Review / Przegląd

Hydrogen peroxide (H$_2$O$_2$): a review of its use in homemade explosives

Nadtlenek wodoru (H$_2$O$_2$): prekursor improwizowanych materiałów wybuchowych

Grzegorz Rarata*, Mitja Vahčič**, David Anderson, Michael Berglund, Dimitris Kyprianou, Giovanni Emma, Gabriela Diaconu

European Commission, Joint Research Centre,
Retieseweg 111, 2440 Geel, Belgium
E-mails: * grzegorz.rarata@ec.europa.eu; ** mitja.vahcic@ec.europa.eu

Abstract: This article presents an overview of hydrogen peroxide and its use in the illicit production of homemade explosives. Hydrogen peroxide is used extensively around the world in many industries, including aerospace. It is also used as the main ingredient in some household cleaning products. However, it has been illicitly used to create both primary and secondary homemade explosives in recent numerous terrorist attacks across Europe. In this article, we describe the historical background and the characteristics of the substance, the aspects concerning its manufacture and present-day use as a main explosive component or direct chemical precursor of homemade explosives, and the options for detection.

Streszczenie: W artykule zostały omówione najważniejsze, improwizowane materiały wybuchowe, których chemicznym prekursorem jest nadtlenek wodoru. Roztwory nadtlenku wodoru są intensywnie używane w wielu dziedzinach życia, poczynając od przemyślu kosmicznego, a kończąc na wybielaczach stosowanych w gospodarstwach domowych. Niestety, medium to zostało także wykorzystane do uzyskiwania nielegalnych materiałów wybuchowych, których użyto miedzy innymi w atakach terrorystycznych w Europie Zachodniej kilka lat temu. Dlatego też w prezentowanym tutaj przeglądzie przedstawiamy historyczny rys dotyczący tego interesującego związku chemicznego, ale także aspekty związane z jego użyciem jako prekursora nielegalnych materiałów wybuchowych. Opisane zostały również podstawowe sposoby detekcji tychże związków.

Keywords: hydrogen peroxide, improvised explosive device, IED, homemade explosive, HMD, oxidiser, organic peroxide, TATP

Słowa kluczowe: nadtlenek wodoru, improwizowany materiał wybuchowy, IED, HMD, utleniacz, nadtlenek organiczny, TATP

1. Introduction

The first known appearance of hydrogen peroxide was reported over two hundred years ago [1]. Nowadays, various solutions of hydrogen peroxide have numerous industrial and domestic applications [2]. Moderately concentrated
solutions of hydrogen peroxide are illicitly used for synthesising some of the organic peroxides that may act as home-made explosives (HMEs). Even more concentrated solutions are required for preparing explosive mixtures containing hydrogen peroxide (e.g. Hydrogen Peroxide – Organic Matter, HPOM) [3]. Among those HMEs, triacetone triperoxide (TATP, C₉H₁₈O₆, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, CAS number 17088-37-8) has been the terrorist’s explosive of choice, for decades. TATP may be classified as a primary explosive in terms of its sensitivity. The compound is characterised by rather poor stability characteristics and relatively high vapour pressure at room temperature [4]. TATP was discovered in 1895 by German chemist Richard Wolffenstein at the Technical University in Berlin [5]. Although the synthesis of TATP is quite straightforward and the precursors are readily available, it was never utilised in practice by professional entities such as military. Generally, it can be formed by mixing moderately concentrated solution of hydrogen peroxide with acetone in acidic solution (addition of an acid acts then as a catalyst).

Hexamethylene triperoxide diamine (HMTD) is another explosive peroxide that was discovered around the same time by German chemist Ludwig Leger [6]. There are a few more crystalline solid chemical compounds (organic peroxides) which involve the use of hydrogen peroxide in their production that may be used as illicit explosives. The homologue of TATP – diacetone diperoxide (DADP, C₆H₁₂O₄, 3,3,6,6-tetramethyl-1,2,4,5-tetroxane, CAS number 1073-91-2) or the compound known as tetramethylene diperoxide dicarbamide (TMDD) – are two of the well-known ones. There is also a peroxide derivative explosive which occurs as a colourless, oily liquid called methyl ethyl ketone peroxide (MEKP). Structures of DADP and TATP can be seen in the Figure 1 and their melting points and vapour pressures are shown in Table 1.

