HERA

Human & Environmental Risk Assessment
on ingredients of household cleaning products

Hydrogen Peroxide
CAS No: 7722-84-1

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1. Abstract

Hydrogen peroxide (H_2O_2, CAS No: 7722-84-1) is a high production volume (HPV) chemical, for which a European Union Risk Assessment has recently become available (European Commission, 2003). This EU risk assessment includes both an environmental risk assessment for the entire EU tonnage of hydrogen peroxide, and also human health risk assessments covering the use of several household cleaning products containing hydrogen peroxide which are within the scope of HERA.

HERA is determined to avoid any duplication of effort and to discourage effort for the sake of marginal improvements. However, HERA believes that HERA Risk Assessments should be carried out where significant additional risk information can be obtained, and where a refinement of the existing assessments would yield new or significantly different conclusions in particular for the detergent use scenario.

This document refers to the information in the EU Risk Assessment which covers hydrogen peroxide use in the household cleaning products which are within the scope of HERA. It also contains additional, recent exposure information which broadly supports the figures provided there.

Human Health

Products used in HERA applications may contain between 4% and 8% hydrogen peroxide. The main application of those products is the bleaching of textiles in the washing machine, but the use of hydrogen peroxide in surface- or toilet cleaners has also been reported. These uses give rise to a variety of possible consumer contacts.

The EU Risk Assessment concludes that there is no need for further information and/or testing for acute toxicity, sensitisation, repeated oral toxicity, repeated dermal toxicity, mutagenicity and carcinogenicity for all exposure scenarios concerning consumers.

The only relevant potential human health concern identified by the EU Risk Assessment is that of skin and eye irritation. Concentrated solutions of hydrogen peroxide are irritant to skin and eyes. The irritation potential of aqueous solutions of hydrogen peroxide depends on concentration. Local effects of hand wash solutions containing hydrogen peroxide do not cause concern given that it is not a contact sensitiser and that the concentrations of hydrogen peroxide in such solutions are well below those expected to be irritating to eye or skin. Laundry pre-treatment or surface cleaning tasks, which may translate into brief hand skin contact with higher concentrations of hydrogen peroxide, may occasionally result in mild irritation easily avoided by prompt rinsing of the hands in water. Accidental spillage of neat product into the eye is to be avoided as can be expected to result in likely irritation.

In the view of the extensive database on toxic effects and the low exposure values in the intended use patterns of the HERA applications, it can be concluded that the use of Hydrogen peroxide in household cleaning products raises no safety concern for consumers.

Environment

A quantitative risk assessment was performed for aquatic organisms and microorganisms. The assessment concludes that there is no need for further information and/or testing for any of the generic scenarios. The conclusion that no further information or testing was required also applies to the sediment, terrestrial, and atmospheric compartments. Also, the conclusion that no further information or testing is required was found for the other consumer exposure scenarios. Thus, the uses of hydrogen peroxide in products which are covered by HERA are not a subject of concern in the EU, with regard to the environment.

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2. Introduction

Hydrogen peroxide (H_2O_2) is a high production volume (HPV) chemical, for which a European Union Risk Assessment has recently become available (European Commission, 2003). This HERA 'short version' report summarises the human and environmental risk assessment of the use of hydrogen peroxide in household cleaning applications, supplementing the EU risk assessment with current usage information (AISE, 2002).

3. Substance information

Substance Identification
This summary covers hydrogen peroxide (H_2O_2), CAS No: 7722-84-1, which has a structure H-O-O-H and a molecular weight of 34.02 g/mol (European Commission, 2003).

Physical-chemical Properties
The physical properties of hydrogen peroxide are given in Table 1 (European Commission, 2003). Hydrogen peroxide is normally handled as an aqueous solution. Commercial solutions must be stabilised with additives to prevent possible violent decomposition due to catalytic impurities or elevated temperatures and pressure. The danger of vapour phase explosion on storage of liquid hydrogen peroxide will be encountered only with concentrated H_2O_2 solutions above 74% at elevated temperatures. Solutions used in HERA applications are below the level of concern, as shown in Table 2.

Table 1. Physical and chemical properties of pure hydrogen peroxide (100%)[1]

Property	**Value**
Melting point	-0.40 - 0.43°C
Boiling point	150-152°C decomposition
Density	1.4425 g/cm3 (25°C)
Vapour pressure	3 hPa (25°C)
Water solubility	miscible in all proportions
Log Kow	-1.5 (calculated)
pKa	11.62 (25°C)
Henry's law constant	$7.5.10^{-4}$ Pa m3/mol (20°C) measured

[1] pure hydrogen peroxide (100%) does not exist in practice

Occurrence
Hydrogen peroxide has both natural and anthropogenic sources. Environmental releases from anthropogenic sources may take place during production, formulation, processing and consumer use of products. Natural hydrogen peroxide may be formed by photochemical, chemical or biochemical process (European Commission, 2003).

