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Introduction

As part of Solvay's declared commitment to RESPONSIBLE CARE®, SOLVAY INTEROX works ceaselessly at minimising the risks of its products to people and the environment. These efforts include the provision of many different types of information and advice on all aspects of operations. Numerous other activities include inspections, design, analyses and trials.

Our principle is to work in partnership with customers and others to achieve our mutual objective of safe and effective peroxygen products.

This manual presents information on the safety, handling and storage of commercial solutions of hydrogen peroxide up to 70 % w/w.

Other safety information available from SOLVAY INTEROX is listed on page 26 of this manual.
Hydrogen peroxide has been produced by SOLVAY INTEROX for more than forty years, and during this time much experience has been gained in the handling, storage and use of this important industrial chemical.

In the early days of its industrial production, the principal use of hydrogen peroxide was as a bleaching agent, but in recent years many other applications have been found such as, for example, in chemical synthesis, water treatment, soil remediation, environmental applications, surface treatment of metals, electronics and disinfection.

One of the major advantages of hydrogen peroxide over most other oxidising agents used in industry is that it is non-polluting by itself since its principal reaction by-product is water.

The purpose of this publication is to provide general information and advice, which, if followed, will help the user to handle and store concentrated hydrogen peroxide solutions safely and without incident.
2. Physico-chemical properties

2.1. Physical properties

(For a more detailed account see SOLVAY INTEROX Data Manual on Hydrogen Peroxide).

Hydrogen peroxide is a clear, colourless, liquid miscible with water in any proportion. Its molecular weight is 34.02.

Hydrogen peroxide is marketed in the form of aqueous solutions and the following table shows the principal characteristics of some of these.

In addition to the Data Manual, SOLVAY INTEROX technical services are at the complete disposal of customers for further clarification of the physico-chemical data.

| % W/W H\textsubscript{2}O\textsubscript{2} content | g/100 g | 3.0 | 10.0 | 20.0 | 27.5 | 30.0 | 35.0 | 50.0 | 60.0 | 70.0 |
| % W/V H\textsubscript{2}O\textsubscript{2} content at 20°C | g/100 ml | 3.0 | 10.4 | 21.4 | 30.3 | 33.3 | 39.6 | 59.8 | 74.5 | 90.2 |

| Volume of gaseous oxygen (litre) given off per litre of solution at 20°C (0°C and 760 mm Hg or 101,325 kPa) | l/l | 10 | 34 | 71 | 100 | 110 | 130 | 197 | 246 | 298 |
| Active oxygen content | g/kg | 14.1 | 47.0 | 94.1 | 129.3 | 141.1 | 164.6 | 235.2 | 282.2 | 329.2 |
| Freezing point | °C | -1.6 | -6.4 | -14.6 | -22.6 | -25.7 | -33.0 | -52.2 | -55.5 | -40.3 |
| Boiling point at 101.325 kPa (760 mm Hg at 0°C) | °C | 100.4 | 101.5 | 103.6 | 105.5 | 106.3 | 107.4 | 113.9 | 119.0 | 125.5 |
| Density at 0°C | kg/dm\textsuperscript{3} | 1.012 | 1.039 | 1.080 | 1.112 | 1.123 | 1.144 | 1.211 | 1.258 | 1.307 |
| 25°C | kg/dm\textsuperscript{3} | 1.007 | 1.032 | 1.069 | 1.098 | 1.108 | 1.128 | 1.191 | 1.236 | 1.284 |
| 50°C | kg/dm\textsuperscript{3} | 0.997 | 1.020 | 1.055 | 1.082 | 1.091 | 1.110 | 1.171 | 1.214 | 1.260 |

2.2. Toxicological properties

Concentrations of 5 % W/W and above can cause irritation or burns, with the severity increasing with concentration.

Splashes of dilute H\textsubscript{2}O\textsubscript{2} in the eyes cause pain. With solutions of 6 % W/W and above severe and permanent damage may occur.

The ingestion of H\textsubscript{2}O\textsubscript{2} can cause burning of the mouth, throat, oesophagus and stomach, and internal distension from evolved oxygen. In some instances, ingestion of commercial strengths can be fatal.
Inhalation of H₂O₂ vapours or mists is irritating to the respiratory tract. The occupational exposure limit (TLV) is 1.0 ppm (1.4mg H₂O₂ /m³ air) for a normal 8 hour/day and 40 hour/week working period.

For further information see the current SOLVAY INTEROX MSDS.

