced threat to staff as is virtually non-toxic. Therefore, 98% hydrogen peroxide is the primary oxidizer being explored as the hypergolic alternative to hydrazine-based propellants. However, for maximum performance, a relevant fuel which is supposed to be ignited on contact with 98% hydrogen peroxide should be promoted by the appropriate additives to ensure low ignition delay time. Additionally, one has to bear in mind that the oxidiser is a kind of high energy material that has a strong tendency towards catalytic decomposition and formation of sensitive, explosive mixtures with some organics (potential fuels).

References


Received: May 18, 2017
Revised: December 20, 2017
Published: December 28, 2017