Production and Use

Hydrogen Peroxide is mainly used for pulp bleaching (48%) and manufacture of other chemicals (38%) such as sodium perborate, percarbonate and peracetic acid. The remaining 15% of the total volume consumed in Europe is used for different applications including textile bleaching, environmental applications, metal etching, sanitisation of chemical instruments and surfaces, metal semiconductor chips manufacturing, disinfection of drinking water, disinfectant in aseptic packaging and bleaching of certain foodstuffs. Less than 1- 4% of the production volume is for personal and domestic use e.g. hair bleaching, dying or fixing of hair perm, household cleaning, tooth bleaching, food processing, disinfection of wounds and mouth and disinfection of eye contact lenses. Also cosmetics, toothpastes and deodorants contain or have contained hydrogen peroxide (European Commission, 2003).

Uses in household cleaning products, the scope of HERA, include use as a laundry additive (liquid bleach/gel), and in hand dishwashing detergents, hard surface cleaners and toilet cleaners. The ranges of hydrogen peroxide in these products are shown in table 2.

The total consumption of H_2O_2 in HERA applications in the 15 European Union Countries in 2002, plus Iceland, Switzerland and Norway, by formulating companies who contributed data to AISE in 2002 was 7696 tonnes per annum. As HERA formulators represent approximately 80% of the European market, it is estimated that less than 9700 tonnes per annum hydrogen peroxide was used in household applications in 2002 (AISE, 2002). This compares with the EU production tonnage of 750 000 tonnes per annum which was used in the EU risk assessment for hydrogen peroxide (European Commission, 2003). The tonnage estimated for use in applications covered by HERA is at the lower of the 1-4% of total hydrogen peroxide production volume which is estimated to be due to domestic and personal use in the EU Risk assessment (European Commission, 2003).

Table 2: Household applications and finished product concentrations of Hydrogen peroxide (AISE, unpublished data, 2002)

Product application	Range of H_2O_2 level in finished product, % by weight
Regular laundry detergents	0
Compact laundry detergents	0
Fabric conditioners	0
Laundry additives - Liquid bleach/gel	0 - 8.5%
Machine dishwashing detergent	0
Surface cleaners	0 – 5 %
Toilet cleaner	4.6%

4. Environmental Risk Assessment

Environmental fate
The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that the general characteristics of H_2O_2 that are relevant for the exposure assessment are:
Degradation
• Abiotic degradation: Abiotic degradation of H_2O_2 is due to either reaction with itself (disproportionation), or reaction with transition metals, organic compounds able to react with H_2O_2, reaction with free radicals, heat or light. Hydrogen peroxide is normally a short-lived substance in the environment but half-lives vary greatly depending on the circumstances. Thus, no abiotic half-life in water or soil has been determined. The estimated half-life in the atmosphere is ca. 24 hours.
• Biodegradation: Standard ready biodegradation tests are not applicable to inorganic substances like hydrogen peroxide. However, the data set available is regarded as sufficient to draw conclusions upon the degradation of H_2O_2. Enzymes produced by aerobic bacteria convert hydrogen peroxide to water and oxygen. Based on specific degradation data, a biodegradation rate constant of 21 h^{-1} (half-life 2 min) in STP is used. In surface waters a realistic worst-case half-life of 5 days is used.
Distribution
A Henry's Law constant of 7.1×10^{-4} Pa·m^3/mol at 20°C was measured. This indicates that volatilisation of H_2O_2 from surface waters and moist soil is expected to be very low. Using the measured log K_{ow} of -1.5, a K_{oc} of 0.2 can be estimated according to the Technical Guidance Document (TGD) (European Commission et al., 2003). Based on this value, hydrogen peroxide is expected to be highly mobile in soil.
Accumulation
There are no experimental results on bioaccumulation available. Hydrogen peroxide is reactive and a short-lived polar substance and no bioaccumulation is expected. This is supported by the calculated log K_{ow} of about -1.5. BCFs calculated according to the TGD for fish and earthworm are low, 1.4 and 3.3, respectively.

The EU risk assessment for hydrogen peroxide (European Commission, 2003) used the information above to determine that, for hydrogen peroxide in products covered by HERA, the local Predicted Environmental Concentration (PEC) values in various environmental compartments are as shown in Table 3.

