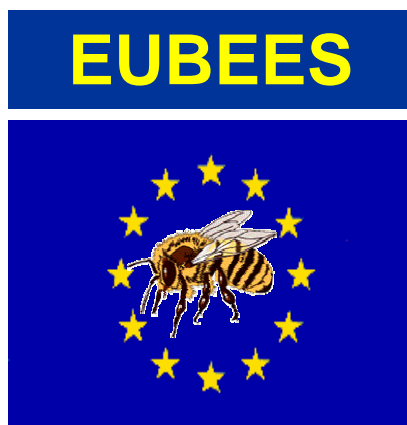


**Supplement to the methodology for risk
evaluation of biocides**

**Environmental Emission
Scenarios for biocides used as
In-can Preservatives
(Product type 6)**

European Commission DG ENV / RIVM

January 2004



This report has been developed in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2).

The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commission's financial support of the project is gratefully acknowledged (Ref. B4-3040/2001/326154/MAR/C3)

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FOREWORD

The European Parliament and the Council adopted in 1998 the Directive 98/8/EC on the placing of biocidal products on the market (Biocidal Products Directive, BPD). The background for the directive is a need for harmonisation of the legislation of the Member States regarding this type of chemicals, which are intended for exerting a controlling effect on higher or lower organisms. The Directive requires an authorisation process for biocidal products containing active substances listed in positive lists (Annex I and IA). Active substances may be added to the positive lists after evaluation of the risks to workers handling biocides, risks to the general public and risks to the environment. The risk assessments are carried out for the life cycle of the biocide: risks during and resulting from the application, risks associated with (the use of) the treated product and risks resulting from the disposal of the biocide and the treated product.

For the environmental risk assessment the environmental exposure needs to be evaluated. Within the risk assessment of industrial chemicals, emission scenario documents have been developed for a number of Industrial Categories (IC) that are included in section IV of the Technical Guidance Document (EC 2003a). For Product type 6 covering 'In-can Preservatives', various applications and processes are expected to be similar to those for the industrial chemicals. These emission scenario documents were checked on their suitability for use in the context of the BPD.

This report has been developed by Royal Haskoning, The Netherlands, in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2). The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commissions financial support of the project is gratefully acknowledged (Ref. B4-3040/2001/326154/MAR/C3).

For quick reference a summary of the available scenarios is given in Section 3.

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1 INTRODUCTION

1.1 Background

In the Technical Guidance Document on risk assessment (UE-TGD, EC 2003a) emission scenarios are described that can be used to evaluate the environmental emission of chemical substances. In this document the suitability of the emission scenarios for industrial chemicals is checked for use in the evaluation of biocidal products covered by Product type 6 (PT6), In-can Preservatives as distinguished in the Biocidal Products Directive (BPD).

Biocidal products of Product type 6 are used for the preservation of manufactured products, other than foodstuffs or feeding stuffs, in cans, tanks or other closed containers by control of microbial deterioration to ensure their shelf life.

Relevant applications include (Van der Poel and Bakker, 2001):

- Washing and cleaning fluids (professional use), human hygienic products, (professional and non-professional use)
- Detergents (professional and non-professional use)
- Paints and coatings (professional and non-professional use)
- Fluids used in paper, textile and leather production (professional use)
- Lubricants (professional use)
- Fuels
- Glues and Adhesives

There is a potential overlap with product type 7 (film preservatives) and PT9 (preservatives in fibre, leather, rubber and polymerised materials preservation) for products stored in cans and applied in films, such as paints, coatings and glues. Another area of overlap may be the lubricants (product type PT13).

In the EU Technical Guidance Document various documents are available on Industrial Categories (IC) that relate to the categories covered by Product type 6. In addition, in projects in various EU member states environmental emission scenarios were developed for relevant industry categories with particular emphasis on the use of biocides. These have already been discussed in the EUBEES Working Group. It should be realised that the scenarios for the Industrial Categories in the TGD are 'living documents': the developments go on and updated versions are circulating in the EU member states and in the OECD. For the purpose of this document, the versions as published in the TGD (EC 2003a) have been used.

According to Annex VI of the Biocidal Products Directive the risk assessment shall cover the proposed normal use of the biocidal product together with a 'realistic worst case scenario'. The documents describing the emission of In-can Preservatives to the primary receiving environmental compartments were identified. The calculation of a realistic worst case PEC using environmental interactions, for example subsequent movement of emissions to secondary environmental compartments (e.g. from soil to ground water), is the result of fate and behaviour calculations and models and is therefore considered outside the scope of this document.

This report was discussed in the working group for the EU project "Gathering, review and development of environmental emission scenarios for biocides (EUBEES 2)".

1.2 Available scenario descriptions

PT 6 relates to the use of In-can Preservatives. Table 1.1 presents the environmental emission scenarios available in the EU TGD (EC 2003a) that may apply to PT 6. In addition, some documents are included that are being discussed within the member states.

