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THE HANDLING HAZARDS OF PROPELLANTS HYPERGOLIC WITH HYDROGEN PEROXIDE

ASPEKTY BEZPIECZEŃSTWA MATERIAŁÓW PĘDNYCH HIPERGOLICZNYCH Z NADTLENKIEM WODORU

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The hazards and risks related to the handling, transportation and storage of hypergolic propellants based on highly concentrated hydrogen peroxide as an oxidiser have been analysed and discussed in the paper. The main focus have been placed on the assessment of all possible hazards and prevention methods for the protection of technical staff and hardware due to the fast development of new green hypergolic propellants with 98% hydrogen peroxide. The basic risks connected with the use of incompatible materials, human errors or propellant properties have been described. The dangerous incidents or even catastrophic accidents hitherto known with hypergolic propellants are related mainly to the toxic compounds based on the hydrazine derivatives and dinitrogen tetroxide. The conclusions and remarks derived from the available literature have been discussed and transferred into a kind of handling procedures for green hypergols. Therefore, the data, comparison to existing literature and authors' experience presented in this paper try to illustrate what may, and sometimes have to be done, during various research operations in the laboratory environment when working with rocket hypergolic propellants. There are many ways to prevent unwanted events but implementing some of them is necessary in order to avoid or mitigate possible unforeseen technical problems, incidents or even accidents. Some of the most important factors for risk minimization when working with 98% hydrogen peroxide and hypergolic fuels have been presented.

Keywords: hydrogen peroxide, HTP, hypergolicity, ignition, propulsion, oxidiser

Słowa kluczowe: nadtlenek wodoru, HTP, hipergoliczność, zapłon, napęd, utleniacz

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 period of two decades after the World War II [1]. However,

hydrogen peroxide used as a rocket oxidiser for previously developed propulsion systems, always needed to be decomposed by a suitable catalyst bed prior to its exhaust products could be used for obtaining combustion with a chosen fuel [2]. Recent research activities conducted mainly by Rusek et al. [3], Pourpoint et al. [4], Gostowski [5], Ulas et al. [6], Melof et al. [7], Sippel et al. [8], Yuan et al. [9], Kang et al. [10] and the authors [11] [12] have shown that high performance and hypergolic fuels with highly concentrated hydrogen peroxide can be developed and then successfully applied in the laboratory scale bipropellant test rocket engines.

In order to achieve a direct ignition and then combustion of 98% hydrogen peroxide with a chosen fuel, the activation energy of such composition has to be significantly decreased. Then, the hypergolic phenomenon of such propellant composition creates the opportunity of its application in the rocket and space propulsion systems.

Currently utilised hypergolic propellants are very toxic fluids that react spontaneously and vigorously when they directly contact each other. Therefore, the alternative, less or even non-toxic hypergolic propellants to be used with 98% hydrogen peroxide, are under intensive development at the Institute of Aviation. Although hypergolic propellants are intended to be storable and stable (e.g. as a couple: a selected fuel and 98% hydrogen peroxide), they still may be very hazardous, taking into account their chemical nature (98% hydrogen peroxide is a kind of high energy material). Unlike the currently used toxic hypergols the new combinations of hypergolic fuels with highly concentrated hydrogen peroxide can additionally seriously reduce the costs and risks related to the safety and services procedures on the ground segment. Generally, the greatest operational risk is connected to possible human errors, hardware and material failures or still unknown reactivity of some fuels with 98% hydrogen peroxide.

Hydrogen peroxide of propulsion grade has a significant heritage of the long term of 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 next after liquid oxygen (LOX). Besides, the substance is characterised by greatly reduced toxicity, low storage and handling costs and relatively simple thruster or engine design [10].

