

Hydrogen Peroxide - The Safe Supply and Handling of HTP

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The Solvay Interlox group of companies has been involved with the manufacture and supply of high test peroxide (HTP) for 40+ years. The historical and current situation is reviewed and comments on current development work in this area are provided. The principal hazards and properties of HTP are overviewed in the context of safe transportation, storage and handling.

Introduction

Hydrogen peroxide was discovered by Thenard in 1818 and has been manufactured commercially by a variety of processes since about 1885. Today it is a versatile chemical, with numerous applications and it is routinely transported and stored in bulk quantities. As of January 1997, the worldwide production capacity for H₂O₂ was ca. 4.9 billion lbs. per year (expressed as 100% H₂O₂).¹

Major current end uses include pulp & paper and textiles bleaching, chemical synthesis, environmental treatment and metals processing. These applications utilize hydrogen peroxide products which are generally considered as "standard" or "industrial grades". These materials are routinely shipped and stored in the US at 70% concentration, particularly as part of the distribution network. The most commonly-used concentration, however, is 50%, with customers diluting the 70% material prior to on-site storage.

There are also several specialty applications which demand either specially formulated stabilizer packages, for example cosmetic grades for consumer products, or very high levels of product purity (but not concentration) as required by the semiconductor industry. For the latter, hydrogen peroxide is typically supplied at a 31% concentration level.

While the manufacture and use of hydrogen peroxide which is high in both purity and concentration (i.e. > 70% H₂O₂) is by no means new, the recent merchant demand for such products has been small, if not non-existent, at least in the United States. However, the latest growth in interest in the use of highly concentrated H₂O₂ (HTP) for propulsion applications perhaps holds the promise of significant future demand.

Following is a discussion of the past, present, and possible future role of the Solvay Interlox group of companies in the manufacture and supply of HTP. With an increase in development work utilizing HTP it is important that the new and existing users are fully aware of the properties and hazards of such material. In support of this requirement, a review of the principal hazards of concentrated H₂O₂ is provided.

Brief History of Solvay Interox

The Solvay Interox group of companies is currently the world's largest producer of hydrogen peroxide with a 24% capacity share of the world market and 18 manufacturing sites that focus exclusively on hydrogen peroxide and its derivatives. Today, Solvay Interox, Inc. is 100% owned by Solvay America, Inc. which is in turn 100% owned by Solvay S.A., a chemical and pharmaceutical company with operations in 41 countries, employing more than 35,000 people, and headquartered in Brussels, Belgium. The origins of the current group of companies, however, date back to the initially independent operations of Solvay (Belgium) and of Laporte, a UK based chemical company. The latter company actually began production of hydrogen peroxide more than 100 years ago. In 1970, Laporte and Solvay formed a worldwide joint venture in peroxygen chemicals by creation of the Interox group of companies. In 1992, Solvay acquired a 100% interest in the H₂O₂ activities of Interox, leaving Laporte to focus on some of the more highly specialized peroxygen compounds such as organic peroxides.

With this long history of involvement in hydrogen peroxide, the Solvay Interox group of companies looks forward to continuing leadership by providing a variety of H₂O₂ products, services, and technologies to the world's peroxygen markets. As a global chemical manufacturer committed to the principles of Responsible Care® we strive to ensure the safe supply and handling of hydrogen peroxide in all concentrations.

Manufacture and Supply of HTP

The use of high strength hydrogen peroxide as a rocket propellant can be traced back to Helmuth Walter and developments in Germany during the 1930's.² At that time, 80% hydrogen peroxide was first produced on a limited scale to support these developments. Such high strength peroxide is now commonly referred to as high test peroxide or HTP.

HTP is still produced in Germany today. Solvay Interox has one of its two HTP producing facilities located near Munich and this site has produced up to 86% H₂O₂ for many years, primarily for captive use in the manufacture of organic chemicals. The other facility is located in Warrington, England and is a former Laporte site.

Laporte first began production of hydrogen peroxide in the late 1800's using a barium peroxide process to generate solutions of 3% H₂O₂. This was later replaced with an electrolytic process which provided 35% H₂O₂, some of which was concentrated via distillation to produce 85% HTP. As new production capacity was added to the growing business, a switch to the organic oxidation process was made (commonly referred to as auto-oxidation or AO process). Today, all major producers of H₂O₂ utilize AO process chemistry in their plants.

Laporte built its first AO process plant at Warrington in 1958 and it was this plant which supplied all of the 85% HTP for the British rocket development programs, including the Black Knight Rocket.³ Today, 40 years later, production of HTP at the Warrington site continues, again primarily for on-site captive use in the production of chemical intermediates.