Table 3: Local PEC values for hydrogen peroxide in products covered by HERA

	Local PEC in surface Water (mg/l)	**PEC for microorganisms** (mg/l)	**Local PEC in soil** (mg/kg)	**Local PEC in air** (mg/m3)
Consumer use II: Household cleaning agents	0.00425	0.0125	$1.09.10^{-4}$	$2.25.10^{-6}$

Environmental effects assessment
The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that, in the aquatic environment, there are short-term toxicity data for fish,

invertebrates and algae. In addition to algal studies, long-term data are available for zebra mussels. The lowest long-term aquatic toxicity test result is the NOEC of 0.1 mg/l for algae. According to the TGD an assessment factor of 50 should be used for deriving the Predicted No Effect Concentration (PNEC) in water. However, based on the data on natural background concentrations (typically <1 – 30 µg/l) it is obvious that this would overestimate the toxicity. Furthermore it is not probable that further long-term studies would show higher toxicity than the NOEC for the most sensitive group of organisms, i.e. algae. Therefore an assessment factor of 10 is considered to be appropriate. The extrapolation with the factor of 10 results in a **$PNEC_{water}$ of 10 µg/l**.

The EU risk assessment for hydrogen peroxide (European Commission, 2003) extrapolated the PNEC for microorganisms from the EC_{50} activated sludge respiration test (466 mg/l) using an assessment factor of 100. This results in a **$PNEC_{microorganisms}$ of 4.66 mg/l.**

For the sediment compartment, The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that hydrogen peroxide does not adsorb to sediment and is rapidly degraded there. Thus the report concluded that **sediment dwelling organisms are adequately protected by the PNEC for water phase.**

The EU risk assessment for hydrogen peroxide (European Commission, 2003) calculated the PNEC for the terrestrial compartment based on the equilibrium partitioning method, as no suitable studies are available on the effects of hydrogen peroxide on soil-dwelling organisms. The results gave **a $PNEC_{terrestrial}$ of $1.19.10^{-3}$ mg/kg wwt.**

Although some experiments are available on fumigation of plants with H_2O_2, no NOEC or EC_{50} levels were determined in these tests. Thus the EU risk assessment for hydrogen peroxide (European Commission, 2003) found that **a quantitative assessment for the atmosphere cannot be performed.**

A quantitative risk assessment was performed for aquatic organisms and microorganisms. The EU risk assessment for hydrogen peroxide (European Commission, 2003) gives the PEC/PNEC ratios shown in Table 4 for hydrogen peroxide in the uses covered by HERA. The assessment concludes that "There is no

Table 4. PEC/PNEC ratios for hydrogen peroxide

Scenario	Aquatic organisms	Microorganisms
Consumer use II: Household cleaning agents	0.425	0.00267

need for further information and/or testing: **conclusion (ii) for this use.** The conclusion that no further information or testing was required also applies to the sediment, terrestrial, and atmospheric compartments. Thus **hydrogen peroxide use in products which are covered by HERA are not a subject of concern in the EU, with regard to the environment.**

5. Human Health

Consumer exposure

The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that bleaching, disinfection and cleaning are the main uses of H_2O_2 in consumer products. Many consumer products, such as household cleaning and bleaching agents, hair dyeing and bleaching products, tooth bleaching agents, mouthwashes, disinfectants, contact lens disinfectants, and even food contain H_2O_2.

Table 5, taken from Table 4.2 of the summary report of the EU risk assessment for hydrogen peroxide (European Commission, 2003), gives data for the consumer exposure to H_2O_2 from the scenarios relevant for products covered by HERA. The duration and frequency of exposure and values for the external, route-specific doses/concentrations are given. Note that the concentrations given in table 5 are somewhat higher than the recent concentrations given in table 2 (AISE, 2002).