Hydrogen peroxide was discovered nearly two hundred years ago but its special properties - especially exhibited by its concentrated solutions - have started being utilised in practice just before the World War II by German researchers [14]. At that time it also has been reported as the first monopropellant – utilised for air-independent propulsion systems in Germany since the middle of 1930's [14]. During World War II the compound gained even more significant applications, especially in the form of more concentrated and relatively quite pure solutions, that may be called now as HTP grade. The Germans were able to obtain fairly clean solutions of up to 85% by weight by the vacuum fractional distillation techniques. The solutions were then used as working fluids for steam generation and turbo-pump driving systems in such famous application as in the first rocket ballistic missile V-2 (A4). In 1935 Hellmuth Walter was the first one who 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-substance or T-Stoff. One of the first application of that medium was its use in the Heinkel aircraft He176 - the aircraft to be propelled solely by a liquid rocket engine [16]. The first successful experiments with hypergolic propellants were also performed by Germans during the World War II [17]. The most successful propellants at that time were used in the first world rocket-powered aircraft fighter, the famous Messerschmitt Me-163 [18].

The post World War II period was the most profitable for concentrated hydrogen peroxide as its intensive development as the 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-1940's, with the seizure of German hydrogen peroxide propulsion technology [19]. After the Second World War the new concepts for hydrogen peroxide utilization were invented and further developed. It is worth to note that the medium was the first propellant used in the monopropellant thrusters for attitude control systems not only on satellite platforms but also on experimental aircrafts and further for launchers. Hydrogen peroxide of HTP class 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 monopropellant for attitude controls. The hypersonic rocket-powered aircraft X-15, Scout missile, Centaur missile and Mercury capsule spacecraft utilised 90% hydrogen peroxide that was decomposed by 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 done also in England during the years after World War II, altogether with improvements in its stability, through the use of appropriate stabilisation agents and increased purification methods during production. For this reason also in the UK hydrogen peroxide became the primary monopropellant and rocket oxidiser that was used for underwater propulsion, aerospace propulsion, space launchers and auxiliary power units [16] [18].

KEY FINDINGS FROM THE LITERATURE REVIEW

Based upon the review of the available literature for the last two decades, the authors have noticed that accidents with hypergolic propellants based on the hydrogen peroxide were not registered or at least are not so far publicly revealed. Probably it is mainly due to the long experience gained before, connected to the prior application of hydrazine and their derivatives in space propulsion systems. The only accidents that are described in available reports concern leakages, spills and errors made with construction materials used for tanks, seals and valves and concerns the WWII period [21]. Nonetheless, all of these accidents led to serious damages of the test sites and even personnel injuries happened [21]. Due to the lack of literature information on any confirmed accidents involving the handling of green hypergolic propellants, the literature review presented in this paper includes events concerning toxic hypergols. The long term of heritage in handling of toxic hypergolic liquids in form of safety procedures, hardware requirements, monitoring systems or rescue and decontamination methods can be successfully transferred to the newly developed hypergolic fuels with 98% HTP.

Therefore, according to the literature review, the available and reliable sources describing dangerous events with hypergolic propellants come mainly from the relevant U.S. reports. However, the toxic hypergols have also been widely used in Europe, Russia, Ukraine and China since the 1960's [17]. Nonetheless, any detailed information or reports related to the accidents with hypergolic liquids from some of the countries are practically not available in open literature sources.

Typical incidents and accidents involving the use of traditional hypergolic propellants (fuels and oxidisers) from the past are mainly connected to the leakages and spills during the storage (danger and can cause fires or poisonings) and transportation or more commonly to the ground testing campaigns (transfer operations) rather than improper handling [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 several additional and quite unique properties that may cause extra potential hazard. For example, the vapours of nitrogen tetroxide (which is in a liquid in equilibrium with nitrogen dioxide vapour which) are approximately three times heavier than air and immediately fill out any available volume (Fig. 1). Besides, liquid nitrogen tetroxide evaporates about five times faster than water at room temperature [23].