Over the last decade or so, however, only limited drum quantities of 85% HTP have been provided by Solvay Interlox to aerospace and defense related companies for propulsion applications. This product continues to be available in Europe to qualified end users and can be imported into the US on an as-needed basis.

However, during this period the demand for HTP has been, in practice, very small which explains the current absence of commercial HTP production in the US.

Historically, US demand had been more significant, and both Shell Chemical Company and FMC Corporation were producers of 90% H₂O₂, the latter company also producing some 98% H₂O₂ for a period of time. Shell's hydrogen peroxide business was ultimately acquired by Interlox and FMC ceased its production of HTP in the early to mid 1980's.

Current Developments

With the recent resurgence in interest in HTP amongst the aerospace community for propulsion applications, Solvay Interlox has focussed some of its development efforts in this area. We have developed the technology to safely and economically produce up to 99% H₂O₂ and have demonstrated the technology on the pilot scale. We are currently completing hazard evaluation work on 90 - 99% H₂O₂, the results of which will enable us to analyze the safety risks associated with manufacturing, transporting, storing and using products of various concentrations in this range. This, in turn, will enable us to define the appropriate risk management measures required for an acceptably safe business.

Concentrated H₂O₂ Hazards

Following is a review of the principal potential hazards and properties of concentrated hydrogen peroxide. For purposes of this discussion, this refers to concentrations of H₂O₂ of 70% to 86%. Anyone conducting research and development work or using such material should be completely familiar with its properties and behavior and fully aware of appropriate handling, storage and disposal procedures, as well as necessary personal protective equipment. Hydrogen peroxide producers have various safety materials available to assist in this training effort.

Potential Health Effects

The potential health effects of hydrogen peroxide are essentially the same for 70% and 85% concentrations. The following excerpts are taken from Solvay Interlox material safety data sheets for a) 60 - 73% H₂O₂ and b) 84 - 86% H₂O₂.

General:

corrosive to mucous membranes, eyes and skin
the seriousness of the lesions and the prognosis of intoxication depend directly on the concentration and duration of exposure

Inhalation:

nose and throat irritation
cough and difficulty in breathing
in case of repeated or prolonged exposure: risk of sore throat, nose bleeds, chronic bronchitis
(for 85% H₂O₂) risk of pulmonary oedema
(for 85% H₂O₂) nausea and vomiting

Eye Contact:

severe eye irritation, watering, redness and swelling of the eyelids
risk of serious or permanent eye lesions
risk of blindness

Skin Contact:

painful irritation, redness and swelling of the skin
risk of severe burns

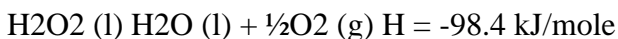
Ingestion:

may be fatal if swallowed
paleness and cyanosis of the face
severe irritation, risk of burns and perforation of the gastrointestinal tract accompanied by shock
excessive fluid in the mouth and nose, with risk of suffocation
risk of throat oedema and suffocation
bloating of stomach, belching
nausea and vomiting (bloody)
cough and difficulty breathing
risk of chemical pneumonitis from product inhalation

Whilst the effects of H₂O₂ vapor are generally only moderate at ambient temperature, the vapor above stable solutions in tanks can give rise to breathing difficulties. The mixture of oxygen and vaporized hydrogen peroxide given off during decomposition is highly irritating to the mucous membranes and respiratory tract and could be a major problem in a confined space if decomposition did occur.

Decomposition

Solutions of hydrogen peroxide always exhibit a degree of instability, regardless of the concentration, continuously decomposing to form water and oxygen with the evolution of heat.



Several factors affect the rate of decomposition, including temperature, degree of contamination, surface activity, pH, and to a lesser extent concentration. For example, the decomposition rate increases approximately 2.3 times for each 10 °C rise in temperature. However, the normal rate of decomposition for commercial grades of hydrogen peroxide stored in compatible equipment (see later for comments on class 1 materials) is extremely low, typically less than 1% loss (relative) per year.

Pure concentrated hydrogen peroxide is quite stable. In fact, concentrated H₂O₂ is generally more stable than a dilute solution (when uncontaminated). However, the particular resistance of any grade or concentration of H₂O₂ towards contamination is very dependant on the level (and type) of stabilizers used. Industrial grades of H₂O₂ (e.g. Solvay Interlox 70% Technical and Chemical grades) are stabilized with various additives in order to provide a certain level of protection against the typical (low) levels of contaminants that may be experienced during transportation and storage in standard (passivated 304 or 316 stainless steel) equipment. This stabilization, however, is not able to protect against "gross" contamination (which may mean levels below 1 ppm for certain contaminants, for example, Fe, Cu, Cr, or Mn ions, particularly in combination with each other) and in such instances decomposition of the product will commence.

