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RISK REDUCTION STRATEGY

Tert-butyl hydroxyperoxide (TBHP)

CAS no.: 75-91-2

EINECS no.: 200-915-7

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(environment part only)

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Rapporteur for TBHP is the Ministry of Housing, Spatial Planning and the Environment (VROM) in consultation with the Ministry of Social Affairs and Employment (SZW) and the Ministry of Public Health, Welfare and Sport (VWS). Responsible for the risk evaluation and subsequently for the contents of this report is the rapporteur.

This report has been prepared by the Chemical Substances Bureau. The rapporteur is responsible for the contents of this report.

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Summary

TBHP is primarily used in the chemical industry as starting material (or intermediate) and as a reactive ingredient (catalyst, initiator or curing agent).

In the environmental risk assessment for TBHP, a local risk to the aquatic (including waste water treatement plants) and/or soil compartment was identified for a limited number of production and/or processing sites.

It is stressed in the risk assessment report that from a scientific perspective a refinement of the risk assessment is the most appropriate action. However, Industry has not supported to provide additional exposure data or to conduct additional ecotoxicological studies and thereby implicitly accepted a conclusion (iii) for a number of sites. It is recommended that competent authorities in the Member States concerned, verify to what extent the risks identified are realistic

With regard to the risk reduction strategy it is recommended:

- that competent authorities in the Member States concerned should lay down, in the permits issued under Council Directive 96/61/EC , conditions, emission limit values or equivalent parameters or technical measures regarding [TBHP], in order for the installations concerned to operate according to the best available techniques(BAT) taking into account the technical characteristic of the installations concerned, their geographical location and the local environmental conditions.
- that Member States should carefully monitor the implementation of BAT regarding [T] and report any important developments to the Commission in the framework of the exchange of information on BAT.
- to facilitate permitting and monitoring under Council Directive 96/61/EC (Integrated Pollution Prevention and Control) [TBHP] should be included in the ongoing work to develop guidance on 'Best Available Techniques' (BAT).
- local emissions to the environment should, where necessary, be controlled by national rules to ensure that no risk for the environment is expected.

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1 Background

1.1 Introduction

Tert-butyl hydroxyperoxide (TBHP) is a priority substance on the 3rd priority list in the framework of Council Regulation (EEC) 793/93 on the Control and Evaluation of the Risks of Existing Substances. TBHP was selected as a priority substance because a possible risk to the aquatic environment had been identified by the OECD, and because of workplace concerns put forward by the Dutch Occupational Hygiene Society (NVvA). The Netherlands acts as the rapporteur for TBHP.

The production of TBHP is located at three sites in the European Union. The total EU production volume is around 14,500 tonnes/year. The total EU processing volume is around 14,200 tonnes/year. Import into and export outside the EU are 143 and 164 tonnes/year, respectively. The difference of about 300 tonnes/year between production volume and processing volume is thought to be caused by the difference in the year of record of the reported amounts (based on data submitted).
The annual market growth in the European Union is expected to be below 3 percent in the near future as indicated by industry.

1.2 Production process

The production of TBHP takes place in a closed batch or closed continuous process. The main types of production of TBHP are:

- Direct reaction of isobutane and liquid oxygen.
  (Used by one of the three EU producers. Overall reaction: $(CH_3)_3CH + O_2 \rightarrow (CH_3)_3CO\text{-}OH$. This reaction produces numerous minor by-products such as t-butyl alcohol and di-butyl peroxide which are removed during the purification by distillation which involves a TBHP-water azeotrope. Decanting of the aqueous

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phase of the distillation process leaves an organic phase containing around 70% TBHP and 30% water.).

- Preparation from tertiary-butyl alcohol and 30% hydrogen peroxide in presence of sulphuric acid

  (Used by one of the three producers. Overall reaction: $(CH_3)C\text{-}OH + H_2O_2 \rightarrow (CH_3)CO\text{-}OH$.)
- Oxidising of tertiary-butylmagnesium chloride.
- Epoxidation of propylene catalysed by a molybdenum complex.
- Oxidation of t-butyl alcohol in a 50% hydrogen peroxide solution with a reaction catalyst of silicotungstic acid.

1.3 Use pattern

TBHP is primarily used in the chemical industry (HEDSET, 1997). TBHP is used as starting material (or intermediate) and as a reactive ingredient (catalyst, initiator or curing agent).