Table 1.1. Available emission scenario documents

Applications in PT 6 – ‘In-can’ preservatives	Available scenario documents
Washing and cleaning fluids (professional use), human hygienic products (see PT1), (professional and non-professional use) Detergents (professional and non-professional use)	EU – TGD (EC 2003a) IC-5 Personal/Domestic and IC-6 Public Domain. Assessment of the environmental release of soaps, fabric washing, dish cleaning and surface cleaning substances PT-2 Private and public health area disinfectants and other biocidal products. Assessment of environmental release of private and public health area disinfectants used for sanitary purposes and disinfectants for use in the medical sector. EUBEES1&2 PT-1 Human hygiene biocidal products (Van der Poel and Bakker 2001, Van der Aa and Balk 2003)
Paints and coatings (professional and non-professional use)	EU – TGD (EC 2003a) IC-14 Paints, laquers and varnishes industry. Assessment of the environmental release of chemicals from the paints, laquers and varnishes industry. OECD (OECD 2003) Emission Scenario Document for Wood Preservatives, Part 1-4. INERIS/F and EUBEES 1/2: PT-10 Emission scenario document for biocides used as masonry preservatives. (Migné 2002) EUBEES 2 PT-7 Film Preservatives (Van der Aa et al. 2003) OECD/EU PT-21. Harmonisation of environmental emission scenario for Antifouling Products (Van der Plassche and Van der Aa 2003) EA/UK: National R&D Project P2-203: Development of emission scenario documents for use in environmental risk assessment. Coating materials industry: paints, lacquers and varnishes (EA-UK 2002)
Fluids used in paper, textile and leather production Paper	EU – TGD (EC 2003a) IC-12 Pulp, paper and board industry. Assessment of the environmental release of chemicals used in the pulp, paper and board industry. PT-6,7&9 Biocides used as preservatives in paper coating and finishing. Assessment of the environmental release of biocides used in paper coating and finishing

Applications in PT 6 – ‘In-can’ preservatives	Available scenario documents
	RIVM/NL and FEI/Finland ESD for biocidal products applied in the paper and cardboard industry (Van der Poel and Braunschweiler 2002).
	EUBEES 2 Harmonisation of Environmental Emission Scenarios for Slimicides (PT-12) (Van der Aa and Balk 2003b)
Textile	EU - TGD (EC 2003a) IC-13 Textile processing industry. * BPT-9 Biocides used as preservatives. Assessment of environmental release of chemicals from the textile finishing industry
Leather	EU – TGD (EC 2003a) IC-7 Leather processing industry. * PT-9 Biocides used as preservatives. Assessment of the environmental release of chemicals from the leather processing industry
Metal working fluids (professional use)	EU – TGD (EC 2003a) IC-8 Metal extraction industry, refining and processing industry. EUBEES 2 PT-13. Preservatives used in metalworking fluids (Van der Aa 2003)
Fuels	Emission scenario descriptions in the EU Risk Assessment Reports for the Existing Chemicals Regulation: Based on available emission models: - pentane - cyclohexane Based on model and on measured data: - tert-butyl methyl ether (CAS 1634-04-4) Based on generalised emission scenarios: - benzene, C10-13-alkyl derivatives (CAS 67774-74-7) - toluene (see ECB website http://ecb.jrc.it/Risk-Assessment/NOMAP/ra_summary_report_txt.htm)
Glues and additives	No Emission Documents available

* : Document has been submitted to OECD for discussion and further developments. In this document the version in the TGD (EC 2003a) has been used.

A very short description of the contents of some of these and other documents is given in Appendix 1. These should be considered as helpful documents but the EUBEES group does not give any recommendation on their use.

Within the context of the EUBEES 2 project, the aim was to check ESDs for industrial chemicals in the TGD for their suitability for biocidal products falling under PT6. As shown in table 1.1, for most of the subgroups covered by in PT6 there is an overlap with other Product types under the BPD. If In-can Preservatives are used as a preservative in the products listed above, their emission pattern is similar to the emission of the preservatives used to protect the products during service life and

often the same products are being used. For the applications overlapping with other Product types in the BPD, the relevant IC documents for industrial chemicals in the EU TGD (EC 2003a) have already been checked by the EUBEES Working Group. As a consequence this document will shortly describe the use area and applications within PT6 and then give guidance in selecting the various documents to estimate the emission to specific compartments.

2 DESCRIPTON OF PRODUCT TYPE 6

2.1 Description of use area and application of In-can Preservatives

In-can Preservatives are used for the preservation of manufactured products in cans, tanks or other closed containers by control of microbial deterioration to ensure their shelf life. According to Van Dokkum et al. (1998) In-can Preservatives may be used to prevent biodeterioration of aqueous fluids, which may cause:

- pH-reduction
- loss of viscosity
- evolution of gas
- coagulation
- sfoul smell (biological degradation)
- colour changes
- breaking of emulsion
- colonies on surface

Borderline cases may arise where In-can Preservatives are used to preserve products that are covered by another Directive, cosmetics or medicinal products. The discussion of these so-called borderline cases is documented in several Guidance documents agreed between the Commission services and the competent authorities of Member States for the BPD and various other products.

Borderline documents and other guidance on scope issues relevant to Biocides Directive 98/8/EC:

- Biocidal products and plant protection products;
- Biocidal products and proprietary medicinal products and veterinary medicinal products;
- Biocidal products and milk hygiene legislation;
- Biocidal products and cosmetic products (draft);
- In-situ generation of biocidal active substances.

These document are available on:

<http://europa.eu.int/comm/environment/biocides/index.htm>

“Borderline case disclaimer”

The reader should check the original borderline guidance documents in each case if his product falls under the scope of the BPD because in this ESD for PT 6 the scope borderlines are not presented in detail and also because the scope borderline documents may have changed in time. The hierarchy is that the Guidance Documents sets the general rules and the Manual of Decisions summarises the discussions on various issues on a case by case basis.

