

NOVEL LIQUID COMPOUNDS AS HYPERGOLIC PROPELLANTS WITH HTP

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Abstract

The paper presents both an experimental investigation and an up-to-date literature review over the hypergolicity of highly concentrated hydrogen peroxide with various liquid mixtures or novel chemical compounds that may be a potential candidate for rocket applications. Moreover, the coverage contains both, a historical and modern approach to hydrogen peroxide based hypergolic propulsion systems. In addition, the advantages of the oxidizer, especially in the form of 98% solution of hydrogen peroxide, are profiled in detail against the toxic ones that are currently utilized. Equally, the potential replacements for hydrazine, monomethyl hydrazine, unsymmetrical dimethyl hydrazine, dinitrogen tetroxide or their combinations, as propellants in rocket applications, are collected and discussed thoroughly in terms of their propulsive performance, availability on the market, storability, handling and general safety conditions for the technical staff as well as environmental compatibility. The ignition mechanism of the two main fuel groups, catalytically and energetically promoted, that reveal fast, spontaneous ignition with the highly concentrated hydrogen peroxide, is described too. Furthermore, the example that results from the simple drop tests are shown with special focus laid on the comparison of the minimum ignition delay time as the key parameter for the discussed fuel compositions. Lastly, the most prospective fuel combinations are discussed as desirable alternatives for the near-future bipropellant propulsion systems for the rocket or satellite applications, or other that demand high energy density.

Keywords: 98% hydrogen peroxide, HTP, hypergolic ignition, propellant, rocket oxidizer

1. Introduction

Liquid rocket propellants have been used extensively for space and military applications for several decades now. Similarly, concentrated solutions of hydrogen peroxide are among the first rocket propellants that were used as both – monopropellants and oxidizers. Along with the rapid development of liquid rocket engines during the World War II, the idea of using the fuel and oxidizer that spontaneously ignite upon the contact had appeared. It was the beginning of the exploitation of hypergolic propellants – materials, which spontaneously self-ignite when, are in direct contact. Since the beginning, such propellants have turned out to be very advantageous for rockets and satellites – mostly due to the fact that they provided reliable and repeatable ignition without any additional source of energy or catalyst bed – the only thing that is required is a special procedure for opening/closing the valves to mix the fluids in the combustion chamber. Therefore, the propellants currently used in a vast number of satellite platforms that utilize bi-propulsion systems are hypergolic – the reaction can be initiated or terminated simply by opening or closing appropriate valves. However, the existing rocket engines used by spacecrafts mostly operate on very dangerous and volatile substances, and thus they are difficult and costly in storage and handling. Specifically among them hydrazine and its derivatives (such as monomethyl hydrazine, MMH) together with dinitrogen tetroxide (NTO) or mixed oxides of nitrogen (MON) present state-of-the-art fuels and oxidizers, being hypergolic and applicable for many satellite propulsion systems. Apart from their toxicity and corrosivity, these compounds exhibit excellent energy

performance, storability and ignition characteristics. Therefore, they have been utilized intensively for the last few decades. Nevertheless, there is currently a strong tendency to avoid or at least minimize the disadvantages of the above mentioned liquid hypergolic rocket propellants (considering health and environmental restrictions), and thus many new kinds of replacements have been proposed and investigated with hydrogen peroxide so far, including mixtures with strong reducing agents or so called ionic liquids. It is worth noting that highly concentrated hydrogen peroxide seems to be the most popular rocket oxidizer tested with the new hypergolic fuel formulations that currently are being developed by the researchers.

It is a rather well known fact for the aerospace community that concentrated hydrogen peroxide has a rather long history of applications in rocket propulsion and other power systems as monopropellants and/or as oxidizers with high density, storability, relatively low toxicity and ease of handling.