In contrast, lightly stabilized H₂O₂, such as that required by aerospace applications, is much more sensitive to contamination than the industrial grades due to the very limited amount of additives present. In order to ensure adequate stability for transportation and on-site storage, the choice of acceptable materials may be more restrictive and the use of standard industry equipment may be inappropriate.

In addition to the homogeneous decomposition effects described above, users should be aware of the heterogeneous decomposition of hydrogen peroxide that occurs on all material surfaces. The magnitude of this effect can be quite large depending on the particular material and the surface condition. It is for this reason that only a few materials are suitable for long term contact with H₂O₂ (see later) and careful attention must be paid to the preparation and conditioning of these surfaces. For example, silver is one of the most active surfaces, which is actually a useful property exploited by the developers of decomposition catalyst systems for

HTP/propulsion systems. In contrast, certain grades of polyethylene and PTFE are quite inert. For any given material, smooth surfaces are always less active than rough ones. Hydrogen peroxide compatible metal surfaces always require passivation and conditioning prior to use.

When considering materials compatibility, the effect of the peroxide on the material is generally much less important than the material's effect on the peroxide. Hydrogen peroxide does not normally give rise to significant corrosion problems, although H₂O₂ can dramatically accelerate chloride ion corrosion effects on aluminum and its alloys and stainless steel. Nevertheless, peroxide can attack many materials to varying degrees and the effect should be considered in the design of equipment.

Since H₂O₂ decomposition is a significantly exothermic process (ca. 23 Kcal /mole H₂O₂ @ 25 OC), the temperature of the decomposing solution will continue to rise if the generated heat can not be effectively dissipated to the surroundings. This increase in temperature will increase the rate of decomposition resulting in a self-accelerating system or "boil-off". This applies to all concentrations of hydrogen peroxide. However, the magnitude of the consequences of H₂O₂ decomposition depends upon the initial concentration.

Large volumes of oxygen are evolved as hydrogen peroxide decomposes. If the peroxide strength is high enough, the material will boil and large volumes of steam will also be generated. For concentrations up to 64.7% H₂O₂, the maximum adiabatic decomposition temperature that may be experienced is 100 OC; i.e. there is sufficient water present to absorb the total heat of decomposition by generation of steam. For concentrations above 64.7%, the final adiabatic temperature that may be attained increases with increase in initial H₂O₂ concentration. For 70% H₂O₂, the heat of decomposition is 474 cal/g solution and the adiabatic decomposition temperature is 233 OC, with a volume expansion of 2,500 times the starting volume. For 85% H₂O₂, the heat of decomposition is 586 cal/g with a potential adiabatic temperature of 613 OC and a volume expansion ratio of 4,500.

Continuous/Emergency Venting of Tanks/Vessels

Because all solutions of hydrogen peroxide are continually decomposing, albeit at a normally very low rate, a vent should always be provided for hydrogen peroxide storage and handling systems, regardless of the amount of product that is stored - never confine hydrogen peroxide solutions, even in sample containers:

For normal/continuous venting, the following should be provided:

- a filtered vent for non pressurized systems
- a pressure safety valve for pressurized or vacuum systems

For emergency venting of concentrations up to 86%, a minimum of 200 cm² of venting for each tonne of 100% H₂O₂ equivalent should be provided through:

- a free lift manway cover for tanks
- a rupture (or bursting) disk on pressurized and vacuum vessels.

All pipelines in which hydrogen peroxide may be locked off (i.e. between valves) must be fitted with a relief valve. The cavities of valves which could trap peroxide when in the closed position should be vented. Drilled ball valves are recommended for H₂O₂ service. Lines and tanks should be designed to vent at the lowest practical pressure. They should not be allowed to experience over-pressurization.

Construction Materials

Because the effects associated with materials in contact with hydrogen peroxide can vary widely, a method of classification according to likely performance in service has been devised as follows:

Class 1: Materials that are fully compatible with hydrogen peroxide and suitable for long term contact such as storage tanks.

Class 2: Materials that are satisfactory for repeated short term contact with hydrogen peroxide prior to storage or use. Contact time should be quite short prior to storage. Contact time should not exceed four hours at 160 OF or one week at 70 OF prior to use.

Class 3: Materials that are suitable for short term contact only, prior to prompt use.

Class 4: Materials that are unsuitable or hazardous for any use with hydrogen peroxide.

