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## Explosives based on hydrogen peroxide - A historical review and novel applications

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**Abstract:** *Highly concentrated hydrogen peroxide solutions have been widely known and used as rocket mono-propellants and oxidisers in the aerospace industry. However, the use of hydrogen peroxide is becoming more and more important in other fields of modern industry – being applicable to novel formulations of base high explosives for use in mining as a kind of industrial “green explosive”.*

*The authors, explain the facts and dispel some of the myths concerning both the medium and the potentially explosive mixtures based on it. The method of preparation and safe handling of 98%+ hydrogen peroxide is briefly presented and advocated by some of the experimental and literature examples. The paper contains both historical and modern approaches to concentrated hydrogen peroxide based mixtures that have been reported as undergoing detonation. The safety concerns, especially those related to their potential explosiveness during preparation, handling or utilisation are analysed as well. New potential applications of hydrogen peroxide based mixtures that can be used as industrial explosives with low NO<sub>x</sub> emission levels are presented. The potential of the medium as a “green” and easy to handle oxidising compound that may replace ammonium nitrate in a variety of emulsion and blended ANFO-emulsion commercial explosives that currently constitute the majority of explosives used in the mining industry, is underlined.*

**Keywords:** *hydrogen peroxide, explosive, mining, green, mono-propellant, oxidiser, NO<sub>x</sub>*

### 1. Introduction

The high density, low vapour pressure and low toxicity of concentrated hydrogen peroxide, coupled with ease of handling, performance and versatility in use as a strong liquid oxidiser and monopropellant, means it is being more frequently utilised by the R&D rocket propulsion entities and relevant industry sectors. Concentrated solutions used as rocket oxidisers or monopropellants are typically produced by the additional step of vacuum fractional distillation or, in some cases, by fractional crystallization from preliminary concentrated (up to 90%) solutions. Moderately concentrated (usually up to 60%) industrial grades of hydrogen peroxide have been known and successfully utilised for decades and currently are the most versatile, safe and environmentally compatible oxidizing agents [1]. Similarly, propulsion grade hydrogen peroxide has a significant heritage of long term safe production and use for power and various propulsive purposes [2]. The medium, often termed High Test Peroxide (HTP) (in the USA also known as Rocket Grade Hydrogen Peroxide (RGHP)), continues to offer the aerospace community excellent opportunities. It is an environmentally and personnel friendly, non-cryogenic and almost non-volatile strong rocket oxidiser (compared to liquid oxygen) as well as being a monopropellant. It is characterised by greatly reduced toxicity, significantly lower storage and handling costs and relatively simple thruster or rocket motor design [3, 4].

Although hydrogen peroxide was discovered nearly two hundred years ago its special properties, present in concentrated solutions, started to be utilised just before World War II, by German researchers. The detonable properties of concentrated solutions of hydrogen peroxide were discovered at that time as well [5]. However,

as the pure compound (100% hydrogen peroxide) or in the form of concentrated water solutions, it cannot be classified as a liquid high explosive [5, 6]. This is due to the fact that the detonation of hydrogen peroxide needs to be considered as the processes that occur within three independent groups; as liquids, gases or two-phase phenomena [2]. This article deals mostly with liquid or liquid-solid mixture detonations of formulations based on hydrogen peroxide as the main oxidiser.

It is worth noting that other rocket liquid oxidisers, such as liquid oxygen or nitrogen tetroxide are capable of forming powerful explosives as well. However, explosives based on liquid oxygen or nitrogen tetroxide are particularly unstable; being too shock sensitive and too difficult to handle to find common commercial use. Furthermore, explosives based on nitrogen tetroxide (the Panclastites) produce large volumes of nitrogen oxides during detonation which significantly increases the hazard to personnel and the environment.

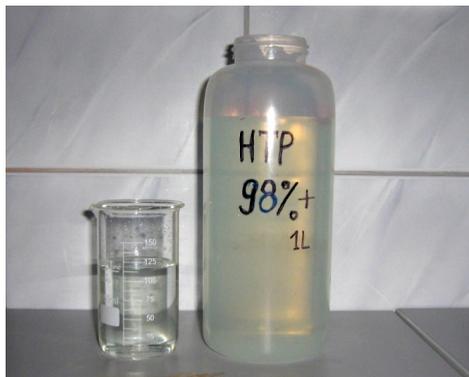
Fumes rich in nitrogen oxides ( $\text{NO}_x$ ) are formed in large quantities in blasting areas where a variety of bulk ammonium nitrate(V) (AN) based explosive products are used [7]. Even in coal blasting it appears to be an industry wide problem. What is more, it seems to occur under a variety of geological conditions, as well as at open cast sites. Nitrogen oxides ( $\text{NO}_x$ ), especially nitrogen dioxide, are toxic gases and can pose serious health risks to exposed personnel. These gases can also adversely affect the environment as they can last for a relatively long time and can drift into nearby populated areas or cause deterioration of vegetation. Fig. 1 is an example of post-blast nitrogen oxide fumes ( $\text{NO}_x$ ). The solution to the problem may be the development and use of industrial explosives that are based on oxidizers other than AN, which are nitrogen free. Currently, hydrogen peroxide seems to be the best choice for such an approach.