2.1.1 Washing and cleaning fluids, human hygienic products

The In-can Preservatives used to preserve washing and cleaning fluids, human hygiene products and similar products will be released to wastewater at the stage of private or industrial use. The ESD for PT1 that was developed by Van der Poel and Bakker (2001) and was discussed by the EUBEES 2 Working Group (Van der Aa and Balk 2003a) is applicable for diffuse releases from households.

2.1.2 Detergents

A detergent can be defined as (1) any of numerous synthetic water-soluble or liquid organic preparations that are chemically different from soaps but are able to emulsify oils, hold dirt in suspension, and act as wetting agents and (2) an oil-soluble substance that holds insoluble foreign matter in suspension and is used in lubricating oils and dry-cleaning solvents (Brittanica (2001) in Van der Poel and Bakker 2001).

Detergents belonging to the first definition are included under washing and cleaning fluids discussed under section 2.1.1. Detergents used in lubricating oils of the second definition belong to the application discussed in section 2.1.5. Dry cleaning solvents contain detergents but do not have to be preserved as they do not contain water.

2.1.3 Paints and coatings

Paints and varnishes are applied for their decorative and/or protective function. The TGD, in IC-14 (EC 2003a), distinguishes paints and varnishes. They may be used as pastes or powders. After physical or chemical processes they form a thin adherent film on the surface of the substrate. The treated substrates are mainly metal surfaces (motor vehicles, metal frames, furniture), wooden surfaces (construction elements, toys, furniture, frames) and miscellaneous surfaces (concrete, road marking paints, anti-fouling). The field of use of paints and varnishes may be divided into two categories, i.e. paints for buildings and decoration (both professional and non-professional) and industrial use. Ingredients of paints and varnishes can be classified into the following main categories: binder, solvent, pigment, colorants, fillers and additives. The latter category, which forms less than 3% in the formulation, include a.o. in-can and film preservatives (EC 2003a).

'Coatings' is a term used to describe any material that may be applied as a thin continuous layer to a surface (Tissier et al. 2001). A UK project specifically focused on the subset of coatings accounted for by paints, lacquers and varnishes. These products are applied to surfaces for both decorative (colour, gloss or optical effects) and protective purposes (EA-UK 2002).

Water-based or latex paints are typically more prone to contamination and need an anti-microbial or biocide to act as an in-can preservative. In-can microbial growth or degradation occurs most frequently from contaminants, bacteria and yeast in the raw materials. The organic paint components act as the microbial food source, causing possible discoloration, gas generation, foul odours, coagulation, rheology changes and can corrosion. A broad spectrum of active substances is used to prevent problems during paint production or in the can during storage.

During the formulation stage the in-can preservative is added to paints and coatings. Next, for a longer period the product is left on the shelf. After application of the product, professionally as well as non-professionally, on average the product (paint or coating) has a long service life. Waste treatment can be very variable; from disposal of the material with the product via the normal routings of municipal waste to stripping off the paint or coating from the material. Some articles (e.g. steel or aluminium) are recycled. Thus the emission of in can preservatives in paints and

coatings during industrial and private use may be estimated using the scenarios developed for the emission of other additives as described in the ESD for IC-14. The EA-UK (2002) report gives emission estimates per sector of the coating industry. The ESD developed for Masonry Preservatives (PT10) and agreed upon within the EUBEES 2 Working Group, and the ESD for Wood Preservatives (PT8) developed by the OECD presents descriptions of the use of paints or coatings in specific applications and thus they may also be used to estimate the emission of In-can Preservatives used in these specific products.

2.1.4 Fluids used in paper, textile and leather production

Paper

Various types of biocidal substances may be used in coating and finishing processes in the paper and board industry. Biocides may be employed in different ways in the paper industry. Biocides used for the preservation of pulp and other aqueous fluids in the paper manufacture (such as slimicides) can remain in the end product. Many of the biocides used in coating additives are used as In-can Preservatives and as Film preservatives. In-can Preservatives must not degrade quickly since they are often used to treat a coating, solutions or slurries of coating binders, speciality additives or the complete coatings that are stored in a tank for a period of time. They extend the shelf life as they retard microbial growth, including bacteria, fungi, and molds. Typically, preservatives would be needed to preserve the following types of preparations involved in paper coating: filler slurry, starch slurry, cooked starch, protein slurry, cooked protein, latex binders, coating thickeners, coating lubricants and pigmented coatings (BPT 6, 7 & 9 in the TGD, EC 2003a). The use of biocides in fluids used in the production of paper is described in various emission scenario documents:

- Biocides used in paper coating and finishing (BPT 6, 7 & 9 in EC 2003a). This document also covers the use of In-can Preservatives;
- Emission Scenario Document for biocidal products applied in the paper and cardboard industry (Van der Poel and Braunschweiler 2002)
- Harmonisation of Environmental Emission Scenarios for Slimicides (PT12) (Van der Aa and Balk 2003b).

