

Section VI.J.

Guidance by source category: Annex C, Part III Source Categories

Textile and leather dyeing and finishing

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# Textile and Leather Dyeing and Finishing

## 1 TEXTILE INDUSTRY

### 1.1 Introduction

The textile industry exhibits one of the most complicated manufacturing chains. It is a fragmented and heterogeneous sector dominated by small and medium sized enterprises, with a demand largely driven by three main end-uses: clothing, home furnishing, and industrial use. As an example, in 2000 and in the European Union, 114,000 companies employed about 2.2 millions people (BREF 2003a).

The textile and clothing chain is composed of a wide number of sub-sectors covering the entire production cycle from the production of raw materials (man-made fibers) to semi-processed (yarns, woven and knitted fabrics with their finishing process) and final/consumer products (carpets, home textiles, clothing and industrial use textiles).

The complexity of the sector is also reflected in the difficulty of finding a clear-cut classification system for the different activities involved. This paper will concentrate on the activities that involve wet processes and thus cover the following three main sectors:

- Wool scouring
- Textile finishing, and
- Carpet sector.

### 1.2 The Textile Production Chain

Woven and knit fabrics cannot be processed into finished goods until the fabrics have passed through several water-intensive wet-processing stages (also known as finishing) such as fabric preparation, dyeing, printing, and finishing. Natural fibers typically require more processing steps than manmade fibers. Relatively large volumes of wastewater are generated, containing a wide range of contaminants that must be treated prior to disposal. Significant quantities of energy are used heating and cooling chemical baths and drying fabrics and yarns.

Fabric preparation requires de-sizing<sup>1</sup>, scouring<sup>2</sup>, and bleaching as well as singeing<sup>3</sup> and mercerizing<sup>4</sup>. Dyeing operations are used at various stages of production to add color and intricacy to textiles and increase product value. Dyes used by the textile industry are largely synthetic. Finishing encompasses chemical or mechanical treatments (US-EPA 1997).

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<sup>1</sup> to remove size materials applied prior to weaving

<sup>2</sup> a cleaning process that removes impurities from fibers, yarns, or cloth through washing. Typically, alkaline solutions are used for scouring

<sup>3</sup> eliminates unwanted colored matter from fibers, yarns, or cloth.

<sup>4</sup> designed to chemically or physically alter the fabric by passing through a 15-20 % solution of caustic soda

The main environmental concerns in the textile industry are about the amounts of water discharged and the chemical load it carries. Other important issues are energy consumption, air emissions, solid wastes, and odors. This document will give a brief overview on the activities in the textile industry but address in more detail only those steps which have PCDD/PCDF relevance.

Figure 1 gives a schematic of the textile production chain. Although there is a multitude of steps in the production chain and environmental concerns do occur, generation of PCDD/PCDF could hardly be associated to individual production steps.

Instead, more attention has to be given to the fact that PCDD/PCDF enter the textile production process through application of pesticides and dyestuffs contaminated with PCDD/PCDF and that the PCDD/PCDF contamination is being carried through the various steps of the production chain. Depending on the individual steps, solvents applied, and the physical environment, PCDD/PCDF either stay in the textile product or are discharged as wastes.

New formation of PCDD/PCDF may occur in production chains where effluents are treated, sludge is being removed and incinerated. Such plants typically are considered to be modern.