Applications are:

- the epoxidation of propylene to propylene oxide (intermediate);
- free radical initiator for polymerisations, copolymerisations, graft polymerisations and curing of polymers (plastic industry);
- free radical initiator to polymerise unsaturated monomers, usually to high polymers. Mainly used by manufacturers of synthetic lattices or water borne dispersions. Also used as a component of catalysts systems for unsaturated polyester resins (resin industry; see Annex 3 for additional data on the use of TBHP in the resin industry);
- the synthesis of other organic peroxy molecules (as a precursor of initiators) such as perester, persulphate, dialkyl peroxide and perketal derivatives;
- the preparation of speciality chemicals required by fine chemical and performance chemical industries, such as pharmaceuticals and agrochemicals (fungicide).

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- the use as an ingredient of hardeners for plastics. These products contain 5 - 20 % TBHP. Hardeners for plastics are also used in the plastic industry.

Industrial and use categories of TBHP

Industrial and use categories of TBHP for the European market in IC/UC terminology being relevant for the environmental exposure assessment are shown below. The quantitative distribution for the processing stage tonnages is around 20% for IC/UC 3-33 and 80% for IC/UC 11-43, based on the data submitted by industry.

Industrial category	**EC no.**	**Use category**	**EC no.**	**Main category**
Chemical industry: used in synthesis	3	Intermediates	33	I b Intermediates stored on site
Chemical industry: used in synthesis	3	Oxidising agents	37	III Multi-purpose equipment
Polymers industry	11	Process regulators	43	Type III, "Wet"

TBHP is commercially available and used mostly as TBHP-70 (T-Hydro), an aqueous solution of approximately 70 weight percent TBHP and 30 weight percent water[1]. TBHP-70 is a highly reactive peroxide with an active oxygen content of about 12%.

1.4 Classification

- EU Classification in Annex I: The substance has not yet been included in Annex I, but the indicated Classification and Labelling (as proposed by the rapporteur) has been approved by the EU Commission Working Group on the Classification and Labelling of Dangerous Substances, in April 2006 (environmental effects) and October 2006 (physico-chemical properties and human health effects), respectively. It is noted that the Working Group did not yet made a final decision on the assignment of R68.

[1] TPHP solutions with a higher purity, up to 90%, are also commercially available (HSDB, 1999)

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- Classification:

  O; R7

  R10

  Xn; R21/22

  T; R23

  C; R34

  R43

  Mutagenic, Category 3; R68 (provisionally)

  N; R51/53

- Labelling:

  Symbols: O, T, N

  R- phrases: 7, 10, 21/22, 23, 34, 43, 68, 51/53

  S-phrases: 3/7, 14, 26, 36/37/39, 43, 45, 60, 61

2 Risks identified in the risk assessment (environment)

2.1 Exposure assessment

TBHP may enter the environment during its production and processing by emission to air and by emission to surface water via effluent from wastewater treatment plants (WWTPs). Furthermore, there may be indirect emission to soil, via deposition from air and/or the application of WWTP sludge on soils.

The environmental exposure assessment of TBHP is based on the expected releases of the substance during the following life cycle stages:

I. production (3 sites, two of which combines production & processing)

II. processing

- IIa. processing chemical intermediate (3/33)(3 sites, one of which combines production & processing)
- IIb. processing in polymer industry (11/43)(14 sites, one of which combines production & processing)

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Both site-specific and generic scenarios have been used for the exposure assessment of TBHP. Site-specific scenarios are based on actual data from industry on emission patterns etc., whereas generic scenarios are fully based on model calculations for a realistic worst case situation. Generic scenarios are used if no data were obtained from either industry or other references.

2.2 Risk assessment results

The following risks were identified in the risk assessment:

Conclusion (iii) was drawn for the aquatic and/or terrestrial environment for one production site, two sites for processing TBHP as a chemical intermediate and eight sites for processing in the polymer industry.

The risk characterisation ratios are summarized below. PEC/PNEC ratios >1 are marked in **bold**.