2. Oxidizer characterization

As previously indicated, 98% hydrogen peroxide solution is considered in this review as the oxidizer for novel hypergolic rocket fuel compounds or fuel mixtures. Actually, concentrated solutions of hydrogen peroxide are currently being thought of as the leading “green” rocket oxidizers. The Nazi Germans, as the first, successfully used them in such applications during the Second World War. However, since the Cold War, escalation started, together with the space race, new oxidizers and fuels with greater performance have been introduced. Although in the majority they have quite unique, but also toxic (e.g. NTO) and corrosive natures (e.g. RFNA – red fuming nitric acid or WFNA – white fuming nitric acid). In the late 1970’s, HTP (High Test Peroxide) was successfully used by the English Space Programme as rocket oxidizing agent in the Black Knight and Black Arrow launch vehicles that transported British satellites into LEO orbit.

The grade of 98% HTP, taking into account its performance, is the second – after liquid oxygen (LOX) – liquid rocket oxidizer. The important advantage is that it remains liquid at ambient pressure at the wide range of temperatures. It can be in a liquid phase even in relatively low temperatures (e.g. such as -40°C – being at an overcooled state). The higher the density of HTP as a propellant, the greater its propulsive efficiency (density specific impulse) is. Anhydrous hydrogen peroxide contains 47% of oxygen by weight. What is more, 2.8 MJ/kg of energy is released during the process of its decomposition into gaseous oxygen and water, and the volume expansion exceeds that of 4500. The decomposition process can occur in both, liquid and gaseous phase.

When 98% HTP is used as a monopropellant, it gives around 20% less performance than hydrazine. However, as a bi-propellant or in a hybrid configuration, its performance may be comparable to other liquid oxidizers such as NTO, RFNA or LOX. Volume specific impulse of 98% HTP is higher than most other propellants due to its high density (approximately 1.44 g/cm^3 at room temperature). Besides, due to low vapour pressure (about 2 mm of Hg at room temperature), the medium is relatively easy to handle – figure below (Fig. 1). A non-flammable and virtually non-toxic (but irritating) liquid easily acts as a powerful oxidizing agent and can cause spontaneous combustion when it comes in contact with many organic materials.

3. Fuels recognized as hypergolic with HTP

In accordance with Semenov theory from 1928 regarding mechanisms of hypergolic chain reactions, the ignition can occur when the heat generated by chemical reactions upon contact with a fuel and an oxidizer is higher than the heat lost to the surrounding media. In other words, such conditions enable ignition and then result in thermo-chemical sustainment of combustion. Nonetheless, this theory is limited only for vaporized propellant systems and does not consider highly energetic reactions in the liquid and liquid-gas phases. Moreover, some of the ignition



Fig. 1. Handling of 98% HTP in the laboratory (IoA)

reactions in liquid phase can be much faster than gaseous ones due to better contact on the molecular level. However, the accurate understanding of this phenomenon is not yet fully discovered and the whole practical model is not available today. It is still not clearly elucidated how the flame kernel is formed and which reactions play the main role in this phenomenon – as the ignition involves gaseous, liquid and gaseous-liquid phases. Therefore, the current methods used to research hypergolicity are based mainly on simple drop tests and more advanced impinging tests. Both of them are used to analyse, in detail, the physical and chemical delays and then optimize them. More advanced methods such as spectroscopy, allow the isolation of pre-ignition reactions and enable observation of the chemical nature of pre-ignition products. Other tests give the capability to determine physical transport properties such as heat and mass transfer.

The ignition delay time (IDT) as a parameter for the hypergolic propellants determination is of crucial importance. The author's experience shows that a given hypergolic fuel mixture may be reduced by increasing the hydrogen peroxide concentration or the initial ambient pressure. In addition, the IDT parameter is more sensitive to the initial temperature of fuel compound than the oxidizer. Another important question when considering hypergolic liquids is the fact that there are two main groups involved – catalytically and energetically promoted fuels with rocket grade hydrogen peroxide. This is due to the fact that the model of hypergolic ignition of catalytically promoted fuels with hydrogen peroxide is quite different from that of energetically promoted fuels. Of particular interest is the dissimilarity of those two fuel groups in terms of IDT value and performance.

Once the 98% HTP droplet comes into contact with the catalytically promoted fuel and intermingles enough with the fuel droplet, a process of hydrogen peroxide decomposition starts and the pre-ignition gases are released as the temperature rises. This process may be seen quite explicitly in the pictures taken by the high-speed camera HX-3 with 10 000 fps and shown in Fig. 2.