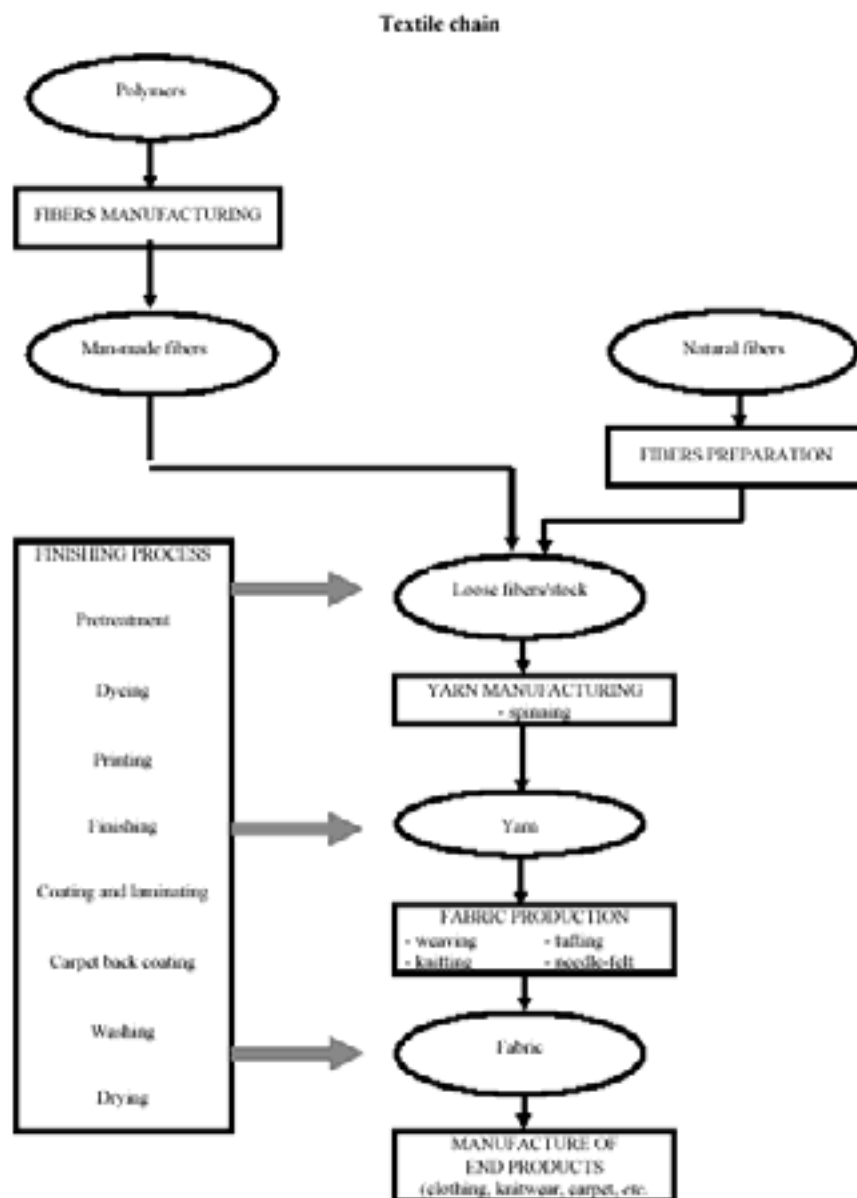


Figure 1: General diagram of processes in the textile industry (adapted from BREF 2003a)

## 2 STEPS/FACTORS TO BE CONSIDERED FOR PCDD/PCDF FORMATION AND RELEASE

General good management practices include staff education and training, maintenance of equipment (and its documentation), chemical storage, handling, dosing and dispensing, improved knowledge of inputs and outputs of the processes.

Knowledge about the textile raw materials is essential in managing pollution transfers. Raw wool fibers may be contaminated with pesticides, sometimes organochlorines pesticides, including pentachlorophenol (PCP), have been applied by the manufacturer. Effective

washing in wool scouring, *e.g.*, with perchloroethylene, will effectively remove all grease and pesticides, which are typically found in the solvent phase.

In the wool scouring process, when evaporation of the effluent and incineration of the sludge is applied, PCDD/PCDF can either be concentrated in the sludge or be formed in the sludge incineration process. Since the effluents may contain elevated concentrations of chlorine, the propensity to generate PCDD/PCDF in badly controlled incineration plants exists.

For pretreatment, bleaching agents such as hydrogen peroxide (modern technology) or sodium hypochlorite (older technology) are used for cotton and cotton blends. Chlorine dioxide (from sodium chlorite or chlorate) is an excellent bleaching agent for synthetic fibers and for flax, linen and other blast fibers that cannot be bleached using peroxide alone.

Dyestuffs used in the dyeing and printing of textiles, *e.g.*, on the basis of chloranil or phthalocyanines, have been shown to be contaminated with PCDD/PCDF. For waste water containing pigment printing paste or latex from carpet backing, precipitation/flocculation and incineration of the resulting sludge is used instead of chemical oxidation (in the Fenton process).

Finally, polybrominated flame retardants, such as polybrominated diphenyl ethers (PBDE) and chlorinated paraffins (C<sub>10-13</sub> chloroparaffins) are used in the textile industry. Both classes of compounds are classified as hazardous chemicals by several organizations (*e.g.*, EC and OSPAR), all halogenated flame retardants are involved in the formation of PCDD/PCDF when submitted to high temperatures (BREF 2003a, \_\_\_\_\_).

### 2.1.1 Chemicals in Raw Materials

Two general categories of fibers are used in the textile industry: natural and man-made:

- |                              |                            |   |
|------------------------------|----------------------------|---|
| - Natural origin fibers      | - animal origin            | <i>e.g.</i> , raw wool, silk fiber, hair  |
|                              | - vegetable origin         | raw cotton fiber, flax, jute  |
|                              | - mineral origin           | <i>e.g.</i> , asbestos (not used in the textile industry)   |
| - Chemical fibers (man-made) | - natural polymer fibers   | <i>e.g.</i> , viscose, cupro, lyocell, acetate, triacetate  |
|                              | - synthetic polymer fibers | - Inorganic polymer, <i>e.g.</i> , glass for fiber glass, metal for metal fiber                                   |
|                              |                            | - Organic polymer, <i>e.g.</i> , polyester (PE), polyamide (PA), acrylic (PAC), polypropylene (PP), Elastane (EL) |

Chemicals can be contained in the fibers for different purposes. Chemicals of relevance for PCDD/PCDF generation that are applied to the fibers are listed below specifying the fiber, the purpose, and the type of chemical (BREF 2003a).

Fiber	Purpose	Chemical of Relevance
Wool (the animal hair from the body of sheep)	Ectopariticides	$\gamma$ -Hexachlorocyclohexane ( $\gamma$ -HCH, lindane) Dieldrin DDT
Cotton	Defoliant, fungicide	Pentachlorophenol (PCP) 2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP) (= chloronitrofen)*
	Dyes	Chloranil-based dioxazine dyes Phthalocyanine-based

\* not in BREF (2003a)

According to the BREF document on textiles (BREF 2003a), all major grower countries have banned the use of organochlorines pesticides for sheep treatment but there is evidence that wool from some former Soviet Union countries and South America contain lindane at detectable concentrations.