First aid: (See page 22)

2.3. Chemical properties

Hydrogen peroxide reacts:
- as an oxidant
- as a reductant
- to form other inorganic and organic peroxy compounds
- to form addition compounds

Examples of such reactions are:

\[ \text{R-S-R} + \text{H}_2\text{O}_2 \rightarrow \text{R-S-OH} + \text{H}_2\text{O} \]

\[ 2 \text{Ce}^{3+} + \text{H}_2\text{O}_2 = 2 \text{Ce}^{4+} + 2\text{H}^+ + \text{O}_2 \]

\[ \text{UO}_2^{2+} + \text{H}_2\text{O}_2 + \text{xH}_2\text{O} = \text{UO}_4^{2-} \times \text{H}_2\text{O} + 2\text{H}^+ \]

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{COOOH} + \text{H}_2\text{O} \]

\[ 2 \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2 = 2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2 \]

2.4. Decomposition properties

A further type of reaction is its decomposition to water and oxygen represented as:

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 98 \text{kJ per gram mole } \text{H}_2\text{O}_2 \]

This can occur under various conditions which are identified hereafter.

In alkaline solution, the rate of decomposition increases rapidly as the pH is increased.

**Hydrogen peroxide and alkali must never be inadvertently mixed.**
Light can cause photochemical decomposition of hydrogen peroxide. The absorption of radiation by hydrogen peroxide solutions occurs over a wide continuous spectrum. Hydrogen peroxide solutions should not therefore be exposed for long periods to light, especially direct unfiltered sunlight.

Apart from self-heating as a result of decomposition, consideration must be given to the effect of temperature rises caused by outside sources of heat. For purely physico-chemical reasons, the rate of the decomposition reaction in solution (homogeneous) will increase 2 to 3 times for every 10°C increase in temperature, and the rate of the surface decomposition (heterogeneous) will increase 1 to 2 times per 10°C. The effect of increased contamination from dissolution of the surface can of course make the situation worse.

**Protect hydrogen peroxide from direct heat.**

Hydrogen peroxide as produced by SOLVAY INTEROX is very pure and the decomposition rate to water and oxygen is normally very low. However, if the hydrogen peroxide becomes contaminated e.g. with salts of metals such as iron, copper, chromium, vanadium, tungsten, molybdenum, silver and metals from the platinum group, then fast decomposition to water and oxygen may follow. This is known as homogeneous decomposition. The most active decomposition catalysts are those giving multivalent ions. Fast decomposition can often be caused by extremely low levels of contaminants, for example a few parts per million. This decomposition is a chain reaction in which the metallic ions are successively oxidised and reduced. This explains why it is possible for small amounts of catalyst to cause extensive decomposition of H₂O₂.

In addition, the effect of pH on the rate of decomposition of contaminated hydrogen peroxide is very marked, even in acid medium.

Fast decomposition may also occur if the hydrogen peroxide is brought into contact with insoluble solids. This is known as heterogeneous decomposition. Hydrogen peroxide will decompose to some extent on any surface even at ambient temperature, although the rate varies enormously with the nature and state of the surface. Thus, the rate of decomposition on silver is 10⁷ times faster than that, for example, on polyethylene, which is one of the common handling materials. Some of the solids which catalyse the decomposition of hydrogen peroxide are the hydroxides and oxides of the heavy metals, as well as the noble metals themselves. The following is a list of the most active catalysts:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Catalyst</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruthenium oxide</td>
<td>RuO₄</td>
<td>Platinum</td>
<td>Pt</td>
</tr>
<tr>
<td>Manganese oxides</td>
<td>Mn₂O₃, MnO₂</td>
<td>Osmium</td>
<td>Os</td>
</tr>
<tr>
<td>Iron oxides</td>
<td>FeO, Fe₂O₃</td>
<td>Iridium</td>
<td>Ir</td>
</tr>
<tr>
<td>Cobalt oxide</td>
<td>CoO</td>
<td>Palladium</td>
<td>Pd</td>
</tr>
<tr>
<td>Nickel oxides</td>
<td>NiO, Ni₂O₃</td>
<td>Rhodium</td>
<td>Rh</td>
</tr>
<tr>
<td>Lead oxide and hydroxide</td>
<td>PbO, Pb(OH)₂</td>
<td>Silver</td>
<td>Ag</td>
</tr>
<tr>
<td>Mercuric oxide</td>
<td>HgO</td>
<td>Gold</td>
<td>Au</td>
</tr>
</tbody>
</table>
These are most active when their specific surface is large as with, for example, colloids and powdered metals. Due to their high activity, some of the metals and oxides in the above tables are used as catalysts when rapid decomposition is required in the use of hydrogen peroxide as a power source, as, for example, in rocket motors. In addition even “compatible” materials of construction can cause accelerated decomposition if the surface is of inadequate quality or has not been properly prepared.

**Never allow hydrogen peroxide to become contaminated.** Bring hydrogen peroxide into contact only with SUITABLY PREPARED compatible materials.

SOLVAY INTEROX adds stabilisers to keep decomposition to a minimum. These are generally of two types, complexing/chelating, and colloidal, which either neutralise small amounts of colloidal catalysts or adsorb/absorb impurities.