The heat released during the decomposition of HTP leads to fast vaporization of the fuel. Therefore, the fuel vapours and gaseous oxygen are mixed together and continuously heated further by the decomposition process. When the auto ignition temperature is reached, fast ignition is observed. It is a typical mechanism for the fuels promoted by the catalytic additives. Nonetheless, due to the complexity of this phenomenon, those sub-processes require more time to initiate ignition. As result, the ignition delay time of such fuel compositions is typically longer than 10 ms.

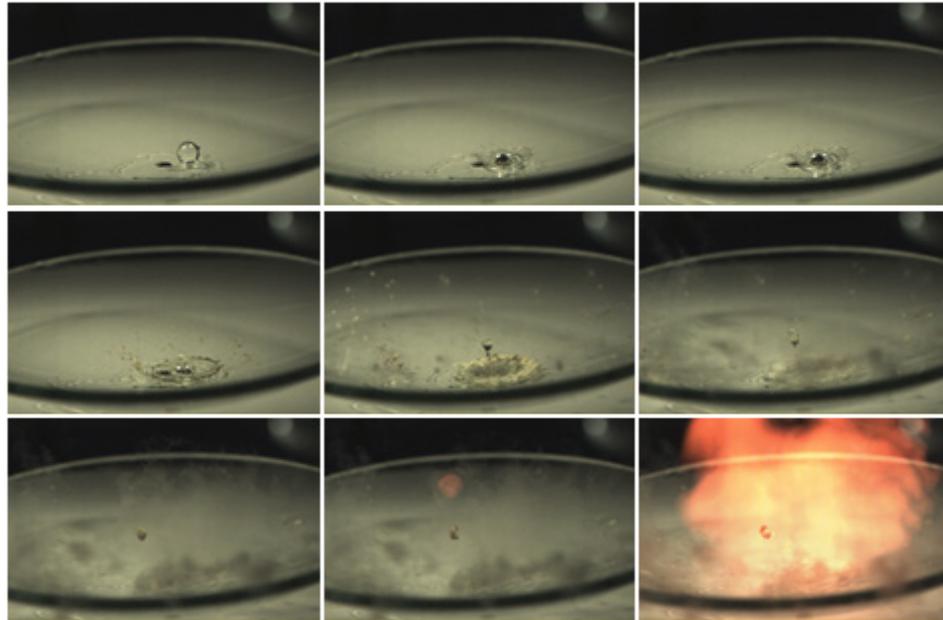


Fig. 2. The droplet test performed on catalytically promoted fuel with 98% hydrogen peroxide – the IDT=16 ms (IoA)

Tab. 1. Mixtures of fuels and additives being hypergolic with hydrogen peroxide

Fuel	Additives	HTP	IDT	Method of Experiment
Methanol	10% MAT	98%	30 ms	Drop Test
Methanol	30% MAT	98%	10 ms	Drop Test
Ethanolamine	5% CuCl ₂	85%	200 ms	Drop Test
Ethanolamine	10%CuCl ₂	85%	30 ms	Drop Test
Ethanolamine	10%CuCl ₂	85%	190 ms	Impinging Test
Ethanolamine ^{40degC}	10%CuCl ₂	85%	130 ms	Impinging Test
Kerosene	Metal Salts	98%	19 ms	Drop Test
dimethylhexolamine	C ₁₆ H ₃₀ CoO ₄	98%	12.7 ms	Drop Test
dimethylbutylamine	C ₁₆ H ₃₀ CoO ₄	98%	9.8 ms	Drop Test
Triglyme	8% H ₄ BNa	88.5%	10.6 ms	Drop Test
Tetraglyme	10% H ₄ BNa	88.5%	12 ms	Drop Test
Dimethyl Formamide	12% H ₄ BNa	88.5%	9.12 ms	Drop Test
Dimethyl Sulfoxide	10% H ₄ BNa	88.5%	14 ms	Drop Test
Triglyme	8% H ₄ BNa	88.5%	9 ms	Impinging Test
Dimethyl Formamide	12% H ₄ BNa	88.5%	7 ms	Impinging Test
Dimethyl Sulfoxide	10% H ₄ BNa	88.5%	7 ms	Impinging Test