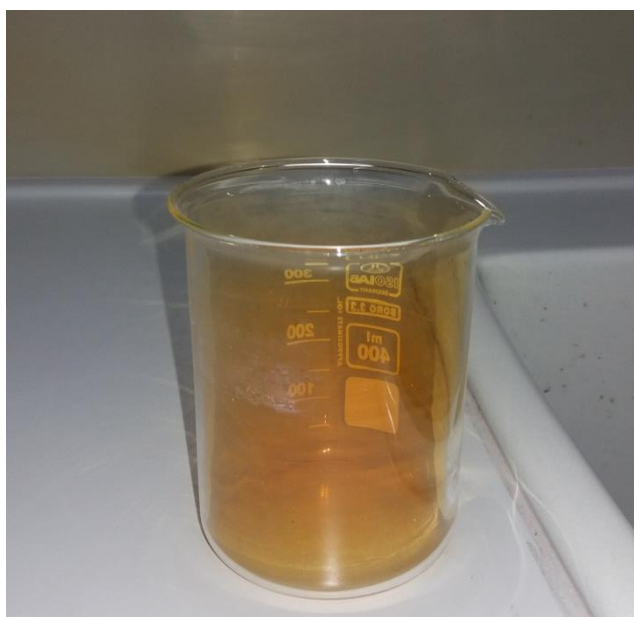


Figure 1. Nitrogen tetroxide in equilibrium with nitrogen dioxide vapour at room temperature (authors)

As it was noticed above, currently utilised hypergolic propellants were introduced in the beginning of the 1950's, both, by the United States and the Soviets. Therefore, it may be stated that the state-of-the-art in bi-propellant rocket hypergolic technology has been in use for nearly sixty years! This is quite unusual case in the aeronautical industry, especially taking into account the nature of the propellants being considered here! The toxicity and corrosivity may be one problem that generates a lot of costs connected to the handling and transportation issues, another one may be potential explosivity of these fluids. The U.S. Bureau of Mines, during the Apollo program, examined the explosivity of residues of MMH (monomethyl hydrazine) 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, unsymmetrical dimethylhydrazine (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 detonation like reaction; the other mixtures exhibited 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 due to the vast explosion of the hypergolic propellants - unsymmetrical dimethyl hydrazine as a fuel and inhibited red fuming nitric acid (IFRNA) as the oxidiser. The proximate cause of the catastrophe was the failure in the electrical system of the engine. However, the underlying issues also involved the numerous unauthorised people close to the launch pad during final technical operations! Besides, the other safety procedures were also ignored or did not exist at that time. Other factors behind that catastrophic event are: poor documentation and design as well as rushed development and design-verification test flight. Moreover, the most common sense safety procedures were also violated, 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 most 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 underneath the sink and the trap exploded. However, no other details were reported on this case.

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 supposed to be assessed to the overall combination of the liquids (as oxidizer and fuel) and with taking into account their possible phase transition into vapours.

Table 1. Types of possible hazards with description and possible protection methods (authors)