Table 5. Consumer exposure data used in the EU risk assessment for hydrogen peroxide (European Commission, 2003)

Scenario	Exposure time		Inhalation (mg/m^3)	Ingestion (mg/kg of bw/d)	Skin / Eye deposition	
	Duration of treatment	Frequency of treatments per year	Estimated	Estimated	Concn. of H_2O_2 in the product	Estimated dose
Textile bleaching	5-10 min	25	0.02-0.13	na	<8 (35) %	0.6 mg/kg bw, on the skin [1]
Cleaning agents	10-20 min	25	<0.13	na	usually about 8%(0.2-35%)	<0.6 mg/kg bw, on the skin [1]

1) 0.6 mg/kg of body weight per day is the potential dermal deposition (estimated by EUSES)

Health hazard data

Toxicokinetics, metabolism and distribution

The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that H_2O_2 is an endogenous product of oxygen reduction in the aerobic cell and passes readily across biological membranes. At high-uptake rates H_2O_2 can pass the absorption surface entering the adjacent tissues and blood vessels where it is rapidly degraded by catalase liberating oxygen bubbles; consequently, mechanical pressure injury and oxygen embolism may be produced. In the view of the high degradation capacity for hydrogen peroxide in blood, it is unlikely that the substance is

systemically distributed, and therefore the endogenous steady state levels of the substance in tissues are unlikely to be affected.

Acute toxicity

The EU risk assessment for hydrogen peroxide (European Commission, 2003) found oral LD_{50} values or lethal doses in rats range between 800 mg/kg for 70% H_2O_2 to more than 5,000 mg/kg for 10% H_2O_2. There are also a number of reported human incidents by oral ingestion of H_2O_2 water solutions, but few reports have given data on the dose. The mechanism of systemic effect has been oxygen embolism. Thus, the substance proved to be harmful if swallowed by a physical mode of action.
The dermal LD_{50} values in animals range between 700-5,000 mg/kg for 90% H_2O_2. The test methods are mostly poorly described, but the studies indicate that H_2O_2 is not acutely toxic after skin application.
Acute inhalation toxicity studies have been performed with aerosols (mice) and vapours (rats and mice). Due to the corrosive nature of the substance after inhalation exposures to highly concentrated aerosols (70% H_2O_2 as "droplets"), lethality occurs at quite low air concentrations (0,92-2 mg/l). The lethal event can be attributed to the substance corrosivity rather than its systemic toxicity. Since exposure to significant concentrations of hydrogen peroxide was not observed in the risk assessment and the predominant human exposures were related to vapors only, vapour experiments were preferred in the hazard assessment. Based on vapour inhalation studies in mice and rats the substance was considered to be harmful by inhalation.

Irritation and corrosivity

The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that in rabbits, H_2O_2 solutions of 10% were slightly irritating to the skin, 35% solutions proved to be moderately irritating and caused delayed epidermal necrosis and sloughing, while 50% solutions and more concentrated solutions were severely irritating and corrosive.
Eye irritation is reported in humans and animals. The effect of H_2O_2 in 5 and 10% solutions are known to cause adverse effects in humans. An 8% solution was highly irritating and caused irreversible effects in the rabbit eye.

Sensitisation

It was concluded in the EU risk assessment that the skin sensitisation potential of hydrogen peroxide is extremely low.

Repeated dose toxicity

A number of repeated dose toxicity studies in experimental animals via the oral and inhalation routes have been reviewed in the EU Risk assessment report (EU, 2003). The oral NOAEL of 26-37 mg/kg bw (100 ppm in drinking water) is based on local effects on the gastrointestinal tract and reductions in food and water consumption in a 90 day drinking water study in a catalase deficient mice strain. Based on irritation of the upper airways (nose) an NOAEL of 2.9 mg/m^3 was derived in a 28-day rat study, while from human occupational data an approximate human NOAEL of 1.4 mg/m^3 was derived.

Mutagenicity

Hydrogen peroxide was mutagenic and genotoxic in a variety of *in vitro* test systems without metabolic acitvation. The responses observed were modified by the presence of degrading enzymes (catalase), the extent of formation of hydroxyl radicals by the Fenton reaction, and the cells repair abilities. In *vivo* genotoxicity studies employing modern methodologies were all negative. The EU risk assessment concluded that the available studies are not in support of a significant genotoxicity or mutagenicity under *in vivo* conditions.

Carcinogenicity

The critical review of a number of publications on the carcinogenicity of hydrogen peroxide by EU, 2003 and consideration of the overall evidence available at this time led to the conclusion that the special nature of a local carcinogenic effect observed the duodenum of a sensitive mouse strain, that furthermore showed a marked tendency of regression and even disappearance after cessation of treatment was of no practical relevance for humans and should not trigger classification.

Toxicity to reproduction

Due to the rapid degradation of hydrogen peroxide in tissues of first contact and blood yielding oxygen and water no studies for reproductive endpoints were requested in the EU risk assessment, as hydrogen peroxide is unlikely to be systemically available to the developing embryo or fetus or the sex organs. Results from animal studies also suggest local toxicity at the point of contact and no systemic effect as the primary mode of action and consequently, although there were gaps in data, reproductive effects by hydrogen peroxide were not deemed to cause any concern.