Textile

For the use of biocides in fluids used in textile the TGD includes a scenario for PT 9: Biocides used as preservatives in the textile wet processing (IC-13, BPT 9 in EC 2003a). Biocides used in the production of textile refer mainly to treatment of the textiles (e.g., moth repellents, biocides against rot and mildew), thus for the preservation of textiles for outdoor applications. Indoor applications are in the protection of woollen articles, shower curtains and mattress ticking. However the use of In-can Preservatives in fluids for textile production is not mentioned. According to Van der Poel and Bakker (2001) this is not surprising as most aqueous fluids will not contain organic chemicals. One of the exceptions is the use of detergents but the application of In-can Preservatives in this type of product is discussed under section 2.1.2. Van der Poel and Bakker (2001) present a simple adaptation taking into account the concentration of the in-can preservative in the fluids used in textile production to estimate the emission to waste water.

Leather

For the use of biocides in fluids used in leather production the TGD includes a scenario for biocides used in the leather processing industry (IC-7, BPT 9 in EC 2003a). The document describes that biocides may be added at various stages during the production of leather to protect it during storage before tanning or finishing steps, but they can also be used during tanning and finishing. It does not explicitly mention the use of In-can Preservatives in fluids for leather production. According to Van der Poel and Bakker (2001) it is not likely that fluids with In-can Preservatives will be used at all. Yet they present an adapted version of BPT 9 taking into account the concentration of the in-can preservative in the fluids used in the leather production to estimate the emission to waste water.

2.1.5 Lubricants or Metalworking fluids

According to Van der Poel and Bakker (2001) the application of In-can Preservatives in lubricants concerns the application in cooling-lubricants used in metalworking. For biocides used in metalworking fluids (PT13) an emission scenario document has been developed during the EUBEES2 project. For the preservation of the fluid to extend the shelf-life the same biocide will work as the active ingredient to preserve the diluted fluid used at metalworking (Van der Aa 2003).

2.1.6 Fuels

Many cases of microbial fouling and spoilage of fuels have been recorded for about 65 years. The common factor in all problems is the presence of water which, because of its higher density and immiscibility, will lie below the fuel as a discrete phase. Fuel (gas, kerosine) is stored in containers. When water enters these containers through seepage or condensation, favourable conditions are created for micro-organisms. They can proliferate in the water phase while feeding on the hydrocarbons in the fuel. They include both aerobic bacteria that may cause sludge and slimy mats and aerobic bacteria that can produce corrosive acids (Van Dokkum et al. 1998). If biocides are used the solubility ratio in fuel and water is a critical parameter and an agent must be selected which has the correct solubility characteristics for the planned use. Emissions into wastewater may occur when the water phase of a storage tank is discharged into the sewer.

No generic emission scenarios for biocides in fuel are available. However, within the scope of the Existing Chemicals Regulation, environmental risk assessment reports have been produced for various components in fuel and more or less generalised emission models could be obtained from these documents (see table 1.1).

2.1.7 Glues and Adhesives

Glues and adhesives are produced in a variety of types and for a variety of purposes. Large amounts are used for short-term applications and/or dry conditions (no microbial attack), for example cardboard packaging materials. In those adhesive products little or no preservatives will be used. For long term applications and/or moist conditions preservatives are required, for example plywood for outdoors use (Van der Poel and Bakker 2001). No emission scenario has been described for the application phase of glues and adhesives.

2.2 Description of types of substances used

A list of active substances currently notified for use as PT 6 In can preservatives preservatives according to the BPD can be found on the ECB Homepage: <http://ecb.jrc.it/biocides/>. For PT 6, approximately 150 substances have been notified.

Examples of substances used as In-can Preservatives are (Baumann et al 2000):

- etheric oils (for example thyme oil, rose oil)
- alcohols (for example benzyl alcohol, bronopol)
- carboxylic acid esters and amides (for example chloroacetamid)
- carbamic acid derivatives (for example 3-iodo-2-propenylbutyl carbamate)
- dibromodicyanobutane
- formaldehyde
- slow-release formaldehydes (for example n-formale, o-formale)
- isothiazol derivatives (for example methylisothiazolinone)
- mercaptobenzothiazoles
- organic acids
- phenol derivatives (for example 3-methyl-4-chlorophenole)
- quaternary ammonium salts (for example benzalkonium chloride)

In-can Preservatives in human hygiene products may range from 0.02 – 0.5 % (ww) (Board et al. 1987 in Balk et al. 1999).

In detergents, phosphates like for example diethylenetriamine penta (methylene phosphonic acid) (DTPMP) are used to stabilise alkaline hydrogen peroxide solutions. In acidic detergents, citric, glycolic and lactic acid are used. In detergents, polycarboxylates, alcoholethoxylates, soda and as a relatively new development, mono- and triisopropylammonium ethersulphates are used (Baumann, 2000).

Typical and the most important in-can preservative chemicals in paints and coatings include: isothiazolones, and formaldehyde donors. These preservatives (e.g. 5-chloro-2-methyl-2,3-dihydroisothiazol-3-on and 2-methyl-2,3-dihydroisothiazol-3-on (MCI/MI)) are bactericides and their killing action must be quick. Typical in-can preservative dosages are 0,003 % for MIT (2-methyl-2H-isothiazol-3-on) and also for CIT (5-chloro-2-methyl-2HH-isothiazol-3-on) (data from the company THOR, Germany).

Typical levels of In-can Preservatives in paints are 0.5 % by weight of total formulation (1 % by weight in some climates with ideal growth for mildew) 0.05 – 0.2 % by weight typical level of biocides in paints (in can) (Balk et al. 2000).