Results from the analysis of textiles of various origin and fibers gave strong indications that pentachlorophenol has been and perhaps still is being used as a biocide on raw materials, especially on cotton. The PCDD/PCDF pattern clearly reveals that PCP is the major source of the PCDD/PCDF in the textiles.

Although no published information was found that chloronitrofen is applied in the textile industry such use cannot be excluded since CNP has replaced PCP in many applications (Masunaga *et al.* 2001, Toolkit 2003).

### 2.1.2 Bleaching with Sodium Hypochlorite

For ecological reasons the use of sodium hypochlorite is now limited in Europe to just a few particular cases, connected with knitted fabric and, in some cases, bleaching of yarn when a high degree of whiteness is required. Bleaching with sodium hypochlorite leads, in fact, to secondary reactions that form organic halogen compounds, commonly quantified as AOX.

In 1991–1992, Swedish researchers found PCDD/PCDF in sludge from a textile plant that bleached with sodium hypochlorite. However, further investigations showed that pentachlorophenol was present in the hypochlorite (BREF 2003a).

### 2.1.3 Chemical Finishing Treatments in the Textile Industry

Textile finishing processes are typically not sources of PCDD/PCDF formation (Horstmann *et al.* 1993). Rather, the use of PCDD/PCDF-containing dyes and pigments and the use in some countries of pentachlorophenol to treat unfinished cotton appear to be the sources of the detected PCDD/PCDF.

Based on the analyses of 16 samples from Germany, it was concluded that, the PCDD/PCDF concentration will not increase significantly during these finishing processes: mean concentrations found in finished cotton were at  $0.21 \pm 0.10$  ng I-TEQ/kg with a median of 0.20 ng I-TEQ/kg (Horstmann 1994). These results were confirmed by random sample analyses of raw and pre-treated cotton arriving at the Hamburg harbor, which contained 0.03-0.2 ng I-TEQ/kg (Hutzinger *et al.* 1995).

#### 2.1.4 Drying and Curing

The BREF stipulates the following, however, I have not found any evidence that PCDD/PCDF evaporate:

In the drying and curing operation, air emissions are produced due to the volatility of the active substances themselves, to their constituents or are associated with residues of preparations and carry-over from upstream processes, *e.g.*, PCDD/PCDF may arise from the thermal treatment of textiles that have been previously treated with chlorinated carriers or polyethylene (BREF 2003a, page 104).

#### 2.1.5 Aqueous Discharges, Dewatering, and Incineration of Sludges

In wool scouring, incineration is used in conjunction with evaporation of the effluent because the surplus heat from the incinerator can be used in the evaporation process. Incineration of wool scour sludges has potential for air pollution. Since sludges contain relatively high contents of chloride (from suint) as well as organically bound chlorine from ectoparasiticides, *etc.*, there is potential for the generation of PCDD/PCDF, when they are incinerated (catalytic and high temperature incinerators are now available to prevent these emissions) (BREF 2003a, UNEP 2003).

##### 2.1.5.1 *Effluent and Waste Management at a Textile Mill*

The evaporator concentrate entering the incinerator has a calorific value of 9.5 MJ/kg and its combustion is self-supporting (no fuel added from external sources). The operating temperature of the incinerator is 1200 °C in order that PCDD/PCDF are destroyed. The exhaust gases are used to heat the boiler, as already stated, and fly ash is removed from the boiler flue gases in a bag filter system. The ash is extracted with water to recover sodium and potassium carbonate in solution, which is used as a builder in the scour. The extracted ash and the solidified liquid ash from the incinerator are landfilled (BREF 2003a).

##### 2.1.5.2 *Integrated Dirt Removal/Grease Recovery Loops Combined with Evaporation of the Effluent and Incineration of Sludge*

A mill that applies a closed-loop treatment of wool scouring effluents by evaporation/incineration with recovery of water and energy. The integrated evaporator/incinerator/boiler system is self-efficient in energy, which is derived from the sludge. Ammonia is used in a catalytic reactor to remove NO<sub>x</sub> in the incinerator flue gases. Incineration of the evaporator concentrate (9.5 MJ/kg) is self-sufficient in combustion. The temperature of the incinerator is 1,200 °C in order to destroy PCDD/PCDF. Fly ashes are removed in a bag-filter. In the gaseous emissions, 0.02 ng TEQ/m<sup>3</sup> were detected (BREF 2003a, p 278).

##### 2.1.5.3 *Treatment of Mixed Waste Water*

Sludge from flotation is dewatered and then thermally regenerated in a rotary kiln, whose flue gases have a temperature of 450 °C. The flue gas is burned in an after-burner (about 850 °C) and released to ambient air at a temperature of 120 °C. In the off-gases from the regeneration

plant for lignite coke in the sludge plant, PCDD/PCDF concentration of 0.004 ng I-TEQ/Nm<sup>3</sup> (@11 % O<sub>2</sub>) were found (BREF 2003a, p 415-417).

When the sludges containing pigment paste are being burned, due to the presence of chlorides, there exists the probability to form PCDD/PCDF (BREF 2003a, p 426, UNEP 2003).