### 2.5. Effects of decomposition

Even at low dilutions, hydrogen peroxide will decompose continuously into water and oxygen. This rate is very low when hydrogen peroxide is stored in approved materials and is kept free from contaminants. However, if oxygen pressure is not relieved, then high gas pressure may build up.

**Never store hydrogen peroxide in hermetically sealed containers.**

The decomposition of hydrogen peroxide is exothermic and also the rate of decomposition increases with increasing temperature. If the heat of decomposition is not removed at the rate at which it is developed (by heat loss to the surroundings or cooling), the temperature will rise and the rate of decomposition will increase. This can result in a self-accelerating decomposition which, in the case of badly contaminated solutions, may culminate in extremely rapid decomposition or “boil off”.

**Keep the temperature of a storage tank under surveillance.**

Even after the total decomposition of solutions containing up to 64 % W/W hydrogen peroxide, liquid water is still present. Because of this, the final temperature cannot exceed the boiling point of water at the pressure of the system. But under adiabatic conditions the total decomposition of solutions containing over 64 % W/W develops sufficient heat to evaporate all the water to steam and superheat it. For example, if decomposition is complete, and there are no heat losses (i.e. adiabatic), 70 % W/W hydrogen peroxide can reach a temperature of 240°C (513 K). One volume of 70 % W/W solution, when decomposed totally under adiabatic conditions and atmospheric pressure, will produce about 2,500 volumes of gas (see diagram on page 9).

**Design of tanks should allow for adequate venting capacity to permit gases and vapours to escape in case of serious decomposition.**
Volume Expansion Ratio on Total Adiabatic Decomposition of Liquid at Constant Pressure and Initial Temperature of 20°C (293.15 K)

2.6. **Spontaneous combustion of organic substances**

Hydrogen peroxide can cause spontaneous combustion of many organic materials, such as cloth, paper, wood, etc. Even dilute commercial solutions can concentrate by evaporation and spontaneous combustion may occur after a delay period. This effect is common in hot climates.

**Spilt hydrogen peroxide must never be allowed to evaporate but must be diluted with water immediately.**

2.7. **Explosive characteristics**

Commercial hydrogen peroxide solutions up to 70 % W/W are not in themselves explosive.

However, explosions may occur under certain conditions when aqueous hydrogen peroxide of more than 44 % W/W is mixed with organic compounds to form a single phase, emulsion or suspension. The most important factors which govern whether or not an explosion occurs are:

a) the concentration of hydrogen peroxide, water and organic material present,

b) the nature of the organic material,

c) the presence of an initiation source,

d) the temperature of the mixture.

This hazard can occur when using \( \text{H}_2\text{O}_2 \) even at less than 44 % initial concentration, if there is a potential for the concentration to subsequently increase, e.g. by water evaporation.

In addition, hydrogen peroxide reacts with certain organic compounds to form organic peroxides which may themselves have explosive properties. Explosions may also occur if hydrogen peroxide is brought into contact with certain incompatible inorganic materials such as powerful reducing or oxidising agents.

Decomposition of hydrogen peroxide can lead to oxygen enrichment of the atmosphere above it. Under certain conditions, e.g. in the presence of flammable liquids or flammable gases, this can lead to a high risk of fires or vapour phase explosions.

**Investigation of new applications involving hydrogen peroxide and other chemicals should be carried out on a small scale, with adequate precautions taken for dealing with uncontrolled and potentially explosive reactions.**

**If you are in doubt about the safety of your hydrogen peroxide application, then consult SOLVAY INTEROX.**
3. Transportation and packaging

Regulations place various constraints on the way in which hydrogen peroxide solutions can be packed, transported and handled.

It is essential that every person responsible for the transport and handling of these solutions should ensure compliance with the relevant regulations. For instance, under no circumstances should hydrogen peroxide be sent via mail or courier services.

Transport regulations are primarily concerned with the nature and marking of containers, loading methods, vehicle equipment, transport documents, etc. Many countries have signed international agreements concerning the various means of transportation and these agreements apply if transportation takes place over the territory of at least two of the contracting countries.

These agreements include

RID - International regulations concerning the carriage of dangerous goods by rail; forming Annex 1 of the International Convention concerning the carriage of goods by rail (C.I.M.).

ADR - European agreement concerning the carriage of dangerous goods by road, drawn up by the UN Economic Commission for Europe.

IMO - International Maritime Dangerous Goods code, drawn up by the INTERNATIONAL MARITIME ORGANISATION.

ICAO - Technical Instructions for the Safe Transport of Dangerous Goods drawn up by the INTERNATIONAL CIVIL AVIATION ORGANISATION.

National regulations may differ from one country to another, and are being revised continuously. Customers who wish to transport hydrogen peroxide within particular national boundaries should refer to the national regulations which are applicable.

Many countries have drawn up regulations on marking, labelling and packaging of dangerous substances within the framework of safety at work regulations. Reference should be made to national provisions on this subject.