Examples of in-can paint preservatives and their recommended use level are (Rossmore (1995) in Baumann et al. 2000):

- 4,4- dimethyloxazolidine (74.7 % ai)	0.05 – 0.3 %
- 1,2-dibromo-2,4-dicyanobutane (25 % ai)	0.10 – 0.3 %
- 2[(hydroxymethyl)amino]ethanol (100 % ai)	0.10 – 0.3 %
- 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride (69 % ai)	0.01 – 0.27 %
- 1,2-benzisothiazolin-3-one (19 % ai)	0.04 – 0.125 %
- Mixture of CIT (1,15 % ai) and MIT (0.35 % ai) (total 1.5 %)	0.05 – 0.167 %
- hexahydro-1,3,5-triethyl-s-triazine	0.01 – 0.1 %

- 2-hydroxymethyl-2-nitro-1,3-propanediol (50 % ai) 0.02 – 0.3 %

Zinc pyrithione Fungicide is, among others, used for:

- Dry film and in-can preservative for water-based latexes, emulsions, pigment slurries, paints, caulks, adhesives, sealants, grouts, and patching compounds.

According to Baumann et al. (2000) the substances used as In-can Preservatives in the paper, textile and leather production are comparable to the substances of product type 7 film preservatives and product type 9 for the preservation of fibre, leather, rubber and polymerised materials.

The biocidal substances used to preserve the diluted fluid during metalworking act also as an in-can preservative during shelf-life (Van der Aa 2003).

Biocides for the in-can preservation of fuel should meet the following criteria:

- active in low dosage (no dilution of the fuel);
- no interference with the combustion process;
- broad spectrum of effectiveness;
- soluble in water as well as in fuel (low log Kow);
- non-corrosive;
- preferably contain no metal or halogen compounds.

Examples are formaldehyde donors, pyridine-derivatives and heterocyclic N,S compounds (Van Dokkum et al. 1998).

Currently lower concentrations are being established in view of the labelling requirements when higher concentrations are used.

2.3 Identification of the potential points of release in the application and use area

2.3.1 Washing and cleaning fluids, human hygienic products

The environmental emission from biocides used in washing and cleaning fluids and human hygienic products is very diffuse. After application the products will usually be rinsed or washed off immediately or at a later stage. As a worst case it is assumed that 100% is discharged to the sewage treatment plant (TGD, IC5&IC6 in EC 2003a).

Another potential route of emission is the disposal of the packaging material together with the remnant of the product or the disposal of outdated products to a waste dump via the normal routings of municipal waste.

2.3.2 Detergents

See sections 2.3.1 and 2.3.5.

2.3.3 Paints and coatings

Points of release are during industrial use (formulation of products containing preservatives), paint application, service life of the painted product and the waste

treatment stage. Recycling may be a potential stage for some painted articles (e.g. steel or aluminium).

The UK ESD document on coatings and application (EA-UK 2002) gives flow charts used for emission estimates for various coating applications. It considers the emissions to all environmental compartments during the application of the coating/paint, service life and end-of-life of the treated product.

2.3.4 Fluids used in paper, textile and leather production

Paper

According to Tissier and Migné (2001) biocides used as In-can Preservatives in the paper industry are used in coating additives, in solutions/slurries of coating binders, speciality additives or in the complete coatings that are stored in a tank for a period of time. Points of their release during paper production are during industrial production, when the coating including the preservative is applied. The coating is dried and the preservative may be emitted to air. In other processes water may be used for washing and cleaning causing emission to water. Liquid residues of the coatings may be treated separately in a precipitation step of ultra-filtration (Tissier and Migné 2001). Biocides usually represent less than 1% of the sizing solution. Biocides used are ascorbic acid, ascorbates, benzoic acid, sodium benzoate, formic acid, glutardialdehyde, 2-bromo-2-nitropropanediol, isothiazolinones, bromohydroxy-acetophenone, dodecylguanidine hydrochloride. For In-can Preservatives the substance is not designed for fixation onto fibres and it can be assumed that no specific fixation occurs (in Tissier and Migné 2001).

Other emission points are at the end of the life cycle at the disposal of coated waste paper and when the waste paper is being recycled. The releases are emitted to (indoor) air and waste water.

Textile production

According to Tissier et al. (2001), biocides used in the production of textile refer mainly to treatment of the textiles (e.g., moth repellents, biocides against rot and mildew), not in the protection of fluids used in textile production as covered by PT6.

Leather production

According to Tissier and Chesnais (2001), biocides are used in the production of leather for the direct treatment of the leather and not to preserve the fluids used in the processes as covered by PT6.

2.3.5 Lubricants or Metal working fluids

Metalworking fluids are used during a specified period. When the quality becomes poor, the fluid is treated in a physical/chemical system and the remaining water is disposed of to a wastewater treatment system. The oil-phase is treated as chemical waste.

2.3.6 Fuels

Emissions to the environment predominantly occur when the water phase of a storage is discharged into the sewer (Van der Poel and Bakker 2002).

3 EMISSION SCENARIOS FOR IN-CAN PRESERVATIVES

Table 3.1 summarises the availability of emission scenarios for the various life cycle stages of applications of In-can Preservatives. It is meant as a guidance to available documents. In view of the large range of applications of In-can Preservatives, no general statement on the applicability of available scenario descriptions can be given. The relevant emissions during various life cycle stages as well as the receiving compartments are to be determined by the specific applications and characteristics of a particular in-can preservative on a case by case basis.