Local risk characterisation ratios (PEC/PNEC values)

	PEC/PNEC water	PEC/PNEC WWTP	PEC/PNEC soil
Production			
I-a (generic)	0.2	<1	0.033
I-b (site specific data) both production and processing (IIa1)	0.2	<1	0.004
I-c (site specific data) both production and processing (IIb2)	**48**	**420**	**4000**
Processing Cat. 3/33 *(chemical intermediate)*			
II-a1	See production I-b		
II-a2 (generic scenario based on site specific tonnage)	0.5	**3.0**	**29**

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	PEC/PNEC water	PEC/PNEC WWTP	PEC/PNEC soil
II-a3 (generic scenario based on site specific tonnage)	2.2	**18**	**180**
Processing Cat. 11/43 *(process regulator in polymerisation)* - (all generic scenarios based on site-specific tonnages, unless site-specific emission data were provided by industry)			
II-b1	**250**[1)]	**22**	**210**
II-b2	See production I-c		
II-b3	**51**	**4.4**	**42**
II-b4	**32**	**2.8**	**26**
II-b5	**13**	**1.1**	**10**
II-b6	0.2	0	0.008
II-b7	0.2	0.01	0.4
II-b8	**3.3**	0.3	**2.6**
II-b9	0.3	0.02	0.2
II-b10	0.2	0.2	**1.7**
II-b11	**2.3**	0.2	**1.8**
II-b12	0.9	0.06	0.6
II-b13	0.2	0.003	0.03
II-b14	0.9	0.06	0.6
II-b15	0.2	0.04	0.4
II-b16	0.2	0.01	0.1
II-b17	0.2	0.005	0.06
II-b18	0.2	0.008	0.2
II-b19	**3.9**	0.3	**3.2**
II-b20	0.2	0.01	0.1
Regional	0.2		0.004
	PEC/PNEC water	PEC/PNEC WWTP	PEC/PNEC soil

1) This company is known to have three processing sites. Only the total sum of the processing tonnage for all three sites was submitted to the Rapporteur. In the risk assessment it is assumed that the total tonnage is processed within one site (scenario II-b1).

The RAR states that, as a refinement of both the PEC values and the PNEC values may be possible, a conclusion (i) would have been more appropriate. The exposure

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assessment was based on a number of default assumptions, since not all producers and processors did submit site-specific information relevant to the exposure assessment. Furthermore, PNEC values are based on very limited data. However, it can be questioned if all PEC/PNEC values would be lowered sufficiently by a refinement of the PEC and/or PNEC values, as some of the current PEC/PNEC values are far above 1.

3 Current risk reduction measures

3.1 Legislative controls in the European Union

General

According to the available information there are no substance-specific measures at Community level aiming at a reduction of the environmental risks caused by TBHP emissions.

Directive on Integrated Pollution Prevention and Control (96/61/EC)

All exposure scenarios are covered by the IPPC directive:

- Scenario I-c (production) is covered by IPPC category 4.1. "Chemical installations for the production of basic organic chemicals, such as: (...) (b) oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, *peroxides*, epoxy resins".

- Scenario IIa (processing / chemical intermediate) is covered by (a.o.) the following IPPC categories:
    - 4.1. "Chemical installations for the production of basic organic chemicals, such as: (...) (b) oxygen-containing hydrocarbons such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, *peroxides*, *epoxy resins*"
    - 4.4. "Chemical installations for the production of basic plant health products and of biocides"

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- 4.5. “Installations using a chemical or biological process for the production of basic pharmaceutial products”

- Scenario IIb (processing / polymers industry) is covered by IPPC category 4.1. “Chemical installations for the production of basic organic chemicals, such as: (...) (h) basic plastic materials (*polymers*, synthetic fibres and cellulose-based fibres)”

The following *best available techniques reference documents* (BREFs) are available:

- Large volume organic chemicals (http://ec.europa.eu/comm/environment/ippc/brefs/lvo_bref_0203.pdf)
- Organic fine chemicals (http://ec.europa.eu/comm/environment/ippc/brefs/ofc_bref_0806.pdf)
- Polymers (http://ec.europa.eu/comm/environment/ippc/brefs/pol_bref_1006.pdf)

Directive on the Limitation of Emissions of Volatile Organic Compounds (99/13/EC)

“Manufacturing of pharmaceutical products” is among the activities referred to in the directive. Installations need to comply with the following emission limit values:

	Activity (solvent consumption threshold in tonnes/year)	Threshold (solvent consumption threshold in tonnes/year)	Emission limit values in waste gases (mg C/Nm^3)	Fugitive emission values (percentage of solvent input)		Total emission limit values		Special provisions
				New	Existing	New	Existing	
20	Manufacturing of pharmaceutical products (> 50)		20 (1)	5 (2)	15 (2)	5 % of solvent input	15 % of solvent input	(1) If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150. (2) The fugitive emission limit value does not include solvent sold as part of products or preparations in a sealed container.