The requirement for class 1 materials for long term contact is not unique to concentrated H₂O₂ and in fact applies to all concentrations. However, a material that is rated class 1 for storage of 50% H₂O₂, for example, may not carry the same rating for storage of 70% or 85% H₂O₂. For storage of high purity 70% H₂O₂ or 85% H₂O₂, class 1 materials are PTFE lined stainless steel (304L or 316L) or 99.5% aluminum. Other aluminum alloys may be used but the exact composition of the alloy can significantly impact the rate of metal pick-up and hence have an effect on the product stability and purity.

Vapor Phase Explosion (H₂O₂/Water Vapor System)

Although hydrogen peroxide is non flammable, it can nevertheless form explosive vapors under certain conditions (explosion occurring by decomposition of the vapor rather than combustion). This potential hazard is a function of temperature, pressure, and H₂O₂ liquid concentration. At atmospheric pressure, boiling 74% hydrogen peroxide (ca. 130 OC) will give a vapor just at the limit of flammability. This "lower explosive limit" for H₂O₂ vapor is 26 mole % (39 wt. %) at atmospheric pressure. For liquid concentrations higher than 74%, explosive vapors can be generated at temperatures somewhat less than their normal boiling points.

For example, for 85% liquid product at atmospheric pressure, a temperature of ca. 121 OC (ca. 250 OF) is required to generate an explosive atmosphere (cf. a

boiling point of 139 OC).

As the pressure increases, flammable atmospheres are achieved at progressively lower concentrations of boiling liquid, until a pressure of ca. 4 bar is reached. At this pressure, the limit of flammability of H₂O₂ vapor is 33 wt. %, which is in equilibrium with boiling 66.5% H₂O₂. Above 4 bar, the flammable limit of the vapor remains constant at 33 wt. % and the equilibrium liquid concentration falls very slowly as pressure increases.

Decomposition of hydrogen peroxide solutions can, of course, raise their temperature to boiling point and evaporate water and hydrogen peroxide (see above). In the absence of any other reactive substance, the concentration of the boiling peroxide always decreases. The heat of decomposition alone is insufficient to increase the liquid concentration.

Oxygen Enrichment of the Vapor Phase

The presence of hydrogen peroxide enhances the normal hazards associated with flammable liquids, vapors, and gases. This is due to the propensity of H₂O₂ to generate large amounts of oxygen in combination with a significant heating effect as it decomposes. Even if a flammable material is below its flash point and therefore normally considered to be in a safe region, the heat from decomposition of H₂O₂ could raise the material above its flash point and convert a safe system into an unsafe one.

The large volumes of oxygen generated as H₂O₂ decomposes further add to this potential problem. Oxygen enrichment greatly increases the hazards of flammable liquids, vapors and gases as follows:

1. It widens the explosive limits. It does not affect the flash point significantly, so materials below the flash point remain safe (however see comments above). The increase is into the fuel rich area.
1. It greatly reduces the energy required to produce ignition
1. It increases the rate of burning and explosion relief becomes more difficult.
1. Flame traps, flame-proofing of electrical equipment, etc. may become ineffective.

Even dilute hydrogen peroxide can create potential problems. 3% H₂O₂ generates 10 volumes of oxygen for each volume of H₂O₂ decomposed. Oxygen enrichment of confined spaces is therefore a real possibility. Dilution with copious amounts of water is the appropriate response to spillage of hydrogen peroxide. Entrapment in confined spaces must be actively avoided.

Another danger in the event of an upset is the mist explosion or torch effect when a mist or fine droplet spray of an organic liquid is discharged into an oxygen enriched atmosphere. Under these conditions an explosion can occur regardless of whether the organic liquid is above or below its flash point.

Oxygen enrichment can also render flammable some gases and vapors which are not flammable in air, for example ammonia and some halogenated organics.

Condensed Phase Explosibility (as a monoexplosive)

This refers to the ability of H_2O_2 to explode as a liquid (or solid) in the absence of organic contaminants. Over the last 60 to 70 years it has been the subject of numerous studies, which have involved the use of a wide variety of test methods (some of which were standard, many of which were not) and produced a wide range of results, some of which are mutually contradictory. In our analysis of this situation, the most credibility has been given to results from tests which have become generally accepted as standard, i.e. "detonation tube tests", which now figure in the UN book of approved methods.