The European Union member states have adopted directive 67/548/EEC, brought up to date regularly, which defines the form and nature of markings relating to the product, the manufacturer, the risks of the product and advice on precautions to be taken.
4. Storage

Hydrogen peroxide can be delivered in small packs, in intermediate bulk containers (IBCs) or in bulk quantities by rail, road tankers, or in ISO tank containers.

Small containers and IBCs should be stored unopened, in an upright position and taking account of good warehousing practice with respect to stacking height. The breather vents must not be blocked. Storage should be such that faulty containers can be easily detected and removed. They must never be rolled or laid on their side. They may be stored in a building with a concrete floor slightly inclined towards drainage and designed in the form of a shallow sump about 10 cm deep and with a small drive-on ramp to the threshold. The storage area should normally be unheated and adequate ventilation ensured. Although heat sources are to be avoided, in certain circumstances such as extreme climatic conditions, heating may be required, but H₂O₂ containers must not be placed unduly close to sources of heat. Containers may be stored outside, preferably protected from direct sunlight. A canopy may be required in hot, sunny climates. The storage area must be kept clean and free from combustible materials and other incompatible chemicals. A water hose should be available for flushing away spillages and leaks to a safe place. A safety shower and an eye bath should be provided for treatment of personnel who come into bodily contact with hydrogen peroxide. Pipelines, especially those carrying chemicals, must not pass through the storage area.

Returnable empty containers should be kept closed and clean and returned to the storage area as soon as possible. They should not be washed out except with non-contaminated water.

**Hydrogen peroxide containers must never be used for the storage of other materials.**
In addition to local regulations for storage on site, SOLVAY INTEROX recommends a contained concrete area with drain. The storage area, preferably outdoors, must generally conform to agreed standards of accessibility and cleanliness. Particular care should be taken to ensure that the ISO tank cannot be damaged by passing vehicles.

Care must also be taken to ensure that the manhole is kept closed, to avoid sources of contamination. The breather vent must not be blocked or obstructed, otherwise overpressurisation can occur.

ISO tanks must never be washed out or used for the storage of other materials or for any other purpose.

If there are any doubts about procedures with ISO tanks, SOLVAY INTEROX should be consulted.

With an annual usage requirement of, say, 50 tonnes or more of hydrogen peroxide solution, it may become economical to construct a bulk storage unit.

\( \text{H}_2\text{O}_2 \) storage tanks comprise numerous specific design features and fittings. Similarly, associated pipework, pumps, ancillary equipment and instruments are highly specific to \( \text{H}_2\text{O}_2 \).

Other important considerations are the layout and installation, which require expert advice. Factors such as statutory requirements, tank location, correct materials of construction, and preconditioning of equipment to receive hydrogen peroxide are also important.

We strongly recommend that customers planning a storage unit consult SOLVAY INTEROX.
An engineering code of practice and designs for standard tanks of various sizes have been developed by SOLVAY INTEROX.

The site should be chosen so as to avoid contamination and contact with incompatible chemicals, and yet be convenient to the areas of usage. It is preferable, in the interest of safety, that the storage vessel be outdoors. An adequate water supply must be available for eye baths, safety showers and normal washing down, and where appropriate this should be frost protected. For emergency flooding non-contaminated water should be used. Where there is a risk of public access, security fencing and clear marking are required.

The size and material of the tank should be discussed with SOLVAY INTEROX. Features for horizontal and vertical metal storage tanks are shown on these two pages.

It is essential that the tanks be built only by firms which are able to meet the highly specific requirements for producing compatible high integrity tanks and fittings.

The minimum equipment for a hydrogen peroxide storage tank includes a combined manhole and emergency vent, a breather vent with filter, an overflow pipe with downcomer, a level indicator, a filling connection, a hydrogen peroxide outlet, a temperature indicator, drain valve and a bund.

Typical features for a hydrogen peroxide tank (basic equipment)

1. Manhole and emergency vent
2. Overflow pipe with downcomer
3. Level indicator (with alarm)
4. Filling connection
5. Hydrogen peroxide outlet
6. Bund
7. Vent with filter
8. Temperature indicator
9. Drain valve
10. Watersupply for shower, eyewash or spillage dilution
Additional features include level indicator and temperature indicator alarms. These are recommended for safety reasons. Some tanks are also fitted with a dilution connection and a mixing device. Alarm switches and thermometers must not be of the mercury type, and no oil should be used in the thermocouple well.

**The manhole cover assembly should be adequate to provide relief in case of decomposition (recommended minimum surface area is 200 cm² per tonne of 100% hydrogen peroxide).**

It is desirable that manholes be fitted with a loose aluminium or stainless steel wire mesh cover to prevent large objects such as inspection torches, safety helmets, tools and spectacles falling into the tank.

If tanks are fitted with an emergency flooding connection, care must be taken to ensure that it cannot provide a source of contamination. The point of connection to the emergency water supply should be located to allow water introduction during a decomposition without risk to personnel.