3.2 Risk management measures at company level

The European Resin Manufactures Association (ERMA) submitted some general data on the use of TBHP in the resin industry. It is indicated that the chances of TBHP reaching the environment from manufacturing sites are extremely low. This because the peroxide is not only consumed during the process, but also plant washings are

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treated through flocculation processes using metal ions, offering further opportunity to consume any minuscule peroxide residues. Furthermore, in some cases plant washings are combusted through on-site incinerators into carbon dioxide and water. It is emphasised that these general data provide no site-specific evidence that there is no emission to waste water or air.

No company specific information with regard to exisiting or future risk management measures was submitted by the companies concerned. It is not known whether permits are issued with emission limits for furfural.

4 Assessment of possible further risk reduction measures

A general overview of possible measures for reduction of risks is given below.

Possible Risk Reduction Measures for Manufacture and Industrial/Professional Use
• Controls on manufacture; • restrictions on the marketing and/or use of the substance under Directive 76/769/EEC; • re-designing the process itself, or changing the substances or materials used in it; • safe systems of work, such as specified standards of physical containment or extraction ventilation; • application of good manufacturing practice, for example, under ISO standards; • classification and labelling; • separation of personnel; • monitoring and maintenance of equipment; • dust suppression methods, such as the use of substances in tablet or pellet form; • occupational exposure limits and/or air monitoring in the workplace; • accurate hazard information (for example, safety data sheets), and/or better delivery of safety information, such as clearer labelling or the provision of warning signs in the workplace; • biological exposure indices and/or biological monitoring of workers; • medical surveys of workers; • training; • use of personal protective equipment; • licensing of operators of certain operations; • 'end-of-pipe' controls to minimise, neutralise or render less harmful any emissions that cannot practicably be avoided otherwise; • limit values for emission and effluent monitoring; and • environmental quality standards and/or environmental monitoring.

(source: Technical Guidance Document on Development of Risk Reduction Strategies)

A local risk was identified for a limited number of sites. Hence, there will be no need for Community-wide measures.

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Considering the uncertainties in the risk assessment, a first step towards risk reduction is for the local authorities & companies involved to verify to what extent the risks identified are realistic.

When it is concluded that risk reduction measures are appropriate, emission controls are considered a proper means to reduce the environmental risks caused by TBHP. The scenarios for which a risk has been identified are covered by the IPPC directive. It is up to the competent authorities in the Member States concerned to lay down in the permits, conditions, emission limit values or equivalent parameters or technical measures, in order for the installations concerned to operate according to the best available techniques (BAT), taking into account the technical characteristic of the installations concerned, their geographical location and the local environmental conditions. BREFs are available for all scenarios for which a risk was identified.

It is unknown whether in EU member states permits have been issued for industrial installations using TBHP. In the Netherlands, TBHP is not mentioned in any permit. The IPPC directive requires that the existing installations have a permit by the end of 2007. Permits may further allow an interim period of several years for installations to comply with the permit conditions.
Robust enforcement and supervision of permits is a prerequisite for the effectiveness of any permitting system. Using plant permits for reduction of TBHP emissions does not necessitate any additional efforts from enforcement and supervision. The permits must contain obligations to supply the competent authority with data required for checking compliance with the permit.

Environmental Quality Standards do not actually reduce the risks but they can be used to follow up the effectiveness of the risk reduction measures taken and to identify needs for further measures.

5 Further risk reduction measures recommended

It is recommended

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- that competent authorities in the Member States concerned should lay down, in the permits issued under Council Directive 96/61/EC , conditions, emission limit values or equivalent parameters or technical measures regarding [TBHP], in order for the installations concerned to operate according to the best available techniques(BAT) taking into account the technical characteristic of the installations concerned, their geographical location and the local environmental conditions.
- that Member States should carefully monitor the implementation of BAT regarding [T] and report any important developments to the Commission in the framework of the exchange of information on BAT.
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