### **3 LEATHER REFINING**

#### **3.1.1 Introduction**

The tannery industry consists of converting the raw hide or skin into leather, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Among these, tanning is the fundamental stage, which gives leather its stability and essential character. Tanneries very often are small enterprises. The major output for EU tanneries is for production of footwear (50 %) followed by the clothing industry (20 %), and furniture (17 %) (BREF 2003b).

The tanning industry is a potentially pollution-intensive industry with relevant water discharges and uses of certain chemicals as biocides, surfactants, and organic solvents.

The production process in a tannery can be divided into four stages:

- Hide and skin storage and beamhouse operations
- Tanyard operations
- Post-tanning operations
- Finishing operations

#### **3.1.2 PCDD/PCDF Relevance**

So far, there are no reports on PCDD/PCDF contamination at or around leather plants. However, contamination of commercial leather products has been reported and based on the PCDD/PCDF pattern, it can be assumed that principally the findings identified in the textile industry are also responsible for the occurrence of PCDD/PCDF in leather products and in emissions (Toolkit 2003).

The primary source of contamination seems to be PCP. This assumption is underlined by the fact that since the ban of PCP in Germany in the year 1989<sup>5</sup>, the PCDD/PCDF concentrations in leather goods decline (EC 1996).

In contrast to textiles, PCP once applied on leather is not so easily removed by washing processes. In leather “breast-wallets” concentrations of PCDD/PCDF up to 430 ng I-TEQ/kg, in leather shoes up to 6,400 ng I-TEQ/kg were found (Malisch 1994). Although in many countries, the use of PCP has decreased, at least in shoes, the PCDD/PCDF concentrations did not decrease: in Germany, peak concentrations of 2,100 and 3,000 ng I-TEQ/kg, respectively, were detected in leather shoes bought in 1991. In the year 1996, highly elevated concentrations continued to exist (Klasmeier and McLachlan 1997). For leather goods, the

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<sup>5</sup> Which sets a maximum concentration of 5 mg PCP/kg in the final product



PCP concentrations correlate with PCDD/PCDF concentrations at least qualitatively and the homologue and congener profiles and patterns strongly indicate that PCP is the major source of the PCDD/PCDF contamination.

## 4 CONCLUSIONS

So far, there is no strong evidence that the production steps in the textile and leather finishing industry are generators of new PCDD/PCDF. The occurrence of PCDD/PCDF in the textile and leather industries are due to:

- Use of chlorinated chemicals, *esp.* PCP, to protect the raw material (cotton, wool or other fibers, leather, *etc.*);
- Use of dioxin-contaminated dye-stuffs, *e.g.*, dioxazines (chloranil-based) or phthalocyanines; and to a much lesser extend through
- Formation of PCDD/PCDF during finishing.
- Finally, formation of PCDD/PCDF may occur upon incineration of sludges.

Plants with capture of aqueous discharges, concentration of sludges, and subsequent incineration of these sludges from dirt removal/grease recovery loops have the potential to generate PCDD/PCDF since the sludges typically contain chlorine, organic carbon and are incinerated in the presence of air (oxygen). In such cases, adequate equipment must be present and good combustion practices must be applied. In general, the rules for BAT/BEP for the incineration of sewage sludge should be followed.

PCDD/PCDF contamination has been found in both textile and leather products. Within the textiles, very often cotton products contained high concentrations of PCDD/PCDF but also in synthetic fibers and wool products, PCDD/PCDF have been identified. For example, 244 ng I-TEQ/kg were detected in bleached polyester, 370 ng I-TEQ/kg in blue cotton (Horstmann 1994), and 86 ng I-TEQ/kg in wool (Mayer 1997). The homologue profiles of all highly contaminated samples were dominated by the higher chlorinated PCDD and PCDF (Cl<sub>7</sub> and Cl<sub>8</sub>). These are indicators for either the use of the biocide pentachlorophenol or chloranil-based dyestuffs as the source of the contamination.

However, there is no simple indicator to identify dioxin-contaminated fibers, wools or textiles. Several analyses confirmed that there is no correlation between PCP and PCDD/PCDF concentrations in textiles although the dioxin patterns gave strong indications that PCP should be the source. These findings make sense as PCP is water-soluble and will be removed in the finishing process and final washing processes whereas the PCDD/PCDF adsorb to the fiber and will stay in the textile. For leather products, at least in most cases, there was at least a qualitative correlation between PCP and PCDD/PCDF.

Finally, it should be noted that experiments had demonstrated that from highly contaminated cloths, a small percentage of PCDD/PCDF can be gradually transferred to the skin. In addition, since PCDD/PCDF are removed during the washing of the textiles, heavily contaminated textiles can contaminate other textiles (Horstmann and McLachlan 1994).

## 5 ANNEXES

This Annex contains specific and detailed data for information. The data given are not thought to represent any threshold or limit. Also note that some of the information is quite old (in terms of PCDD/PCDF science) and may no longer apply to the present situation. Nevertheless, for historic evaluation and since the presence of some of earlier produced batches may still be used or consumer goods treated with these chemicals may still be found in some parts of the world, the information included here may be valuable.