70% hydrogen peroxide solutions are not explosive, even when boiling at atmospheric pressure. Strengths of 80% and above can be made to explode but only with difficulty. The current conclusion of Solvay Interlox is that 85% H_2O_2 is capable of detonation at temperatures of 45°C and above if significant initiation sources are also present. These conclusions are derived primarily from tests which employed initiation by a combination of No. 8 detonator and 50 gram booster charge. This energy of initiation is not judged to be realizable from normally encountered sources associated with chemical handling on a plant (e.g. water hammer, pump malfunction, impact, thermal shock...), rather an actual adjacent detonation would be needed (e.g. a mixture of 85% H_2O_2 /organic or some stronger H_2O_2 alone). The question of whether a H_2O_2 vapor explosion (see above) can transmit into a liquid phase detonation has been recently considered by Solvay Interlox and it is our understanding that this event is not possible, or at worst, extremely remote.

It is clear that for lower energies of initiation, the H_2O_2 strength and temperature requirements for detonation will be somewhat higher. Of interest in this sense, is initiation by a No. 8 detonator without a booster charge, which is judged representative of a safe threshold with respect to the normally encountered initiation sources mentioned above which are achievable in typical chemical handling operations. Solvay Interlox work has shown that, at ca. 75°C , 88 % H_2O_2 with 1.5g/L carbon did not detonate under the stimulus of a No. 8 detonator alone. Therefore, without an adjacent booster detonation as initiator, 85 % H_2O_2 will not pose a detonation risk at least below ca. 80°C and perhaps not even at higher temperatures.

Condensed Phase Explosibility with Organics

Hydrogen peroxide is a very reactive, extremely powerful oxidizer. The product will oxidize virtually all organic materials and it is this property which presents the most dangerous potential hazard. Explosive mixtures can be made with organics and aqueous hydrogen peroxide where the strength of the hydrogen peroxide is less than 50%. Mixtures made with higher strength H₂O₂ can have an explosives power equivalent to 100% TNT, or even close to that of nitroglycerine, and approach nitroglycerine in terms of the sensitivity to shock (see Table).

Substance	Explosive Power	Sensitivity (kg.cm.)
Nitroglycerine	52	2 - 5
85.5% H ₂ O ₂ /Glycerol	46	10 - 15
70% H ₂ O ₂ /PEG	30	22
Picric Acid	32	75
TNT	30	150

Explosion data for mixtures of organic materials with hydrogen peroxide solutions are frequently presented on ternary diagrams (see below).

Inspection of the areas delineated in the diagram above shows that so long as the aqueous H₂O₂ strength is not above 40%, or the overall amount of H₂O₂ in the mixture is below 20%, there would appear to be no risk of explosion up to moderate temperatures.

It is also clear from the diagram, that both 70% and 85% H₂O₂ are capable of generating a detonation hazard if allowed to mix with only a relatively small amount of organic material.

Secondary containment should always be provided for storage vessels and the containment area must be kept clean and free from organic material. Spills or leaks of

hydrogen peroxide should be immediately diluted with large amounts of water to prevent uncontrolled contact with organic materials.

Fire Raising Potential

Although hydrogen peroxide is non flammable, it is a strong oxidizer and can readily start fires when in contact with combustible materials, particularly solid natural materials such as wood, leather, cotton, etc. The mechanism of fire initiation has previously been considered to be due to concentration of H₂O₂ to a critical level via evaporation of water. However, a combination of decomposition of the hydrogen peroxide and oxidation of the substrate by the hydrogen peroxide may be required for effective onset of a fire⁴. In general, the higher the strength of the peroxide, the more readily fires will initiate but fires with concentrations of H₂O₂ as low as 16% have been reported. Cleanliness of all areas where hydrogen peroxide is stored and handled is key to the avoidance of fires and all spills should be immediately flushed with large amounts of water. If fires involving hydrogen peroxide do occur, they should be fought with water in order to provide both cooling and dilution and because oxygen from decomposing peroxide will cause re-ignition in flame supporting environments.

Conclusions

Hydrogen peroxide is a safe and versatile chemical if handled and stored properly. With the correct materials of construction, properly prepared and conditioned, the chemical is very storable, normally decomposing at extremely low rates.

Solvay Interlox is a global manufacturer committed to the principles of Responsible Care® and dedicated to the joint development of mutually profitable business with responsible customers.

References

1Source - SRI market report

2Clark, J.D., in "Ignition! An Informal History of Liquid Rocket Propellants", Rutgers University Press, 1971, pp. 10 - 13.

3Andrews, D., "Advantages of Hydrogen Peroxide as a Rocket Oxidant", Journal of The British Interplanetary Society, Vol. 43, 1990, pp. 319 - 328.

4Mackenzie, J., "Hydrogen Peroxide Without Accidents", Chemical Engineering, June 1990.