Table 3.1 Available emission scenarios documents for Biocides used as In-can Preservatives. Codes refer to documents listed in table 1.1.

Applications in	Life cycle stage	Surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
Washing and cleaning fluids (P+N)	service life disposal	- -	- -	- -	- + 1)	PT 1, PT2 -
Detergents (P+N)	service life disposal	- -	- -	- -	- + 1)	PT 1, PT 13 -
Paints and coatings (P+N)	application	-	EA-UK, IC-14	PT 8, PT10, IC-14	EA-UK, IC-14	PT 10, EA-UK, IC-14
	service life	PT8, PT 21	-	PT 8, PT 10 EA-UK	-	-
	disposal	-	-	IC-14	EA-UK, IC-14	-
Fluids used in production (P) of paper	application	-	BPT 6,7,9	-	-	IC-12, BPT 6,7,9 PT 12 RIVM/FEI
	service life	-	-	-	-	-
	disposal	-	-	-	1)	IC-12, BPT 6,7,9
textile	application	-	-	-	-	IC-13, BPT 9
	service life	-	2)	-	-	IC-13, BPT 9, 2)
	disposal	-	-	-	1)	-
leather	application	-	-	-	-	IC-7, BPT 9
	service life	-	2)	-	-	2)
	disposal	-	-	-	1)	-
Lubricants (P) – Metalworking fluids	service life	-	-	-	-	PT13
	disposal	-	-	-	-	-

Applications in	Life cycle stage	Surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
Fuels	pre-service service life disposal	3)	3)	3)	3)	3)
Glues and adhesives	application service life disposal	- - -	- 2) -	- 2) -	- - 1)	- 2) -

'+' : relevant; '-' not relevant

P: professional use; N: non-professional use

1) Section on 'Waste disposal including waste treatment and recovery' in TGD (EC 2003a)

2) Section on 'Emissions during service-life of long-life articles' in TGD (EC 2003a)

3) Suitable emission scenarios may be found in RARs carried out for various substances in fuel in the context of the Existing Chemicals Regulation (see list in table 1.1)

4 REFERENCES

Balk F, A Roorda, ALM Rutten, M Th de Kok, 2000. Identification and description of biocidal product types and establishment of scores based on the level of exposure of humans and the environment. Biocides Study DG XI/E2/ETU/980056, April, 2000.

Baumann, W, K Hesse, D Pollkläser, K Kümmerer, T Kümpel (2000). Institute for Environmental Research (INFU), University of Dortmund, UBA Berlin: Gathering and review of Environmental Emission Scenarios for biocides.

EA-UK 2002. Development of Emission Scenario Documents for Use in Environmental Risk Assessment. Coating Materials Industry: Paints, Laquers and Varnishes". Risk and Policy Analysts Technical Report P2-203/TRI. Environmental Agency UK.

EC (2002a). Borderline between Directive 98/8/EC concerning the placing on the market of biocidal products, Directive 2001.83/EC concerning proprietary medicinal products and Directive 2001/82/EC concerning veterinary medicinal products. Guidance document agreed between the Commission services and the competent authorities of Member States, 30.7.2002.

EC (2002b). Borderline between Directive 98/8/EC concerning the placing on the market of biocidal products and Directive 76/768/EEC concerning cosmetic products. Draft Guidance document agreed between the Commission services and the competent authorities of Member States. 4.1.2002.

EC 2003a. Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Parts I, II, III, IV. 2nd edition.

PART IV:

IC-5 Personal/domestic and IC-6 Public domain. Assessment of the environmental release of soaps, fabric washing, dish cleaning and surface cleaning substances.

IC-7. Leather processing industry &

BPT 9. Biocides used as preservatives

Assessment of environmental release of chemicals from the leather processing industry

IC-8. *Metal extraction industry, refining and processing industry*. Assessment of environmental release of chemicals used in metal-cutting and -forming fluids.

IC-12. Pulp, paper and board industry. Assessment of the environmental release of chemicals used in the pulp, paper and board industry.

BPT 6,7 & 9. Biocides used as preservatives in various applications. Emission scenario document for biocides used in paper coating and finishing

IC-13 Textile processing industry &

BPT-9 Biocides used as preservatives in the textile wet processing

Assessment of the environmental release of chemicals from the textile finishing industry.

IC-14. Paints, laquers and varnishes industry. Assessment of the environmental release of chemicals from the paints, lacquers and varnishes industry.

BPT-2 Private and public health area disinfectants and other biocidal products.

Assessment of environmental release of private and public health area disinfectants used for sanitary purposes and disinfectants for use in the medical sector.

EC (2003b). Manual of decisions for implementation of Directive 98/8/EC concerning the placing on the market of biocidal products. (used version: 18.6.2003).

Migné V. 2002. Supplement to the methodology for risk evaluation of biocides: Emission scenario document for biocides used as masonry preservatives (product type 10). INERIS-DRC-02-25582-ECOT-VMi-n°02DR0270.doc.