**Fig. 1.** Cloud of nitrogen oxides formed during rock blasting [8]

## 2. Explosiveness and detonability of HTP

It is a well known fact that equilibrium vapour concentrations of hydrogen peroxide above 26% mol (40%) become explosive at a temperature range below the boiling point of the liquid. On the other hand, based upon the experimental evidence, liquid hydrogen peroxide, even in its purest form (as 100% liquid), cannot be classified as a high explosive [1]. This is due to the fact that it requires a relatively high input energy for it to undergo detonation. In practice, an ordinary blasting cap is not sufficient to initiate a solution of 98%+ hydrogen peroxide, and an additional booster (in the form of a secondary explosive charge) and some significant confinement conditions must be applied to obtain an appropriate detonation process with a velocity close to 7000 m/s [5]. As a result, solutions of 98%+ HTP have been routinely used by the aerospace industry and research entities for decades with very little risk of unintended explosion or detonation [2] (Fig. 2).



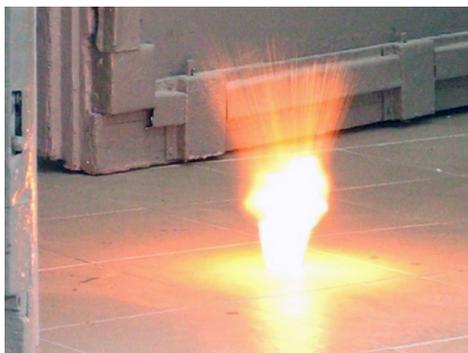
**Fig. 2.** A sample of 98%+ HTP to be used for rocket propulsion experiment

Nonetheless, people unaccustomed to the special properties of hydrogen peroxide may include explosive like events (*e.g.* explosion caused by over-pressurization or violent, unintended decomposition) as detonations – figure below (Fig. 3).



**Fig. 3.** Decomposition of a sample of HTP caused by potassium permanganate

Thus, almost any kind of contamination can increase the rate of HTP decomposition and in some extreme situations can cause a detonative event. An example is the contact of concentrated hydrogen peroxide with strong reducers, such as metallic sodium (Fig. 4).



**Fig. 4.** Reaction between metallic sodium and 98%+ HTP

The situation may change significantly when HTP is mixed with miscible fuels (*e.g.* organic liquids). The sensitivity as well as the explosive strength of such mixtures can increase considerably, as has been observed in the case of hydrogen peroxide and ethanol mixtures [9].

### 3. Historical review

The German research program on the detonability of hydrogen peroxide when mixed with organic fuels (for use as mono-propellants) began before World War II. The first successful experiments were reported in literature in 1927 [10]. A 89% solution of hydrogen peroxide was used together with cotton and petroleum jelly in subsequent research [9]. However, the sources do not provide data on detonation velocities of those formulas. Shortly after World War II, simple formulas of concentrated hydrogen peroxide mixed with glycerol were further researched by Shanley [11]. Although Shanley did not provide much data (including a lack of velocities of detonation), the concept was further investigated and in the 60s the first patents appeared (Ref). The outcome of this early work by Shanley was the determination of detonation ranges of hydrogen peroxide/glycerol/water mixtures. Other substances such as methanol, ethanol, iso-propanol, ethylene glycol, mannitol, ethyl acetate, cane sugar, diethylene glycol, diethyl ether, acetone, dioxane, aniline and many others appeared to be too sensitive when mixed with concentrated hydrogen peroxide and are outside practical utilisation (Fig. 5).