![Figure 1. The reaction leads to formation of TATP or DADP is depicted](image)

| Compound | DADP | TATP |
|----------|------|------|
| Melting point [°C] | 133-135 | 94 |
| Vapour pressure at 298 K [Pa] | 17.7 | 7.8 |
2. Short history of the use of hydrogen peroxide

Hydrogen peroxide was discovered by a French chemist Louis Jacques Thenard in 1818 when he was working on voltaic cells [1]. He noticed that during the reaction of barium peroxide with cold nitric acid resulted in the formation of a new liquid substance that he described as “oxidised water”. Later, sulphuric acid was included in order to precipitate the by-product of barium sulphate produced. Thenard was also the first one to discover some of the characteristic features of this new substance – its tendency to decompose when exposed to certain substances and its ability to form supercooled solutions. These reactions of decomposition were later described by Berzelius as typical catalytic ones [7]. Thenard was also able to apply for the first time a vacuum distillation technique in order to increase the concentration of this new compound [7]. However, higher concentrations were not available for him at that time, due to the presence of metallic and organic impurities which readily catalysed the decomposition of hydrogen peroxide.

The first improvement to the original Thenard’s method of obtaining hydrogen peroxide was made by Pelouze in 1832, who proposed to use fluorosilicic acid instead of nitric one [6]. The process suggested by Pelouze resulted in production of barium fluorosilicate precipitate and in practice offered shorter time of hydrogen peroxide preparation. Therefore, the process was popular for many years as less skill was necessary to form an easily separable precipitate with fluorosilicate acid than with sulphuric acid. It took several decades before Thenard’s compound was obtained in a 100% form. Chemically pure hydrogen peroxide was first obtained in 1894 by the above-mentioned chemist Richard Wolffenstein. He prepared it by distillation technique under reduced pressure and clean conditions [7].

Hydrogen peroxide has been in practical use for over a century now – at first mostly for medicinal purposes and textile and pulp bleaching. It has been manufactured commercially by a variety of processes since the end of 19th century. At the beginning of 20th century, its production by an electrolytic process was also possible. In fact, a variety of methods of hydrogen peroxide preparation were proposed during that period, however most of them were not of commercial interest. Nevertheless, the scale of hydrogen peroxide manufacture and use has increased markedly since about 1925 – when electrolytic processes were gradually introduced to the United States and new industrial bleach applications were developed. By the end of the 1920s, nearly all solutions of hydrogen peroxide in the United States were manufactured by the electrolytic process by companies such as E. I. DuPont and Buffalo Electro-Chemical Company [1].

Since the early 1930s, the physical and chemical properties of hydrogen peroxide solutions were known well enough to put it into some of the very first propulsion applications. This is mainly due to the vast amount of work done by Helmuth Walter – a German engineer who pioneered research into rocket engines and gas turbines that utilised hydrogen peroxide [1]. The compound in the form of weak water solution (typically 3%) had been known for decades as so called “oxygenated water”. However, the substance is also naturally present in water and air although in very small concentrations (trace amounts). Chemically speaking, the substance is in fact the simplest peroxide.

Today it is commercially available for the public as aqueous solution, but at relatively low concentrations. At higher concentrations (up to 60%), it is commonly used by the pulp, paper and fibre industry around the world as an environmentally friendly oxidising agent. It is also used as a chemical reagent for the preparation of other peroxides or chemicals.

3. Use of hydrogen peroxide in explosives

3.1. Molecular peroxides

Any grade of pure hydrogen peroxide cannot be considered as a flammable, explosive or toxic substance but as an oxidiser. At some concentrations, however, it may be used as starting reagent for preparing explosive mixtures (type oxidiser-fuel, similarly to ANFO) or synthesis of explosive compounds (organic peroxides), especially homemade explosives (HMEs). In fact, moderately concentrated solutions of hydrogen peroxide have been known for a relatively long time as a starting material for them.
Most conventional high explosives contain nitro groups within their molecules. However, there are few homogeneous explosive compounds that are based totally on organic peroxides as explosophore groups, such as TATP (C₉H₆O₆, trimer). In fact, it has gained notoriety as a chemically simple primary like explosive compound that can be obtained from hydrogen peroxide.