OECD 2003. Emission Scenario Document for Wood Preservatives. Part 1 to 4. OECD series on Emission Scenario Documents no. 2. Environmental Directorate. Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

Tissier C and V Migné, 2001. INERIS report DRC-01-25582-ECOT-CTi/VMi-no. 01DR0183. Supplement to the methodology for risk evaluation of biocides. Emission scenario document for biocides used in paper coating and finishing (product type 6, 7 & 9). Included in the TGD (EC 2003a).

Tissier C, M Chesnais and V Migné, 2001. INERIS report DRC-01-25582-ECOT-CTi/VMi-no. 01DR0176. Supplement to the methodology for risk evaluation of biocides. Emission scenario document for biocides used as preservatives in the textile processing industry (product type 9 & 18). Included in the TGD (EC 2003a).

Tissier C and M Chesnais, 2001. INERIS report DRC-01-25582-ECOT-CTi-no. 01DR0165. Supplement to the methodology for risk evaluation of biocides. Emission scenario document for biocides used as preservatives in the leather industry (product type 9). Included in the TGD (EC 2003a).

UBA, 2003. OECD ESD on textile finishing industry. Draft. Revision by Thomas Schäfer (incl. comments of TEGEWA, 5 November 2002) Version 24 January 2003. UBA Germany.

Van der Aa E and F Balk, 2003a. Environmental Emission Scenarios for Biocides used as Human Hygiene Biocidal Products (Product Type 1). Royal Haskoning 4L1784.A0/R011, Report to the EUBEES 2 Working Group.

Van der Aa E, I Kuppen and F Balk, 2003. Environmental Emission Scenarios for Biocides used as Film Preservatives (Product Type 7). Royal Haskoning 4L1784.A0/R014, Report to the EUBEES 2 Working Group.

Van der Aa E and F Balk, 2003b. Harmonisation of Environmental Emission Scenarios for Slimicides (PT-12). Royal Haskoning 4L1784.A0/R009, Report to the EUBEES 2 Working Group.

Van der Aa E, 2003. Harmonisation of Environmental Emission Scenarios for biocides used as metalworking fluid preservatives (Product type 13). Royal Haskoning 4L1784.A0/R008, Report to the EUBEES 2 Working Group.

Van der Plassche E and E van der Aa, 2003. Harmonisation of environmental emission scenario, Antifouling Products. Royal Haskoning 9M2892.01/R0003. Report to OECD Antifouling Steering Group for European Commission DG ENV Service contract No. B4-3040/2002/348010/MAR/C3.

Van der Poel P and Bakker J, 2001. Emission Scenario Document for Biocides: Emission Scenarios for all 23 product types of EU Directive 98/8/EEC. RIVM report 601 450 009.

Van der Poel, P and H Braunschweiler, 2002, Emission Scenario Document for biocidal products applied in the paper and cardboard industry National Institute of Public Health and the Environment (RIVM), Finnish environment Institute (FEI). Draft RIVM report.

Appendix 1: Available sources of information for PT 6

AVAILABLE SOURCES OF INFORMATION FOR PT 6

The following documents are the main sources of information for the present document:

1) *EU TGD IC-5 (and 6): Personal/Domestic and Public Domain*

This document contains a simple scenario for the release of detergent chemicals to raw sewage water during the use of these detergents. The scenario assumes that 100% of the used detergent chemicals ends up in sewage water. The treatment of the sewage water is not considered part of this scenario. It is expected that this model can also be used for the emission of biocides used in products of PT6.

2) *EU TGD IC-14: Paints, Lacquers and Varnished industry*

This document contains information on:

- the use of paints and varnishes,
- the components in paints and varnishes,
- the concentration of In-can Preservatives in paints and varnishes,
- the releases of chemicals in paints and varnishes to the environment during application of paints and the disposal of painted goods.

In addition, tables are provided, where release fractions for different kinds of paints and varnishes and for different life cycle stages are given. The paints are divided in:

- volatile,
- non-volatile and water soluble,
- and non-volatile and non water soluble components.

The information for these tables comes from several companies in various European countries (CEPE, 1993).

3) *Van der Poel and Bakker 2001, RIVM report 601 450 008*

This document is divided in sections for the different subgroups in PT6 (for example detergents). For every subgroup the life cycle scheme is given.

It includes:

- washing and cleaning fluids: a pick-list for average consumption per inhabitant per day and per application, number of applications and the fraction of inhabitants using the product;
- detergents
- paints and coatings (only in water based products): scenarios for In-can Preservatives used in paints at the stages of formulation of the paint, industrial use and waste treatment (scenario from TGD). No scenario is available for the stage of private use.
- fluids in paper, textile and leather production:
 - paper: somewhat modified scenario descriptions of Tissier and Migne (2001) are described
 - textile: Tissier et al. (2001) do not mention the use of In-can Preservatives in fluids for textile production. According to Van der Poel it is not surprising as most aqueous fluids used will not have organic chemicals in them. However a simple scenario is presented here.
 - leather: Tissier and Chesnais (2001) do not mention the use of In-can Preservatives in fluids for leather production. According to Van der Poel it is not likely that fluid with In-can Preservatives will be used at all. However a simple scenario is presented here.

- lubricants: the biocides that are used to preserve the metalworking fluid before usage are the same biocides that are used to preserve the fluid during metalworking. These preservatives are discussed for PT13: Metalworking preservatives.
- machine oils: Van Dokkum et al. (1998) mention the application of In-can Preservatives in machine oils. No information could be obtained on (water based) machine oils containing preservatives and use of such oils. Therefore, no ESD has been developed.