Tanks should be surrounded by a retaining wall or bund which is capable of containing at least the whole content of the tank in case of rupture, and in any case comply with local regulations.

Catwalks and rails are not shown, but should be included where necessary. The tank should be labelled as required (e.g. warning signs, product name and concentration) and the tanker coupling should also be clearly marked, to prevent delivery of a different substance which could be extremely dangerous.

**Typical features for a hydrogen peroxide tank (fully equipped)**

1. Manhole and emergency vent
2. Overflow pipe with downcomer
3. Level indicator (with alarm)
4. Filling connection
5. Hydrogen peroxide outlet
6. Bund
7. Vent with filter
8. Temperature indicator (with alarm)
9. Spare branch
10. Sparge (optional)
11. Drain valve
12. Water connection
All transfer lines should be self-draining. Preferably the lines should not pass over wooden floors or other combustible areas. Particular care should be taken to prevent the liquid in the receiving vessel being returned into the upstream pipework and storage tank by siphoning or any other means. A siphon breaker must be fitted if such an event is considered to be a possibility. Flange bolts and gaskets should not be greased.

Minimize the number of valves although more than one valve is usually necessary on the outlet systems of static storage tanks, and arrangements to prevent pressure build up between valves must be made. Only valves that are capable of venting gas should be used (see page 20). Valves located in the bund should be installed so that they can be reached from outside the bund.

The design should avoid any possibility of pumping against a dead end (see pages 20 and 25).

**Trapping of hydrogen peroxide between valves and in pumps must be avoided.**

The flow of hydrogen peroxide from large storage vessels may be measured in a number of ways, for example, via a dynamic flow meter or measuring tanks. These arrangements should be discussed with SOLVAY INTEROX when the installation is designed.

The cleaning and passivation of metallic tanks and all other components of these installations is a specialist operation and should be discussed with SOLVAY INTEROX.

Small containers must not be emptied by pressurising them. They may be emptied by pouring, siphoning or pumping out.

ISO tank containers are usually equipped with a top discharge. They can be emptied by a pump or by pressurising the container in accordance with the supplier’s instructions. The gas (either compressed air or nitrogen) must be clean and free from oil.
5. Product handling

Hydrogen Peroxide should only be handled by trained personnel who are well aware of its hazards and the necessary safety precautions.

Hydrogen peroxide should be handled with care so that no product is spilled during unloading or transfer. If spillage does occur, it must be diluted with water and cleaned up thoroughly, ensuring that all cleaning equipment is thoroughly rinsed after use.

Hydrogen peroxide should be kept in its original container. Handling and transferring must be done only with approved dedicated equipment made of compatible material (see section 6). Once hydrogen peroxide has been drawn from a storage container, it must not be returned since it may have become contaminated.

Hydrogen peroxide must be kept away from heat sources. Hydrogen peroxide should not be contaminated during storage and handling, and contact with incompatible surfaces must be avoided. Scrupulous cleanliness is required when handling solutions of hydrogen peroxide.

Apart from dilute products sold generally in small packs, commercial solutions of hydrogen peroxide present little or no risk of freezing in temperate climates and thus no special protection against frost needs to be taken, except in extreme climates (See page 5, section 2.1., for freezing points).

Dilution water (even some tapwaters) may destabilise $\text{H}_2\text{O}_2$.

**SOLVAY INTEROX should be consulted when hydrogen peroxide is to be stored at a low concentration after dilution by the user.**

All tanks and small packages should be maintained in an upright position during the transfer operation and should not be jolted violently. Neglect of these simple rules can lead to spillages, which may subsequently give rise to hazardous situations.
6. Construction materials for storage and handling of hydrogen peroxide

The selection of materials of construction for equipment to be used in service with hydrogen peroxide must be undertaken with care, otherwise decomposition problems will be encountered.

In cases of doubt, assume incompatibility.

The information given below may not apply to special grades of hydrogen peroxide; for these SOLVAY INTEROX should be consulted.

Many common materials of construction such as iron, steel, copper, brass, nickel and chromium are not suitable for handling solutions of hydrogen peroxide, and recommended materials must be used.

Suitable grades of metals for service with hydrogen peroxide are indicated below.

Aluminium of 99.5 % minimum purity and certain Al-Mg alloys can be used for long duration storage of concentrated hydrogen peroxide, but they are expensive and difficult to fabricate. SOLVAY INTEROX hydrogen peroxide, as delivered, will not significantly corrode aluminium over long periods, and the corrosion products do not seriously affect the stability of the chemical. However, in the presence of chloride ions, serious pitting can occur, so contamination with chlorides from, for example, dilution water must be avoided.

For fabrication work, argon shielded arc welding methods are used with rods of parent metal, with care taken to avoid impressing impurities into the soft metal. It is essential to use only approved fabricating companies.