Types of possible hazards and risks		
Hazards and Risks	Description	Protection and Prevention
Spills and leakages	Incidents during laboratory tests. Spills made by human mistakes. Spills during filling up of oxidizer and fuel tanks.	Special procedures, stable and mechanically resistive laboratory materials, operation under certified fume hoods
Uncontrolled ignition/decomposition	Incidents during preparation/mixing additives with chosen fuels.	Operations with small samples under fume hoods, usage of basic protective equipment, fire extinguish equipment
Poisoning of technical staff, operators or human crew	Technical staff operations without special protective equipment. High LD50 and LC50 of chosen fuel composition.	Application of special protective equipment such as gloves, glasses, suits and masks.
Contamination of external environment	Long biodegraded liquids, toxic for animals and plants, creation of toxic clouds	Usage of special materials for decontamination
Fuel sensitivity on contamination	High sensitivity on organic or inorganic contamination led to exothermic decomposition or even ignition with air.	Maintaining high purity of laboratories and preparation rooms, usage of cleaned or specially passivated vessels, tanks or other laboratory materials.
Oxidiser corrosivity with typical construction materials	High chemical activity with construction metals such as stainless steel, alumina alloy, cooper, Inconel, titanium, etc.	Compatibility tests, usage of long term compatible materials, special protective layers, special elastomers (PTFE, PE, PP)
Oxidiser low energy activation - decomposition, ignition	High activity on contact with impurities. High activity on mechanical disturbances.	Usage of special stabilizers, usage of special vessels and tanks, special storage and transportation conditions
Accumulation of fuel vapours at the top of the storage/service rooms	Liquids with high vapour pressure and gases lighter than air can create vapours at top of the storage/service room. High risk due to ignition by the electrostatic sparks.	Storage and handling propellants in ventilated rooms. Usage of special sensors. Usage of non-sparking electrical devices. Grounded and antistatic floor and other elements.
Uncontrolled and unstable combustion led to detonation	Unknown behaviour of new fuel compounds with energetic additives in some cases can lead to explosion or even detonation.	Experiments with small amount of hypergolic liquids. Usage of special shields and fume hood.
Incompatibility of seal materials for long term storage	Lack of information about long term compatibility may lead to leakage or spills during storage or test site operations.	Performing long term compatibility tests with special sealing materials or usage of proved/certified seals with chosen liquids.
Incompatible protective equipment and handling materials	Usage of incompatible protective equipment and handling materials with chosen oxidiser and fuel compounds can lead to self-ignition or dangerous human injuries.	Usage of special protective equipment if necessary according to MSDS or producer instructions.
Chemically unstable liquids and compositions	Some fuel compositions can be unstable and after some time; can decompose or degrade losing hypergolic properties with 98% HTP.	Usage of special containers or tanks for storage. Containers or tanks should be passivated and stored in special conditions (e.g. under low temperature)

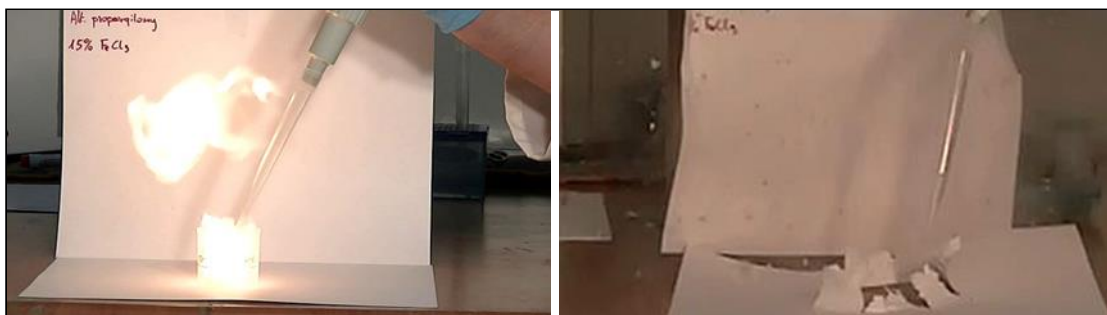


Figure 2. The effect of ignition drop tests with 15% (left) and 4% propargyl alcohol-catalyst mixture (authors)

The oxidative nature of concentrated solutions of hydrogen peroxide must be taken into account when handling this substance during hypergolic ignition tests. Therefore, fires may be started quite easily by dampening combustible materials with contact 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 it with excessive amounts of tap water. What 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 low vapour pressure and quite high density and boiling point.

The situation changes significantly when handling typical hypergolics - as hydrazine derivatives and NTO. Liquid nitrogen tetroxide and its vapours will 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. Reacts with water to produce nitric acid and nitric oxide. Attacks many metals in the presence of water. Therefore, the staff must wear special protective equipment as it can be absorbed into the body by inhalation and in accidental situations a harmful concentration of this vapour in the air may be reached very quickly.

CONCLUSIONS

The development of a novel class of low toxicity fuels that may be used together with 98% hydrogen peroxide creates a new class of hypergolic propellants of increased safety in terms of their toxicity and corrosivity. Bi-propellant hypergolic systems based on 98% hydrogen peroxide as oxidiser produce more environmentally friendly exhaust

products, and the propellants by itself pose greatly reduced threat to the staff. Therefore, 98% hydrogen peroxide is the primary oxidizer being explored as the hypergolic alternatives 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.

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