Explosives like TATP, HMTD and MEKP, have been illicitly used as so-called homemade explosives, mostly in the form of white crystalline powders (or as sensitising additives), as they are relatively easy to be set off. Besides, pure TATP is also one of the most sensitive explosives whereas its explosive power (brisance) is very close (0.7 times) to that of 2,4,6-trinitrotoluene (TNT). It has been shown that during the synthesis of TATP possible variations in the production method (temperature, catalysts) might change the morphology of the explosive or even the resulted product. DADP is the thermodynamically favoured product and TATP is the kinetically favoured one [8]. As it is described above due to its high impact and friction sensitivities, low thermal stability, high vapour pressure and relatively low detonation velocity, it has not found any civil or military application yet, similarly as the other organic peroxides.

The other molecular peroxides (such as MEKP) are in fact also sensitive substances to impact, friction, spark and shock stimuli. DADP in turn, may be considered less sensitive to drop-weight impact than TATP [9, 10]. Nevertheless, these substances should only be handled in small quantities, in explosive facilities, and only by individuals who have proper training and experience with handling primary explosives.

### 3.2. Heterogeneous explosives based on hydrogen peroxide

The other types of explosives based on relatively concentrated hydrogen peroxide solutions are the mixtures of this medium with some fuels (e.g. some organic materials – as mentioned above HPOM type). This is due to the fact that hydrogen peroxide acts as an oxidant with various organic materials in mixtures and provides a higher energy content than detonations of pure hydrogen peroxide. Besides, even the most concentrated solutions of peroxide are not easy to set off. These types of mixtures also may be defined as Hydrogen Peroxide/Fuel (HP/F) ones.

The first detailed studies of these explosives were carried out in a classified military research program on the detonation performance of HP/F explosives in Germany during the World War II era [13]. These explosives, in fact, may be divided further into two main groups: one which contain liquid fuel (so, the whole mixture is also liquid; HP/LF) and the second one, which contain solid organic fuel materials in the form of fine particles dispersed in concentrated hydrogen peroxide (HP/SF). Both types of explosives were also investigated in the USA after World War II and then patented there as cap sensitive explosives for possible industrial use, e.g. [13, 14].

In 1990, mixtures of hydrogen peroxide and resins were patented as packaged explosives [15]. Examples provided in the patent show that some of the mixtures detonated at velocities above 6000 m/s in 33 mm diameter PVC tubes. A few years later, the charges based on 44% solution of hydrogen peroxide and glycerol as fuel (which constituted 83% of explosive mixture, were sensitised by using special glass micro-balloons) were studied by the Australian team lead by Araos [16]. However, the charges had to be initiated with 50 g pentolite boosters in order to obtain a proper detonation. The use of more concentrated peroxide for HP/LF preparation may increase the sensitivity and explosive power of the resulting explosive, as shown by the German research program during the World
War II [12]. Formulations of concentrated hydrogen peroxide with miscible liquid fuels (e.g. primarily alcohols) were later tested. The peroxide concentration was varied from as low as 61% to pure (100%). The results of these experiments showed that the mixtures close to the stoichiometry are easily detonable (blasting cap sensitive); with detonation velocities close to 7000 m/s. A German research team also investigated the explosive hazard of hydrogen peroxide mixed with different alcohols [17]. Therefore, it has been known for a long time that concentrated solutions of hydrogen peroxide may form explosive mixtures that may undergo detonation, especially with some organic (combustible) materials. However, a few possible reactions that must be taken into account when concentrated hydrogen peroxide is mixed with another substance. The most typical reaction is the decomposition of peroxide. It may be a very slow or very vigorous process (even explosive like), depending on the percentage of peroxide and the nature of substance being in contact with it. In some cases, decomposition of peroxide may be more violent or even set a sudden burst of fire. There are also cases when an instant, violent explosion may be observed (e.g. on contact with metallic sodium or hydrazine hydrate). However, there are numerous chemical compounds that do not seem to show any visible signs of reaction when mixed, even with concentrated peroxide, at least initially. Such mixtures may be stable whereas some other may only look as “stable” but in fact pose a great explosion hazard, depending on the individual properties of the organic compound. Such mixtures may be quite stable when stored but detonate violently when stimulated (e.g. by impact). However, the impact sensitivity of liquids is particularly dependent on the degree of confinement and in practice widely different results may be obtained. In any case, when preparing concentrated hydrogen peroxide/liquid organic “fuel” mixture (HP/LF), it is strongly advisable to take extensive precautions. Some of such mixtures may detonate quite easily, for example by dropping them (the container with them) on a hard floor. The power of the resulting explosion may be comparable with that of a corresponding quantity of nitroglycerine. Furthermore, the sensitivity of HPOM mixtures can increase substantially with time [18]. Such explosives are formed when concentrated hydrogen peroxide (typically above 50%) is mixed with a miscible liquid fuel that is not initially readily oxidizable. The most common used liquid fuels are alcohols (especially ethanol) and glycerol. This type of explosive mixtures generate only gaseous products when detonated. For example for HP/glycerol mixtures, the summary reaction may be written as follows:

$$7\text{H}_2\text{O}_2 + \text{C}_3\text{H}_4\text{O}_3 \rightarrow 11\text{H}_2\text{O} + 3\text{CO}_2$$  \hspace{1cm} (1)

The addition into the mixture of sugars or some absorbing polymers is also possible. They act as thickeners (Figure 2). However, the preparation and use of these explosives in practice is not so straightforward. The main problem is chemical stability of such mixtures – it may not be high and can be additionally affected by the presence of many impurities, especially inorganic ones (such as dust). Many metals catalyse the decomposition of hydrogen peroxide and this may lead to self-ignition or even explosion (accidental detonation) of improvised explosives based on mixtures of hydrogen peroxide with liquid or solid fuels. Moreover, the accelerated decomposition of peroxide caused by impurities included in organic material may contribute to decrease its concentration and thereby reduce the explosive properties of a whole mixture.
4. Detection of hydrogen peroxide

Hydrogen peroxide detection is important as it is used in bulk amounts by many industries around the world. Due to this fact, many different and innovative ways have been developed for either detecting liquid peroxide, or its vapours. Generally, there are two main types of detection: qualitative and quantitative. Qualitative detection of hydrogen peroxide is most commonly done by iodine-starch reaction where hydrogen peroxide oxidises potassium iodide into iodine, which then reacts with starch to produce a deep blue colour [19]. Many commercial paper indicators utilizing this reaction have been developed for peroxide detection [20]. However, this reaction is nonselective and will detect any type of peroxide. Therefore, to have a more selective reaction various indigo dyes can be used. For example, the loss of colour in leuco-methylene blue is selective for hydrogen peroxide [21].

The horseradish peroxidase (HRP) catalysed reaction is one of the most popular enzymatic assays used for quantitative determination of hydrogen peroxide [22]. However, this reaction is quenched or restrained by cations, surfactants, and organic solvents, and the reagents are expensive. Other methods for peroxide determination include HPLC, colorimetric methods, amperometry and chemiluminescence [23]. Titanium-based assays (Ti-PAPS reagents) were developed in the 1980’s for spectrophotometric detection of peroxide [24]. The Fox assay was developed in the 1990’s based on ferrous ion oxidation in the presence of the ferric ion indicator xylenol orange under acidic conditions [25].

Peroxide-based explosives (such as TATP or some organic mixtures with moderately or highly concentrated hydrogen peroxide) differ in composition from pure peroxide. With old standard screening or rapid identification methods for explosives, peroxide-based explosives were rather difficult or sometimes even impossible to detect [26]. This is mainly because of the absence of metals or nitro groups within their molecular structures. However, over the last several years, many methods and technologies for detecting explosives that contain organic peroxides have been further developed. Therefore, nowadays these technologies are commercially available.
and deployed operationally at security checkpoints. For instance, in aviation security screening, the European Civil Aviation Conference (ECAC) publishes a list of detection equipment that has passed ECAC testing [27]. For example, explosive trace detection (ETD) equipment typically based on ion mobility spectrometry (IMS) is used to for the rapid and effective detection of TATP. Hydrogen peroxide and its mixtures can be detected by a number of commercially available liquid explosives detection systems (LEDS). This equipment incorporates a wide variety of sensing technologies:

- X-ray transmission,
- radio frequency,
- Raman spectroscopy,
- colorimetric,
- infrared,
- chemiluminescence, and
- nuclear magnetic resonance (NMR).