### 5.1 Brief Overviews on Chemicals Known to Be Contaminated with PCDD/PCDF and Potentially Applied in the Textile and Leather Industries

#### 5.1.1 Pentachlorophenol (PCP) and Sodium Pentachlorophenate (PCP-Na)

Pentachlorophenol (PCP) and sodium pentachlorophenate (PCP-Na) are pesticides and used as a preservative for, *e.g.*, wood (indoor and outdoor), leather, textiles (including cotton or wool). Pentachlorophenol (PCP) is a chlorinated hydrocarbon insecticide and fungicide. The predominant use of PCP was as wood preservative at least until the end of the 1980s. In the USA, 95-98 % of American PCP production is used directly or indirectly in wood treatment. Data from Canada (95 %) and Germany (61 %) confirm the main use of PCP as a wood preservative. In Germany, however, considerable amounts of PCP were used by the textile (13 %), leather (5 %), mineral oil (6 %), and glue (6 %) industries in 1983 (Toolkit 2003).

The sodium salt of pentachlorophenol (PCP-Na) is utilized primarily in aqueous solution. It is used as an antifungal and antibacterial, and has applications in the following areas:

- a wood preservative (fungicide and anti-blueing agent),
- an agent for the impregnation of industrial textiles (fungicide),
- bactericide in tanning and the paper pulp industry,
- a molluscicide in the treatment of industrial water, in particular cooling water,

and sometimes as

- a sterilizing agent.

There are three major processes for the commercial production of pentachlorophenol (Toolkit 2003):

1. The most common method is the direct chlorination of phenol with chlorine gas in the presence of a catalyst. The reaction results in the formation of byproducts such as hydrogen, hydrogen chloride and PCDD/PCDF.
2. Hydrolysis of hexachlorobenzene with sodium hydroxide. PCDD/PCDF are formed as unwanted byproducts. This process was used only in Germany.
3. In China, PCP is manufactured via thermolysis of hexachlorocyclohexane (HCH).

Overall, there are two processes to manufacture PCP-Na:

1. Hydrolysis of hexachlorobenzene (HCB) with sodium hydroxide. This process was applied in Germany until 1984 (then, method (2) with PCP as the starting material has been used).
2. Dissolution of PCP in sodium hydroxide. After filtration, the PCP-Na solution is being concentrated.

Normally, the PCDD/PCDF contamination in PCP-Na is lower as in the PCP as some contamination is eliminated through the filtration process.

The contamination of PCP and PCP-Na with PCDD and PCDF varies from some  $\mu\text{g}$  I-TEQ/kg to 1-2 mg I-TEQ/kg depending on the manufacturing process and the compound. Today many countries have banned the use of pentachlorophenol and its sodium salt.

### 5.1.2 Chloranil

2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (*p*-chloranil) is the precursor for the production of dioxazine dyes<sup>6</sup> (for cotton, leather, and synthetics) and other chemicals (*e.g.*, seeds and fungicides). Depending on the production process, *p*-chloranil can contain high contamination with PCDD/PCDF (Toolkit 2003).

Two production processes are known:

1. The old Hoechst AG process via chlorination of phenol (used until 1990 in Germany). Utilizing this old process, *p*-chloranil was contaminated in the range of several hundred  $\mu\text{g}$  I-TEQ/kg with PCDD/PCDF (mostly PCDF). The contamination of the ortho congener was much lower (around 60  $\mu\text{g}$  I-TEQ/kg).
2. The process developed by Rhône-Poulenc Chimie and used today by, *e.g.*, Clariant (Germany) via chlorination (with HCl) of hydroquinone. This process results in much cleaner products (*p*-chloranil:  $\sim 7$   $\mu\text{g}$  I-TEQ/kg)<sup>7</sup> (Toolkit 2003).

Of the approximately 400 t of chloranil produced per year until 1989, 300 t/a were processed to pigments and 100 t/a to dyestuffs (BUA 1992). In the last year of its production 1990, Hoechst AG produced 300 t/a. Until 1989, 150-200 t/a have been exported and approximately 50-100 t/a have been imported by the Hoechst AG from India. It is known that in India the same process has been applied for the production of chloranil until the mid of 1990. Further imports into Germany have been estimated to be around 50-100 t/a (BUA 1992). Since 1990, the only producer in Western Europe and probably the largest producer of chloranil worldwide is Rhône-Poulenc Chimie of France. Smaller production sites of chloranil have been found to exist in India, which may still use the traditional phenol process. No information could be obtained for productions in Eastern Europe and the Russian Federation. However, it is known that chloranil has been produced in the Russian Federation and has been

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<sup>6</sup> Synthesis of pigments is from reaction of chloranil (or other halogenated benzoquinones) with aromatic amines to diarylaminochloroquinones and oxidative cyclization in high-boiling solvents, such as *o*-dichlorobenzene, in the presence of acyl chlorides or sulfuric acid

<sup>7</sup> The same quality is obtained by Tokoyama Soda (Japan)

imported into Russia as well. There is no domestic production of chloranil in the United States of America (Toolkit 2003).

PCDD/PCDF contamination in the final products made from chloranil, such as dyestuffs and pigments, finally will end in wastes of polymers/plastics, textiles and packaging materials (paper, tin cans, *etc.*) to be disposed of as municipal solid waste or re-entering recycling processes. In the case of paper recycling and textile and leather dyeing, the PCDD/PCDF will be released into water or found in the sludges.