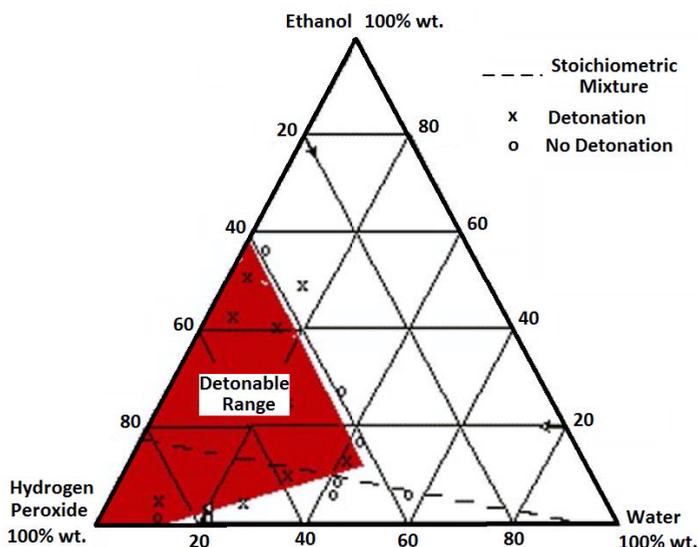


Fig. 5. Typical ternary diagram for the detonation range of HP/ethanol/water mixtures [9]

The first patent on hydrogen peroxide/glycerol high explosive was issued in 1948 in the United States [12]. According to the patent, hydrogen peroxide, water and glycerine were mixed to produce a single phase liquid system which at room temperatures was relatively stable and non-reactive. The end product, provided the water content was maintained below 52 wt.% and the amount of hydrogen peroxide was sufficient to oxidise the glycerine during detonation, was an explosive resistant to initiation by mechanical shock but which would detonate when initiated by a standard blasting cap.

Other explosive mixtures were then developed, some with quite significant practical potential. The use of hydrogen peroxide as an oxidiser with various organic materials, has led to the development of several types of explosives and propellants with a higher energy content than that resulting from the detonation of pure hydrogen peroxide. Examples of such mixtures can be found in a variety of patents, in which hydrogen peroxide is mixed with, for example, flour, sawdust, water, glycerin, ammonium nitrate, gelling agents and more (*e.g.* [13]).

Typically, such mixtures include hydrogen peroxide, usually at concentrations in the range of 60% to 90%, with sawdust, resin and a gelling agent (starch or agar). Mixtures have also been proposed in which hydrogen peroxide is supposed to be used at relatively high concentrations together with hydrazine (or ammonium nitrate) and water, to produce explosive formulas that are rich in gaseous detonation products.

It is also worth mentioning that some “exotic” high explosives may be prepared using lower concentrations of hydrogen peroxide (e.g. 30% solution - known as perhydrol). A well-known example of such an explosive compound is TriAcetone TriPeroxide (TATP). It is an organic peroxide that has received widespread attention in recent years as it can be prepared quickly and relatively easily from inexpensive chemicals. TATP is a ketone peroxide with a relatively high active oxygen content. It is also shock sensitive, with explosive decomposition being easily initiated, and hence is considered to be a primary explosive. However, TATP can be seen as a powerful secondary explosive but with a very sensitive nature and stability problems, but possessing significant detonation power (close to TNT).

## 5. Hydrogen peroxide and its detonable mixtures

In simple terms, detonation is a kind of supersonic combustion characterised by a few significant parameters such as velocity and critical diameter. These parameters are strongly dependent on the general features of a given high energy material (quantity, confinement conditions, geometry, temperature, presence or absence of gas bubbles or impurities, etc.). In the case of highly concentrated hydrogen peroxide solutions, the above parameters have been quite intensively studied [14]. The experimental data confirmed that even the highest concentrations of hydrogen peroxide (solutions 98 wt% or above) are much less sensitive than other typical liquid explosives such as Ethylene Glycol DiNitrate (EGDN) or NitroMethane (NM) [15]. However, solutions of highly concentrated hydrogen peroxide (over 98 wt%) with entrained bubbles become more sensitive to shock initiation [15].

As already mentioned, some of the organic liquids tend to form very sensitive explosive mixtures that can undergo detonation relatively easily. An example of such a mixture is a laboratory investigation of the hypergolic ignition of so called catalytically promoted fuels with 98%+ HTP [1]. The very first step in such research is checking if ignition occurs, which is usually carried out *via* a form of a simple liquid drop-wise addition test. As it turned out, some of the potential liquid fuels exhibited very violent reaction in contact with 98%+ HTP, even resulting in detonation. The mixture of propargyl alcohol with 5%, 10% and 15% of dissolved iron (III) chloride as the catalyst, turned out to be quite a reliable hypergolic mixture, whereas the 4% solution exhibited limited ignition properties. One sample underwent a DDT like process (strong shattering effect of the explosion) when just two drops of fuel came in contact with one drop of 98%+ HTP (Fig. 6).