Relevant homemade explosives contained in cabin baggage can be detected by advanced X-ray tomography equipment referred to as explosives detection systems for cabin baggage (EDS-CB). More information about detection of different explosives is given in [28]. Typically, the simplest way of detecting is performed by applying specially designed accurate field test kits for selected HMEs, such as those for TATP produced by a few companies around the world [29]. This is just one example of the many suppliers of such kits for detecting explosives.

5. EU Regulation on explosives precursors

Hydrogen peroxide of industrial grade is manufactured and imported in the European Economic Area in the order of millions of tonnes per year [30]. The industrial importance and use of hydrogen peroxide as a versatile and environmentally friendly oxidiser is significant and still growing, not only in Europe. However, taking into account its use as an explosive precursor, the EU Regulation on the marketing and use of explosives precursors (No 98/2013) applies to hydrogen peroxide with concentrations levels of 12% or more [31]. This regulation 98/2013 on explosives precursors lists several so-called “high-risk” substances, which are either restricted to general public or whose purchase should be reported. The effect of the Regulation encompasses several of the most common components for the synthesis of HMEs, with hydrogen peroxide at the head of the list. At the time of writing of this paper, the European Commission has already adopted a new proposal [32]. Currently, it is under the discussion at the European Parliament. The limit of 12% for the hydrogen peroxide solutions was confirmed in the new proposed Regulation.

6. Conclusions

In this article, we described the historical background and the characteristics of the hydrogen peroxide, focusing on the aspects concerning its manufacture and present-day use as a main explosive component or direct chemical precursor of homemade explosives (HMEs). The options for its detection have also been described. In recent years, hydrogen peroxide has been used as a main chemical precursor for producing various improvised explosives, also in Europe. Restrictions on the marketing and use of hydrogen peroxide are set out in EU legislation, and a number of technological options for detecting hydrogen peroxide based homemade explosives are currently commercially available not only for civil aviation sector.
References

[1] Constantine M., Cain E. 1967. Hydrogen peroxide handbook. Defence Technical Information Centre, Canoga Park.

[2] Application areas. https://active-oxygens.evonik.com/product/h2o2/en/application-areas/ [accessed on 23.10.2019].

[3] Report JRC Geel on HP based explosives, 2018 [not published].

[4] Matyas R., Chylkova J. 2013. Study of TATP: method for determination of residual acids in TATP. Forensic Sci. Int. 228.

[5] Sceibler H. 1929. Memoriam: Richard Wolfenstein. Angew. Chemie 42 (51): 1149-1151.

[6] Jones C.W. 1999. Applications of hydrogen peroxide and derivatives. Cambridge: Royal Society of Chemistry, ISBN 978-0-85404-536-5.

[7] Schumb W., Satterfield C.N., Wentworth R.L. 1955. Hydrogen peroxide. A.C.S. Monograph 128, New York: Reinhold Publishing Corporation.

[8] Bowden P.R., Tappan B.C., Manner V.W., Preston D.N., Scott B.L. 2017. Characterization of diacetone diperoxide (DADP). AIP Conf. Proc. 1793, 040010 https://doi.org/10.1063/1.4971504 [published online 13.01.2017].

[9] Matyas R., Pachman J. 2010. Study of TATP: Influence of reaction conditions on product composition. Propellants Explos. Pyrotech. 35 (1): 31-37.

[10] Egorshev V., Sinditskii V.P., 2013. A comparative study on two explosive acetone peroxides. Thermochim. Acta 574: 154-161.

[11] Oxley J.C., Smith J.L., Shinde K., Morgan J. 2005. Determination of the vapour density of triacetone triperoxide (TATP) using a gas chromatography headspace technique. Propellants Explos. Pyrotech. 30 (2): 127-130.

[12] Historical survey of hydrogen peroxide/fuel explosives. Sandia National Laboratories and U.S. Department of Energy, Report SAND2015-0133R, 2015.