Concentrations of PCDD/PCDF in chloranils and dye pigments are given in Table 2 and Table 3. Dioxazine dyes and pigments using the old process had concentrations between 20,000 and 57,000 µg TEQ/t (for Blue 106) and between 1,000 and 19,000 µg TEQ/t (Violet 23) (Williams 1992). In the USA, concentrations in chloranil were between 263,000 µg TEQ/t and 3,065,000 µg TEQ/t. The Carbazole Violet (dye-pigment) had 211,000 µg TEQ/t (Toolkit 2003, and see this Annex).

### 5.1.3 Phthalocyanines

There are no congener-specific data available to report PCDD/PCDF concentrations in phthalocyanine dyes. Hutzinger and Fiedler (1991) reported concentrations between 0.5 and 2.7 ppb for Cl<sub>5</sub>DD, Cl<sub>6</sub>DD, Cl<sub>4</sub>DF, Cl<sub>5</sub>DF, Cl<sub>6</sub>DF in nickel phthalocyanine. No PCDD/PCDF were detected in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye at detection limits of 0.1 to 0.5 µg/kg (Hutzinger and Fiedler 1991).

### 5.1.4 2,4,6-Trichlorophenyl-4'-nitrophenyl Ether (CNP)

2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP) or chloronitrofen has been used as an alternative for pentachlorophenol with intensive applications in rice paddies in Japan. CNP has been found to contain high concentrations of PCDD and PCDF. Especially, batches produced in the 1970s and early 1980s had contamination in the range of 240 to 540 µg TEQ/kg; later productions showed lower concentrations in the range of 400 ng TEQ/kg (Masunaga *et al.* 2001). There is no further information on the synthesis and what might have caused the decrease in the contamination level in the more recent batches (Toolkit 2003).

## 5.2 Analytical Data on Relevant Chemicals and Contaminations in Consumer Goods

Table 1: Concentrations of PCDD/PCDF in pentachlorophenol (PCP) and 2,4,6-trichlorophenyl-4'-nitrophenyl ether (CNP, chloronitrofen) (Hagenmaier and Brunner 1987, Hagenmaier 1990, Masunaga *et al.* 2001, Toolkit 2003)

Chemical	Origin/Use	Concentration (ng I-TEQ/kg)	Remark
PCP	Europe, USA	2,000,000	By direct chlorination of phenol or by hydrolysis of HCB with sodium hydroxide

PCP	China	800,000	By thermolysis of hexachlorocyclohexane
PCP-Na		500	Dissolution of PCP in sodium hydroxide or hydrolysis of HCB with sodium hydroxide
PCP - Witophen P	Germany	1853,000	
PCP -Rhône-Poulenc	France	2321,000	
Na-PCP - Dowicide	USA	452,000	406,000 WHO-TEQ
Na-PCP - Preventol		80,000	58,500 WHO-TEQ
PCP-Na - Prolabo	France	3,374,000	Santl <i>et al.</i> (1994)
PCP	Vulcan, 1985	4,445,000	
PCP	Vulcan, 1986	2,736,000	
PCP	Vulcan, 1988	4,173,000	
CNP, old technology	Japan	300,000	
CNP, new technology	Japan	400	

C.I. Pigment Violet 23 (Hoechst AG) and C.I. Pigment Violet 37 (Ciba Geigy AG) are dye pigments used for used for lacquers, polymers, and printing inks (Toolkit 2003).

Table 2: Concentrations of PCDD/PCDF in dye pigments and dyestuffs

Chemical	Origin/Use	Concentration (ng TEQ/kg)		Remark
		ng I-TEQ/kg	ng WHO-TEQ/kg	
<i>p</i> -chloranil	Starting material for production of dioxazine dyes	400,000		<i>via</i> chlorination of phenol
<i>p</i> -chloranil	Starting material	100		<i>via</i> hydroquinone (modern process)
chloranil	Starting material	263,000-3,065,000		From USA
<i>o</i> -chloranil		60,000		<i>via</i> chlorination of phenol
		ng I-TEQ/kg	ng WHO-TEQ/kg	
Chloranil	USA	263,000	31,000	Remmers <i>et al.</i> , 1992
Chloranil	USA	2,874,000	2,532,000	
Chloranil	USA	814,000	85,000	
Chloranil	USA	3,065,000	2,903,000	
Carbazole Violet	dye-pigment	211,000	156,000	
Blue 106	Dioxazine dye	56,428	7,450	using the old process
Blue 106	Dioxazine dye	30,330	3,400	
Blue 106	Dioxazine dye	19,502	2,300	
Blue 108	Dioxazine dye	124	100	Williams <i>et al.</i> , 1992
Violet 23	Dioxazine dye	15,941	8,700	
Violet 23	Dioxazine dye	1,441	600	
Violet 23	Dioxazine dye	18,941	5,600	
Violet 23	Dioxazine dye	12,725	4,200	
Violet 23	Dioxazine dye	2,704	1,100	
Violet 23	Dioxazine dye	2,705	1,000	

Table 3: PCDD/PCDF in chloranil from different producers; concentrations in µg/kg (BUA 1992)