The energetically promoted fuels are usually prepared by mixing a strong reducing agent (e.g. metal hydride or borohydride) with a base fuel (e.g. liquid amines, alcohols or ionic liquids). Such fuels exhibit substantially different pre-ignition mechanisms than catalytically promoted ones. Once a droplet of 98% hydrogen peroxide comes into contact with a drop of such fuel, it mixes and the reactions typically lead to spontaneous ignition that occurs in the liquid phase. Thereafter, a bright flash starts from the liquid phase, as it may be seen in the series of images shown in Fig. 3. The ignition mechanism is very different from catalytically promoted ones and seems to be more energetic. The ignition is initiated just above the liquid phase and HTP is not decomposed. The oxidizer directly reacts with the additive dissolved in the fuel, releasing a high amount of energy and some vapours of the fuel. The energy liberated during the ignition of inherently reactive fuels with hydrogen peroxide can be even eight times higher than in the case of catalytically promoted ones.

Tab. 2. The reactions and level of energy for catalytic and inherently reactive fuels with hydrogen peroxide

Reaction	Heat of Reaction
$\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) + 1/2\text{O}_2(\text{g})$	54 kJ/mol
$\text{H}_2\text{O}_2(\text{l}) + 1/4 \text{ metal hyd.}(\text{s}) \rightarrow 11/4 \text{ H}_2\text{O}(\text{g}) + 1/4 \text{ LiOH}(\text{s}) + 1/8 \text{ Al}_2\text{O}_3(\text{s})$	446.3 kJ/mol

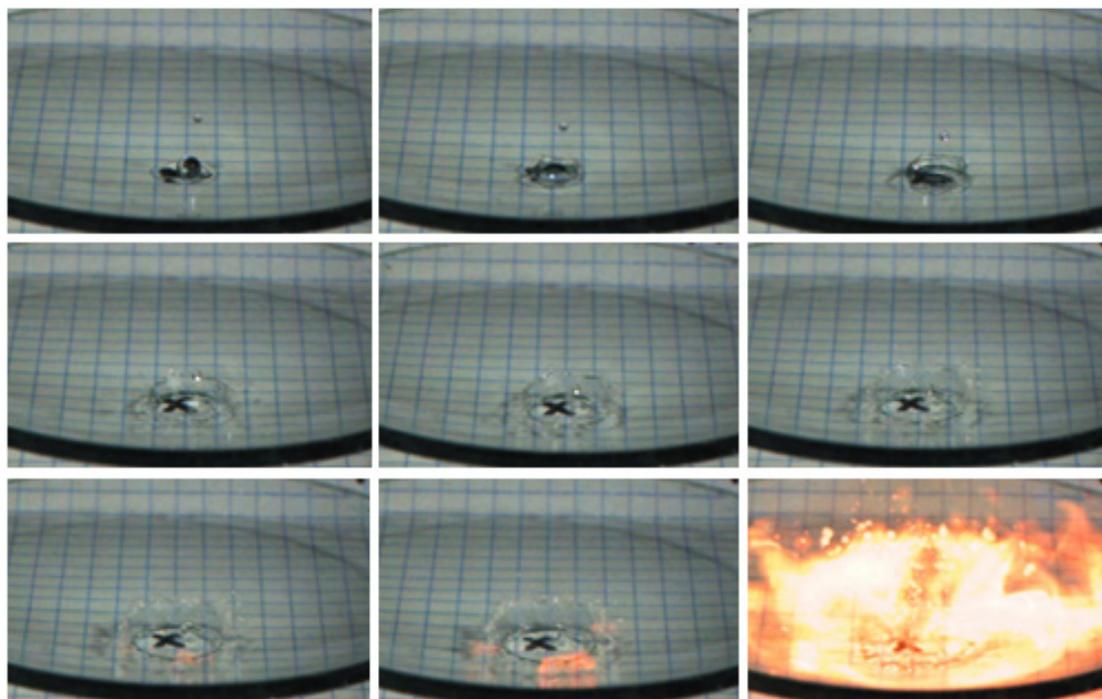


Fig. 3. The droplet test performed on energetically promoted fuel with 98% hydrogen peroxide, $\text{IDT}=3.4 \text{ ms}$ (IoA)