Risk Characterization for consumers

The EU risk assessment concluded that the toxicokinetic evaluation of hydrogen peroxide suggests that only under conditions of very high exposure rates the substance might enter the systemic circulation. When accidental swallowing is excluded, it is unlikely that such high exposures could be reached in any realistic scenario of consumer exposure. It is especially unlikely that the substance deposited on the skin is systemically absorbed to a meaningful degree. Results from animal studies also suggest local toxicity at the point of contact and no systemic effect as the primary mode of action and consequently, although there were gaps in data, reproductive effects by hydrogen peroxide were not deemed to cause any concern.

The EU risk assessment for hydrogen peroxide (European Commission, 2003) found that local irritation and, in extreme and uncommon cases, corrosion of the skin, eye, gingivae or the teeth are the critical adverse effects caused by exposure to H_2O_2. Most of the effects reported are transient or are considered mild. However, even rather dilute solution of H_2O_2 (3%) may cause danger, if swallowed in large enough volume accidentally. Effects of splashes of strong solutions to the eye (> 5%) and skin (> 35%) represent scenarios that may be relevant in terms of consumer exposure.

The EU risk assessment for hydrogen peroxide (European Commission, 2003) concluded that all other endpoints, acute toxicity, sensitisation, repeated dose toxicity, mutagenicity and carcinogenicity were not considered to cause concern for human health of consumers. Thus, the conclusions regarding sensitisation, repeated dose toxicity, mutagenicity and carcinogenicity are **conclusions (ii) – There is at present**

no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Table 6, taken from Table 4.4 of the summary report of the EU risk assessment for hydrogen peroxide (European Commission, 2003), characterizes the risks to the consumer from exposure to H_2O_2 in the scenarios relevant for products covered by HERA. **Eye irritancy is shown to be of concern for products containing H_2O_2 in concentrations ≥5%. Thus for these products Conclusion iii - there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account – is applicable.** The legislation supporting this recommendation can be found in the *Official Journal of the European Union, 2004.*

Table 6 – Risk characterization for consumers for product types included in HERA

Scenario	**Irritation/corrosivity**			**Repeated dose toxicity, oral**	**Acute toxicity; sensitisation; mutagenicity; carcinogenicity others**
	Eye	**Skin**	**Airways**		
Textile bleaching	**iii**[1]	ii	ii	ii	ii
Cleaning agents	**iii**[1]	ii	ii	ii	ii

1) Current data suggest that textile bleaching products and cleaning agents available for consumers normally contain less than 8% of H_2O_2 but in some unusual extreme cases may contain up to 35% of H_2O_2. Eye irritancy is of concern if the actual concentration of H_2O_2 in the substance used is ≥5%

Risks to Consumers from the physicochemical properties of hydrogen peroxide have also been identified in the EU risk assessment for hydrogen peroxide (European Commission, 2003). The risk assessment finds that an accident may occur if H_2O_2 (even diluted) is inappropriately stored in a glass bottle with a tight stopper. In the course of time, overpressure will be generated in the bottle due to slow decomposition of the peroxide and there is the possibility that the bottle may break, rupturing violently.

No risks were identified in the EU risk assessment for humans indirectly exposed via the environment and combined exposures for consumers.

In summary, the only relevant potential human health concern identified by the EU Risk Assessment is that of eye irritation. Concentrated solutions of hydrogen peroxide are irritant to skin and eyes. The irritation potential of aqueous solutions of hydrogen peroxide depends on concentration. Local effects of hand wash solutions containing hydrogen peroxide do not cause concern given that it is not a contact sensitiser and that the concentrations of hydrogen peroxide in such solutions are well below those expected to be irritating to eye or skin. Laundry pre-treatment or surface cleaning tasks, which may translate into brief hand skin contact with higher concentrations of hydrogen peroxide, may occasionally result in mild irritation easily avoided by prompt rinsing of the hands in water. Accidental spillage of neat product into the eye is to be avoided as can be expected to result in likely irritation.

Conclusion:

In the view of the extensive database on toxic effects and the low exposure values in the intended use patterns of the HERA applications, it can be concluded that the use of Hydrogen peroxide in household cleaning products raises no safety concern for consumers.

6. References

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7. Contributors to the report

This dossier has been prepared by the HERA Secretariat. Additional input was provided by experts of the HERA (Environment and Human Health) Task Forces. Volume and exposure information for the use of household detergents and cleaners was gathered among the HERA Formulator Companies and has been aggregated by the Cefic Statistical Service department.