Fully austenitic stainless steels may be used in service with hydrogen peroxide, including storage. However, it must be emphasised that special care is needed with finishing and treatment of surfaces, welding, and stabilisation systems because, if corrosion should occur, the corrosion products would be powerful catalysts for hydrogen peroxide decomposition. The preferred grade of stainless steel for storage and transport vessels is 304 L, 316 L. Equivalents which conform to the alloy composition are also acceptable.

Welding quality and surface finishing are very important, and pre-polished plate is preferred. The welding should be by inert gas shielded processes. Metal inert gas (M.I.G.) is preferred. If other processes are to be used, consult SOLVAY INTEROX first. All welds and weld splashes should be ground and polished to match the surface finish of the plate.
SOLVAY INTEROX have developed detailed engineering codes and specifications covering the fabrication of hydrogen peroxide storage equipment. Advice and assistance are available on request.

Metallic materials have contaminants loosely adhering or sometimes embedded in the surface, and before being used in service with hydrogen peroxide they must be subjected to some, if not all, of the following processes: cleaning and degreasing with detergent, pickling to remove metal and impurities, passivating and conditioning.

Customers should consult SOLVAY INTEROX concerning the precise details of these treatments.

Plastic tanks are suitable for up to 50 % W/W hydrogen peroxide provided they are made of correct polymeric material.

They are subject to embrittlement, environmental stress cracking and “ageing”. They are more susceptible to physical damage than aluminium or stainless steel tanks. Their physical properties can be seriously affected by extremes of ambient temperature, and it is difficult to obtain satisfactory quality control during fabrication.

Customers should consult SOLVAY INTEROX concerning the design characteristics of plastic storage tanks and the type of plastic used.

Piping from plastic tanks may be in aluminium or stainless steel.

Some fluorinated plastics and rubbers can be used in service with hydrogen peroxide, for example, polytetrafluoroethylene, polyvinylidene fluoride such as Solvay SOLEF®, and a co-polymer of vinylidene fluoride and hexafluoropropylene such as VITON®

Plastic compatibility can be grade dependent between suppliers, and the nature of fillers, pigments and other additives is important.

White chemical porcelain and borosilicate glass are both compatible with hydrogen peroxide and are widely used for small scale laboratory apparatus. Due to the risk of breakage, these materials are not generally recommended for large scale apparatus or plants.

Most common lubricants are incompatible with hydrogen peroxide because they can form hazardous peroxide/organic mixtures. This problem may be overcome, for example, by using fluorinated oils, but then these oils tend to be poor lubricants.
Compatible materials of construction must be used for all contact surfaces and all non-contact surfaces where exposure is both foreseeable and dangerous.

SOLVAY INTEROX does not recommend the use of pumps with packed glands but instead advises the use of pumps with mechanical seals. The use of seal faces of ceramic on the one side and glass or ceramic filled PTFE on the other is advised.

The recommended material of construction for pumps is austenitic stainless steel (304L or 316L), although PTFE pumps are acceptable. In diaphragm pumps, a pressure burst may occur if the diaphragm fails. On such pumps, provision should be made for pressure relief on the non-peroxide side of the diaphragm.

For high strength hydrogen peroxide, i.e. above 50 % W/W, the use of double diaphragms with compatible buffer fluid and leak detection is advised.

SOLVAY INTEROX recommends ball-valves with suitable venting arrangements for releasing potential pressure build-up from the decomposition of hydrogen peroxide trapped in the valve. Diaphragm valves can be dangerous if hydrogen peroxide gets into the bonnet, and hence the valve bonnets must be drilled. Plug-type valves need a lubricant, and therefore SOLVAY INTEROX does not advise the use of this type of valve.

Acceptable valves have a seat, usually polytetrafluoroethylene, and a small hole drilled in the ball so that in the off position the channel through the ball is in communication with the shut-off higher pressure side.

Gaskets may be made from polyethylene or polytetrafluoroethylene (PTFE). Compressed asbestos fibre (CAF) gaskets may only be used in a PTFE envelope.
hydrogen peroxide
solution containing up to 70% wt/wt hydrogen peroxide

warning
- Strong oxidant.
- Can cause eye damage and skin burns.
- Reacts with many substances generating heat with fire risk.
- Can decompose generating gas with risk of bursting.