Congener	Rhône-Poulenc Chimie	Fa. Hoechst
2,3,7,8-Cl <sub>4</sub> DD	NQ (0.076)	NQ (0.1)
∑ Cl <sub>4</sub> DD	ND <sup>1)</sup>	0.1
1,2,3,7,8-Cl <sub>5</sub> DD	NQ (0.062)	1.8
1,2,3,4,7,8-Cl <sub>6</sub> DD	NQ (0.11)	NQ (0.1)
1,2,3,6,7,8-Cl <sub>6</sub> DD	NQ (0.10)	3.2
1,2,3,7,8,9-Cl <sub>6</sub> DD	NQ (0.06)	NQ (0.1)
1,2,3,4,6,7,8-Cl <sub>7</sub> DD	NQ (0.09)	ND
∑ Cl <sub>7</sub> DD	ND	240
Cl <sub>8</sub> DD	0.4	180 000 <sup>2)</sup>
2,3,7,8-Cl <sub>4</sub> DF	0.12	NQ (0.1)
∑ Cl <sub>4</sub> DF	ND	0.1
1,2,3,7,8-Cl <sub>5</sub> DF	NQ (0.77)	ND
2,3,4,7,8-Cl <sub>5</sub> DF	NQ (0.11)	NQ (0.1)
∑ Cl <sub>5</sub> DF	ND	12
1,2,3,4,7,8-Cl <sub>6</sub> DF	15.5	ND
1,2,3,6,7,8-Cl <sub>6</sub> DF	NQ (1.5)	0.9
1,2,3,7,8,9-Cl <sub>6</sub> DF	NQ (0.73)	ND
2,3,4,6,7,8-Cl <sub>6</sub> DF	2.5	ND
∑ Cl <sub>6</sub> DF	ND	14
1,2,3,4,6,7,8-Cl <sub>7</sub> DF	440	ND
∑ Cl <sub>7</sub> DF	ND	ca. 450
Cl <sub>8</sub> DF	138	65 000 <sup>2)</sup>
I-TEQ	6.7 <sup>3)</sup>	ND (>246)

NQ = not quantifiable (Limit of quantification in parenthesis)

<sup>1)</sup> ND = not determined; <sup>2)</sup> determined with HPLC;

<sup>3)</sup> calculated with inclusion of half of limit of quantification

Table 4: PCDD/PCDF in textiles (Horstmann and McLachlan, 1995)  
PA = polyamide, PE = polyethylene

	Textile	Colour	Fibre (%)	ng I-TEQ/kg
P1	Socks	white, red rings	64 PA, 36 PAN	0.24
P2	Socks	white, blue rings	81 Cotton, 19 PE	0.17
P3	T-shirt	white	100 Cotton	0.07
P4	Linen	white	100 Cotton	1.31
P5	Body	white-grey	100 Cotton	0.01
P6	Legging	white	95 Cotton, 5 Elasthan	0.11
P7	T-shirt	dark blue	100 Cotton	0.27
P8	T-shirt	light blue	100 Cotton	3.64
P9	Towel	violet	100 Cotton	0.22
P10	Linen	ocker	100 Cotton	0.54
P11	Men's underwear	white	100 Cotton	0.74
P12	Women's underwear	white	100 Cotton	0.05
P13	Shirt (Men)	light+dark blue stripes	65 PE, 35 Cotton	8.42
P14	Jeans	blue	100 Cotton	0.21
P15	T-shirt	orange	100 Cotton	0.59
P16	Socks	blue	100 Cotton	0.22
P17	T-shirt	light blue	100 Cotton	2.11
P18	T-shirt	pink	100 Cotton	0.88
P19	T-shirt	blue	100 Cotton	1.51
P20	T-shirt	dark blue	100 Cotton	0.14
P21	T-shirt	green	100 Cotton	26.8
P22	T-shirt	green	100 Cotton	1.96
P23	T-shirt	violet	100 Cotton	369

It should be noted that from the above mentioned samples, samples P17, P21, and P23 were analyzed for PCP. However, only in P21, PCP could be quantified (2 000 ng/g). Thus, it is not possible to establish a correlation between PCDD/PCDF concentration and PCP occurrence or concentration. The result can be easily understood taking into consideration that the physical-chemical properties of PCP and PCDD/PCDF are very distinct. During the finishing process in the textile manufacturing chain, PCP may be washed out with alkali whereas the PCDD/PCDF stay adsorbed to the fibers.

Table 5: PCDD/PCDF in blue and green cotton T-shirts (Horstmann and McLachlan, 1995)

Sample	1	2	3	4	5	6	7	8	9
Color	Blue	Green	Blue	Blue	Blue	Blue	Blue	Blue	Gr/blue
ng I-TEQ/kg	<0.05	4.1	0.30	0.10	4.1	0.37	<0.05	0.25	1.7

Table 6: PCDD/PCDF in different synthetic material (Horstmann and McLachlan, 1995)

Sample ID	Synthetic material	Concentration (ng I-TEQ/kg)
S1	Polyacrylic	<0.05
S2	Polyamide	0.36
S3	Viscose	<0.05
S4	Acetate	0.49
S5	Polyester-unbleached	240
S6	Polyester-bleached	0.78

The unusually high concentration in sample S5 was characterized by an unusual homolog profile. The pattern was characterized by high concentrations of hexachlorinated dibenzofuran congeners; a source of this contamination could not be identified.