[13] Baker A. W. 1946. Hydrogen peroxide explosives. US Patent 3047441.

[14] Shanley E. S. 1948. Peroxide glycerol explosive. US Patent 2452074.

[15] Bouillet E., Colery J.-C., Declerck C., Ledoux P. 1990. Process for the manufacture of explosive cartridges, and explosives cartridges obtained using the said process. US Patent 4942800.

[16] Araos M., Onederra I. 2013. Detonation characteristics of alternative mining explosives based on hydrogen peroxide as the oxidising agent. World Conf. on Explosives and Blasting, 7th, Moscow, Russia, 182-186.

[17] Schreck A., Knorr A., Wehrstedt K.D., Wandrey P.A., Gmeinwieser T., Steinbach J. 2004. Investigation of the explosive hazard of mixtures containing hydrogen peroxide and different alcohols. J. Hazard. Mater. 108.

[18] Gaskell D.R. 2011. Forensic investigation of explosions. 2nd Ed., Boca Raton: CRC Press; eBook ISBN 9780429250156.

[19] Eiss M.I., Giesecke P. 1959. Colorimetric determination of organic peroxides. Anal. Chem. 31 (9): 1558-1560.

[20] Amelin V.G., Kolodkin I.S., Irinina Y.A. 2000. Test method for the determination of hydrogen peroxide in atmospheric precipitation and water using indicator papers. J. Anal. Chem. 55 (4): 374-377.

[21] Zaribafan A., Haghbeen K., Fazli M., Akhondali A. 2014. Spectrophotometric method for hydrogen peroxide determination through oxidation of organic dyes. Environ. Stud. Persian Gulf 1 (2): 93-101.

[22] Tang J., Wang B., Wu Z., Han X., Dong S., Wang E. 2003. Lipid membrane immobilized horseradish peroxidase biosensor for amperometric determination of hydrogen peroxide. Biosens. Bioelectron. 18 (7): 867-872.

[23] Deadman B.J., Hellgardt K., Hii K.K.(Mimi). 2017. A colorimetric method for rapid and selective quantification of peroxodisulfate, peroxomonosulfate and hydrogen peroxide. React. Chem. Eng. (4):462-466.
[24] Matsubara C., Kudo K., Kawashita T., Takamura K. 1985. Spectrophotometric determination of hydrogen peroxide with titanium 2-((5-bromopyridyl)azo)-5-(N-propyl-N-sulfopropylamino)phenol reagent and its application to the determination of serum glucose using glucose oxidase. *Anal. Chem.* 57 (6): 1107-1109.

[25] Wolff S.P. 1994. Ferrous ion oxidation in presence of ferric ion indicator xylenol orange for measurement of hydroperoxides. *Methods Enzymol.* 233: 182-189.

[26] Xu M. 2014. *Trace vapour detection of hydrogen peroxide: an effective approach to identification of improvised explosive devices*. PhD Dissertation, The University of Utah, Department of Materials Science and Engineering.

[27] European Civil Aviation Conference (ECAC) – Common Evaluation Process (CEP). https://www.ecac-ceac.org/cep [accessed on 2.12.2019].

[28] Liscouski R., McGann W. 2016. The evolving challenges for explosive detection in the aviation sector and beyond. *CTC Sentinel* 9 (5): 1-6.

[29] Explosives testing kits. http://www.identa-corp.com/products/explosives-testing-kits/tatp-peroxide/ [accessed on 23.10.2019].

[30] Substance information – hydrogen peroxide. https://echa.europa.eu/substance-information/-/substanceinfo/100.028.878 [accessed on 23.10.2019].

[31] European Commission – explosives precursors. https://ec.europa.eu/home-affairs/what-we-do/policies/crisis-and-terrorism/explosives/explosives-precursors_en [accessed on 23.10.2019].

[32] Proposal for a Regulation of the European Parliament and of the Council on the marketing and use of explosives precursors. http://www.europarl.europa.eu/legislative-train/theme-area-of-justice-and-fundamental-rights/file-marketing-and-use-of-explosive-precursors [accessed on 23.10.2019].

Received: December 5, 2019
Revised: December 18, 2019
First published online: December 30, 2019