Always have an adequate supply of water readily available.

recommended practice
- Wear safety goggles and gloves. If there is a splashing risk wear face shield, plastic apron and boots.
- Have eye bath available and safety showers if possible. Ensure there is adequate ventilation where peroxide vapours may occur.
- Have water hoses available for fire fighting. Wash spilled peroxide away from handling and storage areas with plenty of water.
- Store in original container in a cool place. Keep containers upright. Ensure vents remain effective.
- Keep storage area free of combustible materials. Use it for peroxide storage only.
- Use clean vessels and equipment constructed from compatible materials. Empty all containers and drain equipment after use. Wash out with water.
- Ensure that peroxide does not become contaminated. Do not return unlabelled product to original container. Dilute it with plenty of water and flush to drain.
- Wash contaminated materials at once. On no account allow them to dry out before rinsing (e.g., clothing).
- Use only vessels or containers fitted with a safety vent in operable condition. Do not confine peroxide in any enclosed spaces (e.g., between closed valves).
- Use clean vessels and equipment constructed from compatible materials. Empty all vessels and drain equipment after use. Wash out with water.
- Use clean vessels and equipment constructed from compatible materials. Empty all vessels and drain equipment after use. Wash out with water.
- Use clean vessels and equipment constructed from compatible materials. Empty all vessels and drain equipment after use. Wash out with water.

emergencies

contact with skin
- Wash affected skin with plenty of water.
- Remove contaminated clothing immediately.
- In case of burns or shock, seek medical attention.

contact with eyes
- Wash out immediately with plenty of water.
- Continue washing for at least 15 minutes.
- Seek medical attention.

leak or spill
- Drench with water. Wash the liquid off all contaminated surface with plenty of water.
- Remove all contaminated clothing and other combustible materials.
- Do not attempt to recover spilled liquid.

fire
- Drench with water only. Do not use foam or dry chemical extinguishers.
- Drench adjacent containers with water by spraying with water.
- Keep adjacent containers cool by spraying with water.
- Keep adjacent containers cool by spraying with water.

ingestion
- Drink plenty of water.
- Seek medical attention.

inhalation
- Move the victim out into the fresh air. Wear an independent breathing apparatus.
- In case of suffocation, seek medical attention.

All information in this document is given in good faith and from best knowledge available. National or local regulations must always be applied.

Emergency telephone No: 00/44/1925/31 200
For detailed information please apply to: SOlVAY INTEROX LIMITED
Baronet Works - Baronet Road
GB - Warrington (Cheshire) WA4 6HB
Tel: 44/1925/651277
Fax: 44/1925/655856
Telex: 0151/627834 SOLIX G
7. Personnel safety instructions

See the SOLVAY INTEROX-Hydrogen Peroxide Safety Data Sheet (MSDS) for further information.

The most important safety points mentioned in this section have been summarised on the SOLVAY INTEROX Hydrogen Peroxide Safety Poster which is available on request.

As a minimum, personnel handling hydrogen peroxide must wear long-wristed plastic gloves and suitable eye protection. PVC aprons are also recommended.

If there is any risk of splashing, then a protective face mask, full body protection, and suitable boots made of polyvinylchloride or rubber must be worn.

Pipetting of commercial solutions should be done mechanically and not by mouth.

Eye wash bottles and showers must be available in sufficient number in the storage and working areas.

The effect of hydrogen peroxide solutions on skin and mucous membranes depends on the concentration, but increases also as a function of the time of contact. Hence, the first immediate action in the event of any skin contact with hydrogen peroxide is repeated rinsing of the affected area with clean water.

In case of splashes in the eye, the opened affected eye must be rinsed with clean water, initially with an eye wash bottle. Rinsing must be done immediately and continuously for at least 15 minutes after which medical advice should be obtained.

Any clothing which has been in contact with hydrogen peroxide must be immediately drenched with water. When large areas of clothing have been wetted with hydrogen peroxide, it is recommended that the clothing be removed under a running shower and then rinsed thoroughly. Never let hydrogen peroxide-contaminated clothing dry without washing since there may be a risk of spontaneous ignition at a later time. Spillage onto or inside shoes is especially dangerous.

In cases of accidental ingestion, it is recommended that copious amounts of water be drunk, and that vomiting NOT be induced. Medical advice must be sought.

Fresh air is the best answer to respiratory irritation caused by hydrogen peroxide. An unconscious person should be brought into the open. Rescuers should wear suitable air-masks if necessary. Medical advice must then be sought.
8. Some common types of incidents

If the precautions outlined in the previous sections are followed, then incidents or accidents with hydrogen peroxide are unlikely to occur. However, it may be helpful to the user to know what types of incident may arise and how best to deal with them. The single most important requirement is to have preplanned emergency procedures. SOLVAY INTEROX can help in defining these.

Personnel called upon to deal with incidents must wear suitable protective equipment.

8.1. Emergency procedures

Small containers used by SOLVAY INTEROX are usually of polyethylene and of a capacity of 25-60 litres. A container may leak because it has been subjected to unduly high mechanical stress such as, for example, by being stacked with too heavy a top loading, or being subjected to a severe mechanical blow from a crane or fork-lift truck. Alternatively the container may have been punctured by a nail or a sharp protrusion.

The container may also leak because it has been tipped over so that the breather vent is covered by liquid. In this position liquid will escape through the vent if there is any slight rise in pressure in the container.

As soon as a leak is discovered it must be dealt with promptly.

