6. Safety

Hydrogen peroxide has a high energy content:

$$H_2O_2(l) \longrightarrow H_2O(l) + 1/2\,O_2(g) \quad \Delta H = -98.30\ \mathrm{kJ/mol}$$

Furthermore, its high oxygen content (47 wt%) is available for combustion reactions and the oxidation of organic compounds. This means that special safety conditions apply in handling hydrogen peroxide. Safety studies can be divided into three groups:

1) examination of the pure vapor phase,
2) examination of the pure liquid (aqueous) phase, and
3) examination of mixtures or solutions of organic compounds with or in aqueous hydrogen peroxide.

Results are summarized below, but the literature must be consulted for details. In specific cases, especially when hydrogen peroxide is used with organic compounds, the intended work area must be checked for hazards if it has not already been certified as safe by a safety examination.

Pure Hydrogen Peroxide—Vapor Phase [5], [116]–[119]. Explosive vapor mixtures are formed at atmospheric pressure when the hydrogen peroxide concentration in the vapor phase exceeds 26 mol%. Figure 16 shows the explosive range as a function of temperature and hydrogen peroxide concentration.

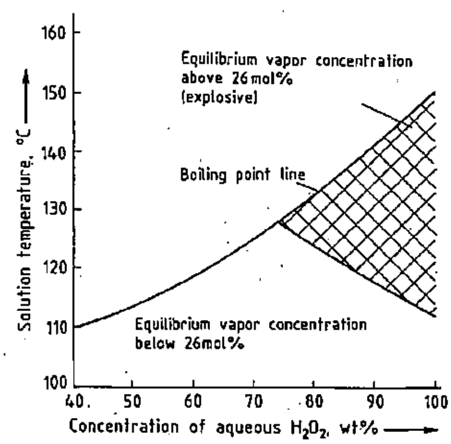

Figure 16. Dependence of the explosive range of the vapor phase (> 26 mol% H_2O_2) on the temperature and the hydrogen peroxide concentration of liquid phase (at atmospheric pressure)

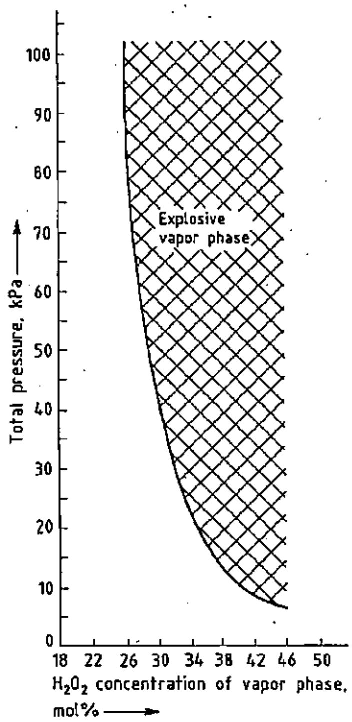

Figure 17. Dependence of the explosive range of vapor phase on pressure

For the industrial concentration of hydrogen peroxide solutions, it is important to note that at reduced pressure the critical hydrogen peroxide concentration of the vapor phase may exceed 26 mol% (Fig. 17).

Pure Hydrogen Peroxide—Liquid (Aqueous) Phase [120], [121]. The explosive risk of pure, highly concentrated hydrogen peroxide solutions has been examined by various methods, but the sometimes contradictory findings are difficult to interpret consistently.

Results are influenced primarily by test conditions and not by hydrogen peroxide concentration. For example, 90.7 wt% hydrogen peroxide in a tube with an internal diameter of 2.67 cm (1.05 inches) could not be exploded by the detonation shock of a tetryl booster, whereas explosion occurred in a tube with an internal diameter of 4.09 cm (1.61 inches). Similarly, 86% hydrogen peroxide in a tube of 4.09 cm internal diameter was exploded by raising the

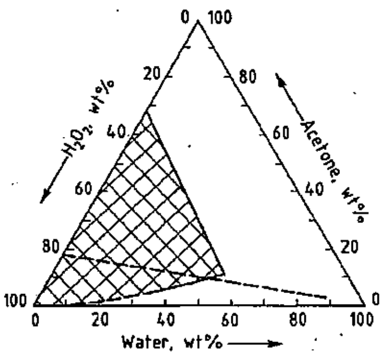

Figure 18. Explosive range (hatched area) of hydrogen peroxide–acetone–water mixtures
Dashed line, indicates the stoichiometry
$8\,H_2O_2 + CH_3COCH_3 \longrightarrow 3\,CO_2 + 11\,H_2O$

temperature above 50 °C [120], [121]. The decisive factors for explosion of pure aqueous hydrogen peroxide seem to be the degree of occlusion, the insulation, and the energy of detonation.

Mixtures or Solutions of Aqueous Hydrogen Peroxide with Organic Compounds [122]–[124]. The hazards associated with mixtures of hydrogen peroxide and organic chemicals are important for its industrial production and, especially, for its uses. As an example, Figure 18 shows results obtained with the hydrogen peroxide–acetone–water system [122]. Many other organic compounds give similar results. The size of the explosive region depends on the organic compound and the test conditions.