The process of ignition described above (of energetically promoted fuels) is very similar to the hypergolic ignition of the toxic propellant composition such as MMH with MON3. The ignition delay of such a propellant mixture is below 3 ms and is currently classified as state-of-the-art performance. The delay is also used as a reference value for the alternative future green hypergolic propellants. The propulsive performance, mainly density impulse, of some of the fuels included in this study is much higher than which occurs for a typical toxic composition of MMH-MON3. The performance of the latter couple is a typical reference value for the new alternative promising fuels. This parameter includes vacuum specific impulse and density. Additionally, it allows for the assessment of the usefulness of chosen fuels for future satellite or rocket applications. The higher the density is, the lower volumes of the tanks are and the lower the mass of the whole system is. The example results are shown in the Fig. 4.

4. Novel promising hypergols

There is a constant effort to find satisfactory fuels (as well as oxidizers) that would be suitable for the present and upcoming requirements of the aerospace industry. Therefore, many novel compounds systems are being considered and tested as potential hypergolic fuels with common rocket oxidizers, including HTP. It is worth notice here that for a long time hydrazine was the only fuel known as hypergolic with HTP. However, since the 1990, a wide variety of fuel compounds and mixtures have been tested with various oxidizers, including concentrated solutions of hydrogen peroxide. Nonetheless, compounds that are characterized by high melting points and rather narrow liquid range temperatures are not very promising. Contrarily, other features, such as relatively low toxicity, viscosity or corrosivity as well as high density or storability, are supposed to be considered during the preliminary selections.