If the container is simply leaking through its vent as a result of having been tipped on its side, then the only action required will be to restore it to a vertical position and to wash the outside of the container and the surrounding area with copious quantities of water.

If the container is obviously damaged, the contents should be diluted with large quantities of water and run to a safe draining location for disposal.

Whilst leaks in pipeline flanges and in ancillary equipment, such as pumps, may occur from time to time, leaks in the wall of static storage tanks are exceedingly rare.

If the leak is large and serious, and cannot be safely stopped by isolating valves, then copious amounts of water should be directed into the affected area.

Care should be taken to introduce a minimum of contamination during repairs. It is essential that the repaired section be properly cleaned and passivated before being put back into service.
If a plastic container appears to be bulging then this is an indication of high internal gas pressure. This may occur after very long storage with a blocked or faulty vent. Alternatively, it may be the result of excessively high decomposition taking place. In such an event the container will at first start to bulge and may eventually rupture. A situation such as this must, therefore, be treated with extreme caution.

The container should not be approached except by competent personnel who are wearing full protective clothing.

The ultimate risk is a violent bursting of the container and widespread ejection of liquid. The first step is to assess the situation from a safe location. Any of the following indications should be considered as a sign of danger, in which case nobody should approach the package.

- noise e.g. gas escaping;
- visible signs of advanced decomposition e.g. steam, liquid escape from vent;
- severe distension of the package;
- increasing extent of distension.

In the absence of any of the above indications then a trained, fully protected person may approach and carefully remove the cap (which may in itself result in an emission of liquid). If any of the danger signs develop, the container must be abandoned. If there are signs, but the situation remains unchanged for a period of 1 day, then the pack should be sprayed with water, before removing the cap as above. If there are any signs of decomposition (e.g. bubbling, warm to the touch), after removing the cap, then the contents should be diluted to drain with copious quantities of water.

Decomposition and subsequent self-heating in tanks can occur if the tank contents become contaminated with a decomposition catalyst. Such catalysts may be introduced in a number of ways, for example:

a) Tools or equipment accidentally dropped into the tank.

b) Airborne contaminants entering the tank, e.g. via an open manhole.

c) Process liquors possibly flowing back into the tank.

d) Contaminated hydrogen peroxide being returned to the tank.

e) Incompatible fittings.

f) Contamination via poor quality dilution water or mixing air.

The first indications of decomposition are that the temperature of the tank contents will start to rise above ambient. Decomposition is normally slow in the early stages and can possibly be controlled by cooling the outside of the tank. After a certain stage when the temperature of the tank contents is rising fast, decomposition can be very rapid and is likely to result in gas evolution, foaming and spraying of hot liquid over a wide area. If the venting facility is not adequate this may lead to pressure build up and even tank rupture.
Under no circumstances should the tank be approached if gassing or jetting is occurring, or if there are any other indications of advanced decomposition, e.g. noise or high temperature.

However, the activation (from a safe location) of a safety system such as dousing or dumping may be carried out. SOLVAY INTEROX will help to define such safety systems.

No attempt should be made to transfer or use decomposing product. It must be diluted and disposed of safely. The tank must not be used for hydrogen peroxide again until the cause of the decomposition has been established and the tank subsequently cleaned and repassivated, if necessary.

Customers should consult SOLVAY INTEROX if poor stability is suspected.

8.2. Other aspects

Hydrogen peroxide solutions, if confined between closed valves, can lead to a pressure burst even when uncontaminated. The problem can be overcome by a number of methods:
- vents,
- pressure relief valves,
- elimination of valves where possible, and locking open certain valves during normal running, where appropriate.

Vents and pressure relief valves must be in suitable materials and directed to a safe place.

Even non-contaminated hydrogen peroxide solutions, in ball valves or diaphragm valves, may lead to pressure bursts if the ball or the bonnet are not vented (see section 6).

If hydrogen peroxide is pumped against a dead end (e.g. closed valve) the heat generated can lead to rapid decomposition with gas evolution, and a pressure burst can subsequently follow. Steps must be taken during the design (e.g. no-flow trip, kickback line or pressure relief) to avoid this happening.

Fires caused by hydrogen peroxide and combustible materials should be fought with water.

In most countries there will be statutory regulations governing the disposal of hydrogen peroxide. Solutions containing less than 0.1 % W/W can normally be flushed down drains. However, in certain cases it may need to be more diluted.
9. Further information

1. SOLVAY INTEROX - Hydrogen Peroxide Material Safety Data Sheet (MSDS).
2. Wall Poster.
4. Design Manual for H₂O₂ bulk storage and handling.
7. Fire and explosion hazards associated with the storage and handling of H₂O₂. R. Merrifield, HSE Technology Division, SIR N° 19.

For further information or detailed technical documentation, please contact your local SOLVAY INTEROX office. (See the complete list of addresses on the opposite page).