4) *Baumann et al. 2000, p.6 (Institute for Environmental Research (INFU), University of Dortmund, UBA Berlin: Gathering and review of Environmental Emission Scenarios for biocides (2000))*

This document contains information on:

- the use of In-can Preservatives used in the different subgroups of PT6,
- and expected emission routes.

The only life cycle stage that is covered by an emission scenario in this document is the waste treatment stage. The emission scenario for a landfill (Van der poel, 1999) is given.

5) *Tissier & Migne (2001), INERIS*

This document contains an emission scenario for products from PTs 6, 7 (Film preservatives) and 9 (incl. Paper and cardboard) in papermaking processes.

Next to the scenario description information is provided on:

- the paper industry and papermaking processes;
- biocides used in papermaking processes;
- expected release routes;
- data and estimates concerning production, process parameters, water consumption and waste water treatment in France, Germany and the EU in general.

6) *Tissier & Chesnais (2001), INERIS*

This document contains an emission scenario for products from PT9 used in the leather industry. In this scenario releases from the most important steps (according to the scenario description) of processing hides and skins are taken into account.

Next to the scenario description information is provided on:

- the leather industry and the processing of hides and skins;
- biocides used in the leather industry;
- expected release routes;
- data and estimates concerning production, process parameters, water consumption and waste water treatment in several EU countries.

7) *Tissier et al. (2001), INERIS*

Tissier et al., 2001 contains an emission scenario for products from PT 9 (incl Fibre, leather, polymerised materials) and PT18 (incl. insecticides) used in the textile processing industry. In this scenario releases from different stages of the textile processing are taken into account.

This scenario is meant for biocides that are applied on textile. The production phase of textile is not taken into account here.

Synthetic fibres are made of polymers and have a specific preparation. During the production phase of synthetic textile, biocides are added (formulation phase of these

polymers). The release of these biocides is treated in the scenario for plastic additives (BRE, 1998).

Next to the scenario description information is provided about:

- the textile industry and the processing of textile;
- biocides used in the textile industry;
- expected release routes;
- data and estimates concerning production, process parameters, water consumption and waste water treatment in several EU countries.

8) *Several scenarios for metalworking fluid preservatives: PT13 (among others IC-8)*

The biocides used in cooling lubricants (metalworking fluids) that are used to preserve the metalworking fluid before usage are the same biocides that are used to preserve the fluid during metalworking. These preservatives are discussed at in the emission scenario document for PT13: Metalworking preservatives (EUBEES2 document, Van der Aa 2003).

9) *EU TGD IC-12*

This document contains a simple scenario for the release of chemicals used in the pulp, paper and board industry. The scenario is applicable for slimicides (PT12) and other types of biocides used in papermaking processes, e.g. In-can Preservatives (PT6), pulp-preservatives (PT9) and coating additives, such as film preservatives (PT7). The treatment of the sewage water is not considered in this scenario. It is to be expected that this model can also be used for the emission of biocides used in products of PT6 for fluids in paper production.

10) *Van der Poel & Braunschweiler 2002, RIVM/FEI draft report Emission Scenario Document for biocidal products applied in the paper and cardboard industry* National Institute of Public Health and the Environment (RIVM), Finnish environment Institute (FEI)

Emission scenario with focus on slimicides intended for use in paper and cardboard manufacturing but it contains also a scenario for PT9 products used for preservation of fibre in paper industry. In the paper and cardboard industry preservatives are used for the preservation of pulp in the paper machine.

11) *Van der Aa & Balk 2003b. Harmonisation of Environmental Emission Scenarios. Biocides: PT 12.* Produced within the scope of the EUBEES 2 project. Scenario for estimating the emission rate of slimicides used in papermaking processes and in the oil industry.

11) *Migne (2002), INERIS: PT10 Masonry preservatives ESD (EUBEES2 document)*
This document is relevant also for PT6 In-can Preservatives for paints and coatings.

12) *OECD (2003): Emission Scenario Document for wood preservatives (PT8)*
Some parts of this ESD could be relevant also for PT6 In-can Preservatives for paints and coatings

13) *UK-Environmental Agency (2002): National R&D Project P2-203: "Development of Emission Scenario Documents for Use in Environmental Risk Assessment. Coating Materials Industry: Paints, Laquers and Varnishes".*

This study aims to review and revise the emission estimates for the coatings materials industry, with emphasis given to paints, laquers and varnishes. Emission estimates are given per sector of the industry on the basis of flow charts. Also overviews of the industry in the UK and the EU are given.

14) OECD ESD on textile finishing industry. Draft. Revision by Thomas Schäfer (incl. comments of TEGEWA, 5 November 2002) Version 24 January 2003. UBA Germany.

The document describes the European textile industry and the main processes in the textile industry. Also the textile auxiliaries, basic chemicals and biocides are described. Furthermore release estimation per process is given, branch specific parameters and emission calculations.

15) Emission Scenario Document Photographic industry IC-10. Assessment of the environmental release of photo chemicals. UBA Germany, February 2003. On behalf of the 10th Meeting of TFEEA.

In this document the use of biocide is mentioned only as an ingredient in photographic material (fungicide). Emissions take place during production of the photographic material, processing of photographic material in the developing processes and the disposal of used photographic material. A simple emission scenario is given for the release estimation for substances from photographic materials at processing.