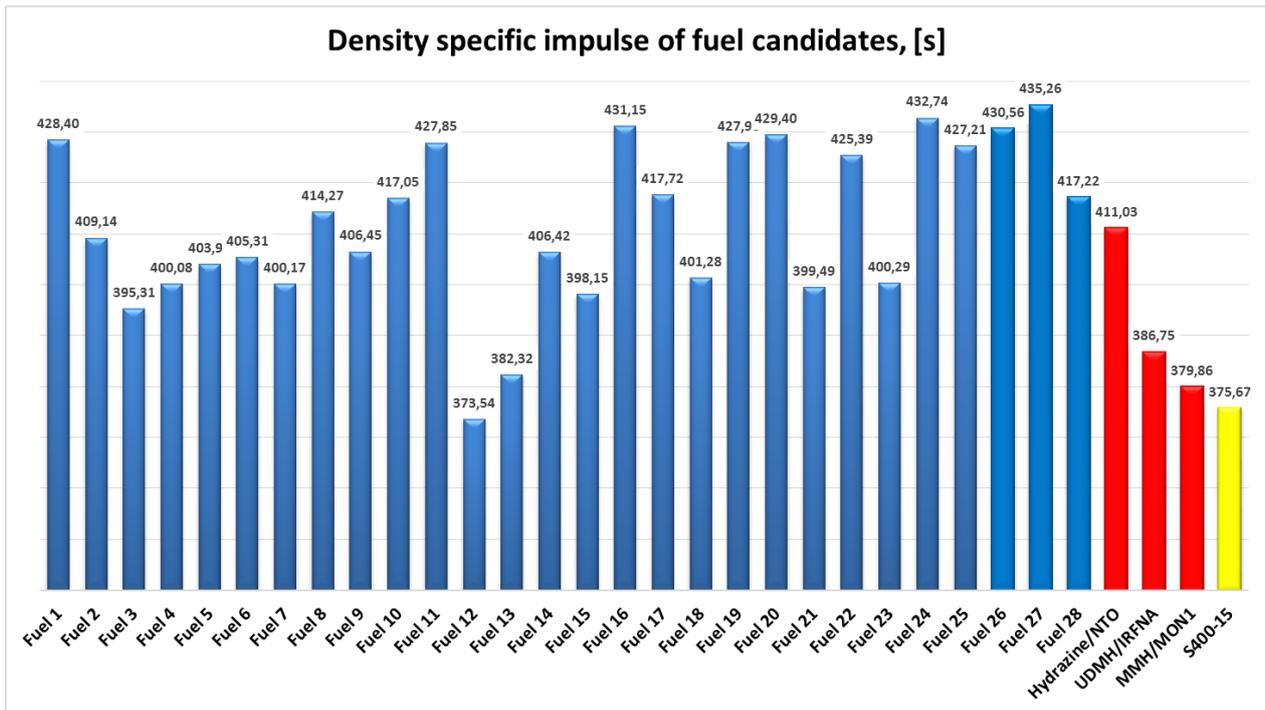


Fig. 4. The calculated density impulse of the fuel compositions based on amines, alcohols and some hydrocarbons

According to the relevant literature, ionic liquids (ILs), especially energetic ones, are now receiving increasing consideration to be potentially hypergolic with HTP rocket fuels. The ionic liquids, in compliance with the well-accepted definition, are chemical compounds of salts with melting points below 100°C. However, only a relatively small group of these compounds demonstrate hypergolic ignition with HTP. The most promising, and therefore being under intensive investigation, are specially tailored ILs that are additionally characterised by high energy densities. The intrinsic properties of some of the ILs qualify them as very promising hypergolic rocket propellants with reduced hazards connected to them in operations such as processing, services, handling or transportation. The most interesting ILs in this approach are those with low melting points, high thermal stabilities and high reactivity (hypergolicity) with HTP – such as borohydride rich formulations – are called hypergolic ionic liquids (HILs).

Generally, HTP, as an oxidizer, is extremely reactive and more easily decomposed than, for example, NTO or RFNA. It lacks the strong acidity. Most metals containing ILs have metal atoms that are completely coordinatively saturated. Such ILs will demonstrate rather weak reactivity with HTP without ignition. However, it is possible to introduce a component of the IL that is an unsaturated coordination compound of a transition metal like Fe, Mn, or Co – all of which catalyse the decomposition of hydrogen peroxide, either to O₂ and water, or to HO•. Another approach may be just dissolving a small concentration of one of these metal salts (perhaps as trifluoromethanesulfonate) in the IL. It would then serve as a catalyst to help initiate fast ignition. However, the ILs intrinsically hypergolic with HTP may be qualified as so-called reactive fuels – in contrast to the catalytically promoted ones. The latter group of fuels is generally made by the addition of a suitable amount of catalyst (e.g. soluble salt of transition metal) to the fuel.

The ILs often reported in literature as potentially hypergolic with HTP belong to the group where anions of these salts appear to play the major role in determining hypergolic properties. The anions of these salts include dicyanamide, dicyanoborate, cyanoborate, azide, nitrate, aluminum borohydride, nitrocyanoamide, etc. Organic cations are heterocyclic with ammonium like functional groups or HILs are hydride-rich bis (borano) hypophosphite-based compounds – typically, there are nitrogen-containing alkyls and aromatic species, e.g., substituted alkyl ammonium, imidazolium or propargyl.

In fact, sodium and potassium borohydrides (as the additives for reactive fuels) are hypergolic with HTP. Therefore, it may be presumed that the synthesis of borohydride ionic liquids should also result in hypergolic properties. The example of such HILs may be the group of tetrahydroborate compounds that already exhibit hypergolic ignition with WFNA.

5. Conclusions

The use of green propellants is a visible trend for near-future space or rocket propulsion systems. Many novel fuel-like liquid mixtures and chemical compounds, such as HILs, demonstrate rather great potential as green hypergolic rocket fuels to replace toxic hydrazine derivatives in rocket bipropellant propulsion systems. Unfortunately, there is rather sparse data in available literature concerning their hypergolicity with higher grades of HTP – as most experiments involve concentrated nitric acids (WFNA or RFNA). Despite this, a new family of fuels enriched with the addition of aluminium lithium hydrides, borohydrides, borohydride ionic liquids and borane compounds dissolved in some ionic liquids may meet nearly all of the desired criteria for hypergolic fuels with 98% solution of rocket grade hydrogen peroxide as oxidizers. This is due to the fact that they generally exhibit low ignition delay times and are characterised by high performance, relatively low toxicity (volatility) and corrosivity.

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