For practical use, safety tests of the intended working area are very important. When systems such as hydrogen peroxide–formic acid–water are used, other products may be formed (in this case performic acid), that are more dangerous than the original mixture [123].

7. Uses

Development of the AO process permitted large-scale production of hydrogen peroxide, which is now used widely in almost all industrial areas. Its main use is in bleaching (→ Bleaching, **A4**, p. 194). Uses in the chemical industry and in environmental protection are increasing because its great advantage is that the degradation product is water.

Hydrogen peroxide is used in the textile industry for bleaching cotton, linen, bast fibers, wool, silk, polyester fiber, and polyurethane fiber. In the pulp and paper industry, it is used to bleach sulfate and sulfite cellulose, wood pulp, and wastepaper, and to brighten wood veneers and wooden structures.

The chemical industry employs hydrogen peroxide for the production of peroxy compounds such as sodium perborate, sodium percarbonate, metallic peroxides, or percarboxylic acids. Hydrogen peroxide is very important in organic chemistry for epoxidation and hydroxylation (manufacture of plasticizers and stabilizers for the plastics industry), oxidation (manufacture of amine oxides as washing-up liquids), oxohalogenation, and initiation of polymerization.

Sulfuric acid solutions of hydrogen peroxide are used for the pickling and chemical polishing of copper, brass, and other copper alloys, as well as for etching and cleaning printed circuit boards. Highly purified hydrogen peroxide is used in the manufacture of silicon semiconductor chips to clean silicon disks and to remove photoresist layers. It is also used for in situ leaching in underground uranium mining.

Hydrogen peroxide is increasingly used in environmental protection to detoxify effluents containing formaldehyde, phenols, or cyanide (e.g., wastewater from mines and tempering works, galvanizer concentrate, photochemical effluents), and to deodorize sulfur-containing effluents. Smoke and exhaust gases containing sulfur dioxide can be completely detoxified with hydrogen peroxide.

Hydrogen peroxide is a highly efficient disinfectant (especially for packaging materials); it is also used as a bleaching agent in hair preparations and as a propellant in space technology.

8. Toxicology and Occupational Health

Toxicity in Humans. In humans, brief contact of hydrogen peroxide with the skin leads to irritation and whitening (cutaneous emphysema), the severity of which depends on concentration. Longer contact or higher concentration can lead to burns.

Contact with the eyes also leads to serious injury. Hydrogen peroxide vapor or aerosol causes irritation or damage of the upper respiratory tract and serious lung injuries [125], [126]. The human reaction to the irritating effect of hydrogen peroxide on the mucous membranes and skin is far more sensitive than that of the rat. The threshold concentration for acute irritative effects of gaseous hydrogen peroxide on the respiratory tract is 60 mg/m^3 in rats but only 10 mg/m^3 in humans; the corresponding values for skin are 110 mg/m^3 for rats and 20 mg/m^3 for humans [127].

Accidental ingestion of hydrogen peroxide (33 wt% solution) in five cases led to stomach and chest pain, respiratory depression, foaming at the mouth, and loss of consciousness. Muscle and nerve disturbances and fever were observed as added complications. However, all affected persons recovered after several weeks [128].

Hydrogen peroxide has not been found to produce teratogenic or carcinogenic effects in humans; mutagenic or chromosomal effects have not been observed. The MAK and TLV–TWA values (1987) are 1 ppm (1.4 mg/m^3).

Toxicity in Animals. Acute toxicities of hydrogen peroxide in animals follow [128]:

LD_{50} (mouse, oral)	2538 mg/kg
LD_{50} (mouse, oral)	2000 mg/kg
LD_{50} (rat, oral)	4060 mg/kg
LD_{50} (mouse, dermal)	1.2×10^4 mg/kg
LC_{50} (rat, inhalation, 4 h)	2000 mg/m^3

Acute dermal toxicity depends on hydrogen peroxide concentration. With 90 wt% hydrogen peroxide, the dermal LD_{50} in rabbit is 630 mg/kg and in rat 4800 mg/kg [129]. So far no indication of a toxic effect on reproduction in animals has been found [130].

Hydrogen peroxide has a mutagenic effect on fungi and bacteria (e.g., Ames test), but not on insects or mammalian cells in vitro [130].

Oral administration of hydrogen peroxide produced tumors in the small intestine of mice [131], [132]. According to the criteria of the International Agency for Research on Cancer (IARC), however, only "limited evidence of the carcinogenicity of hydrogen peroxide to experimental animals" exists [130]. When hydrogen peroxide was given orally to rats, no significant differences occurred between the two test groups and the control group [133]. No evidence of tumor formation was found one year after exposure of mouse skin to 5% hydrogen peroxide [134].

9. References

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Hydrogen Selenide → Selenium and Selenium Compounds
Hydrogen Storage Alloys → Hydrides