Table 7: PCDD/PCDF in wool and wool products (Mayer 1997))

Type	PCDD/PCDF Concentration (ng I-TEQ/kg)
Knitting wool	0.4-86.1
Knitting wool (brown)	0.7-37.0
Diaper pants	0.03-3.7
Socks	0.15-23.2
Hair of lamb skin	0.01-0.08
Untreated wool (sheep)	0.5; 1.1
Untreated wool (lamb)*	0.2; 0.7
Lanoline	0.6-7.2

\* 3 months old, known not to have been treated with disinfectants

Table 8: PCDD/PCDF and PCP in different leather samples (Malisch 1994)

Leather Consumer Good	PCP Concentration (mg/kg)	PCDD/PCDF Concentration (ng I-TEQ/kg)
Money bag (worn around neck)	0.17	3.1
Money bag (worn around neck)	0.21	3.1
Money bag (worn around neck)	10.20	29.3
Money bag (worn around neck)	10.30	56.7
Shoe lining leather	11.30	1,211
Money bag (worn around neck)	11.60	26.2
Shoe leather uppers	16.00	28.8
Money bag (worn around neck)	130	425
Money bag (worn around neck)	220	244
Shoe lining leather	246	353
Shoe lining leather	550	6,388



## 5.3 Country Descriptions

### 5.3.1 Situation Regarding PCP in Europe

In the EU, Directive 91/173/EEC prohibits the marketing and use of pentachlorophenol and its salts and esters in a concentration equal to or greater than 0.1 % by mass in substances and preparations<sup>8</sup>.

### 5.3.2 Situation regarding PCP in the United States of America

US regulation: the wood preservative uses Notice was amended by EPA to establish reliable and enforceable methods for implementing certified limits for Cl<sub>6</sub>DD and 2,3,7,8-Cl<sub>4</sub>DD in registered wood-preservative pesticide products. Concentrations of 2,3,7,8-Cl<sub>4</sub>DD were not allowed to exceed 1.0 ppb in any product, and after February 2, 1989, any manufacturing-use PCP released for shipment could not contain Cl<sub>6</sub>DD levels that exceeded an average of 2 ppm over a monthly release or a batch level of 4 ppm (a gradually phased in requirement). On January 21, 1987, EPA prohibited the registration of PCP and its salts for most non-wood uses. EPA deferred action on several uses (i.e., uses in pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and ecological effects data. On January 8, 1993, EPA issued a press advisory stating that the EPA special review of these deferred non-wood uses was being terminated, because all of these uses either had been voluntarily cancelled by the registrants or had been cancelled by EPA for failure of the registrants to pay the required annual maintenance fees.

Pentachlorophenol (PCP) was one of the most widely used biocides in the United States prior to the regulatory actions to cancel and restrict certain wood and nonwood preservative uses of PCP. PCP was registered for use as a herbicide, defoliant, mossicide, and as a mushroom house biocide. It also found use as a biocide in pulp-paper mills, oil wells, and cooling towers. These latter three uses were terminated on or before 1993). However, the major use (greater than 80 percent of consumption) of PCP was and continues to be wood preservation (US-EPA 2000).

### 5.3.3 Situation Regarding Chloranil in the United States of America; Europe, and Africa

Chloranil is not manufactured in the United States but significant quantities are imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and domestic dye/pigment manufacturers known to EPA, they use chloranil in their products to switch to low-dioxin chloranil. In May 1993, when U.S. stocks of chloranil with high levels of PCDD/PCDF had been depleted, EPA proposed a significant new use rule (SNUR) under

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<sup>8</sup> However, four exceptions are given. The use of pentachlorophenol and its compounds in industrial installations is permitted:

- (a) for wood preservation;
- (b) for the impregnation of fibers and heavy-duty textiles;
- (c) as a synthesizing and/or processing agent in industrial processes;
- (d) for the in situ treatment of buildings of cultural and historic interest (subject to individual authorization by the Member State concerned)

Section 5 of TSCA that requires industry to notify EPA at least 90 days prior to the manufacture, import, or processing, for any use, of chloranil containing PCDD/PCDF at a concentration greater than 20 µg I-TEQ/kg (Federal DF Register, 1993 from US-EPA 2000).

In 1983, approximately 36,500 kg of chloranil were imported into the USA; no newer data were available since 1984 (US-EPA 2000).

In the USA, chloranil has been used as a fungicide and seed-dressing agent between 1937 and 1977. After 1977, all uses of chloranil in agriculture were banned. In Europe, chloranil has not been used as a fungicide nor as a seed protectant. In Africa, chloranil has been used as a fungicide and seed-dressing agent at least until 1984.

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## 7 LIST OF ABBREVIATIONS AND ACRONYMS

a	Year (annum)
AOX	Adsorbable organic carbon
BREF	BAT Reference document (of the EU)
CNP	2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP) (= chloronitrofen)
Co	Cobalt
Cu	Copper
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HCl	Hydrochloric acid
I	International (combined with TEQ)
µg	Microgram (=10 <sup>-6</sup> g)
ng	Nanogram (=10 <sup>-9</sup> g)
Nm <sup>3</sup>	Normal cubic meter
O <sub>2</sub>	Oxygen
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDF	Polychlorinated dienzofurans
PCP	Pentachlorophenol
t	Ton (metric)
TEQ	Toxic equivalent
WHO	World Health Organization