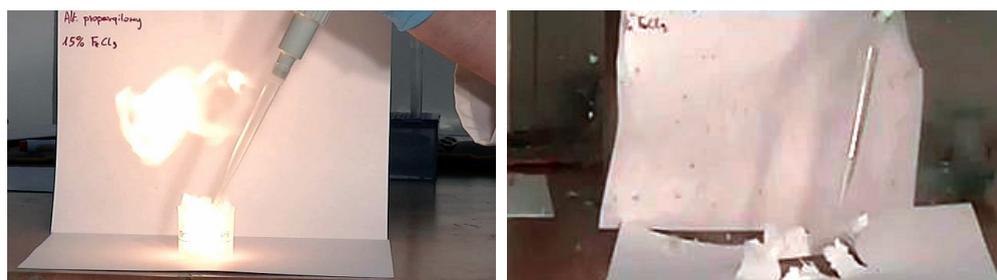


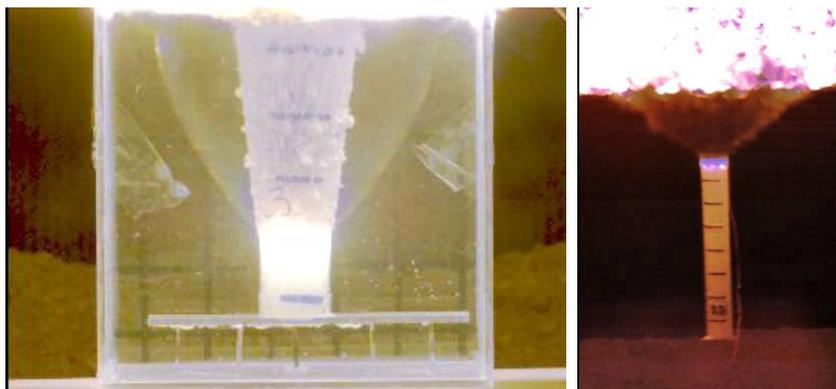
Fig. 6. Effect of ignition drop tests with 15% (left picture) and 4% propargyl alcohol-catalyst mixture [1].

## 6. Novel formulations for the mining industry

The oxidising nature of concentrated solutions of hydrogen peroxide means that they can be used as a component of explosive mixtures. Currently, the Australian mining industry is developing alternative blasting formulations based on HP which have the potential to eliminate the hazard of post-blast nitrogen oxide ( $\text{NO}_x$ ) gases [16]

This would significantly reduce the hazard to workplace health, safety and environmental issues from blasting, connected to the use of AN based explosives and large quantities of  $\text{NO}_x$  emissions, especially those associated with non-ideal detonations of such mixtures.

Results from tests recently performed in Australia, clearly show that the replacement of ammonium nitrate with hydrogen peroxide in some of the commercial explosive mixtures, could be a crucial step and a positive change for the whole industry. According to CRC Mining project leader Dr Italo Onederra, over 160 tests have been conducted to characterise the detonation properties of these new formulations [15]. Stills taken from high speed video recordings are given in Fig. 7. The results have shown velocities of detonation between (2200 – 5500) m/s for a range of densities (0.40 – 1.10)  $\text{g}/\text{cm}^3$ .



**Fig. 7.** Detonation tests for HP/fuel based explosives - the aquarium test (left picture) and crumb rubber tests [16]

Additionally, confined rock breakage tests were conducted and the results presented at the Fragblast international conference in Sydney in 2015 [17].

## 7. Conclusions

The development of a novel class of commercial or even high, military dual component explosives based on hydrogen peroxide, may become a fact in the very near future. The mixtures researched so far have exhibited relatively low nitrogen oxides emissions as well as sufficient explosive power, stability, sensitivity and versatility. Additionally, HP based explosives can be prepared in situ (simply by mixing two components) which eliminates the logistical difficulties usually encountered in shipping and storing high explosives. Both, the fuel component (liquid or in the form of loose material, optionally with the additional activator) and a solution of specially stabilised HP (the liquid phase), can remain in long term non-explosive storage, until required. However, when mixed, the resulting mixture becomes a detonator (or detonator-booster) sensitive high explosive with high gas volume, high bulk energy and consistent detonation velocity - quite appropriate for the mining industry. The mixtures investigated so far appeared to be relatively easy to use and quite adaptable. Additionally, their main ingredients are characterised by their non-explosive nature which may ease shipping and storage restrictions.

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