



# **GUIDELINES ON BEST AVAILABLE TECHNIQUES AND PROVISIONAL GUIDANCE ON BEST ENVIRONMENTAL PRACTICES**

**relevant to Article 5 and Annex C  
of the Stockholm Convention on  
Persistent Organic Pollutants**

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**Textile and leather dyeing (with chloranil)  
and finishing (with alkaline extraction)**



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MAY 2007, GENEVA, SWITZERLAND

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**Part III Source category (j):  
Textile and leather dyeing (with chloranil) and finishing  
(with alkaline extraction)**

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### ■ Summary

Contamination with PCDD and PCDF has been found in both textile and leather products. The occurrence of PCDD/PCDF in the textile and leather industries is due to use of chlorinated chemicals, especially pentachlorophenol and chloronitrofen, to protect the raw material (e.g. cotton, wool or other fibres, leather); and use of dioxin-contaminated dyestuffs (e.g. dioxazines or phthalocyanines). Smaller quantities of PCDD/PCDF may be formed during finishing, and during incineration of process-generated sludges.

Alternatives to the above-listed dye pigments exist and those listed should not be applied.

Possible alternatives to pentachlorophenol and chloronitrofen include 2-(thiocyanomethylthio) benzothiazole (TCMTB); o-phenylphenol (oPP); 4-chloro-3-methylphenol (CMK); and 2-n-octyl-4-isothiazolin-3-one (OIT).

As regards best available techniques, the most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use dioxin-contaminated biocides and dyestuffs in the production chains. Also, if any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals). To the extent possible, burning of textile, upholstery, leather products and carpet should be avoided to prevent PCDD/PCDF formation.

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation, best available techniques should be applied as described in section VI.D of the present guidelines (industrial boilers). However, other environmentally sound techniques should also be explored.

## 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; for example, in 2000 in the European Union, 114,000 companies employed about 2.2 million people (European Commission 2003b). Demand is largely driven by three main end uses: clothing, home furnishing and industrial use.

The textile and clothing chain is composed of a wide number of subsectors covering the entire production cycle from the production of raw materials (artificial fibres) to semi-processed products (yarns, woven and knitted fabrics with their finishing processes) and final or consumer products (carpets, home textiles, clothing and industrial use textiles).

## 1.2 Process description

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 fibres typically require more processing steps than artificial fibres. Relatively large volumes of wastewater are generated, containing a wide range of contaminants, which must be treated prior to disposal. Significant quantities of energy are used in heating and cooling chemical baths and drying fabrics and yarns.

Fabric preparation requires desizing, scouring and bleaching as well as singeing and mercerizing. Dyeing operations are used at various stages of production to add colour and intricacy to textiles and increase product value. Dyes used by the textile industry are largely synthetic. Finishing encompasses chemical or mechanical treatments (EPA 1997).

The main environmental concerns in the textile industry are the amounts of water discharged and the chemical load it carries. Other important issues are energy consumption, air emissions, solid wastes and odours.

Although there is a multitude of steps in the production chain and environmental concerns do occur, generation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) could not be associated to individual production steps.

Instead, more attention has to be given to the facts 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.

## 1.3 Sources of chemicals listed in Annex C of the Stockholm Convention

In the textile production chain, the 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 PCDD/PCDF-contaminated fungicides to treat unfinished raw materials such as cotton appear to be the sources of the detected PCDD/PCDF.

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

Thus, measures that constitute best available techniques and best environmental practices will focus on:

- PCDD/PCDF contamination through introduction of dioxin-contaminated chemicals into the textile production chain;
- New formation of PCDD/PCDF in thermal disposal operations of production-specific wastes.

### 1.3.1 PCDD/PCDF contamination through dioxin-contaminated materials

Chemicals known to be contaminated with PCDD/PCDF are used for the two purposes and include the chemicals listed below (European Commission 2003b):

- Defoliant or fungicide: Pentachlorophenol and 2,4,6-trichlorophenyl-4'-nitrophenyl ether<sup>1</sup> (chloronitrofen);
- Dyes: Chloranil-based dioxazine and phthalocyanine-based dyes.

Results from the analysis of textiles of various origin and fibres 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 revealed that pentachlorophenol was 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, as it has replaced pentachlorophenol in many applications (Masunaga, Takasuga and Nakanishi 2001; UNEP 2003).

### 1.3.2 Formation of PCDD/PCDF in thermal disposal operations

There are several steps in the textile production chain where wastewaters or effluents generate sludges that are incinerated: for example, from effluents evaporated in the wool scouring process, or from wastewater containing pigment printing paste or latex from carpet backing. As with any incineration process, PCDD/PCDF can be formed since these sludges contain relatively high contents of chloride as well as organically bound chlorine from ectoparasiticides such as  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH, lindane), dieldrin or DDT that have been applied to the raw materials (especially wood) (European Commission 2003b; UNEP 2003).

Concerning the probability of the use of lindane, dieldrin and DDT, all major grower countries have banned the use of organochlorine pesticides for sheep treatment but there is evidence that wool from some former Soviet Union countries and South America contains lindane at detectable concentrations (European Commission 2003b).

Finally, polybrominated flame retardants, such as polybrominated diphenyl ethers and chlorinated paraffins ( $C_{10-13}$  chloroparaffins) are used in the textile industry. All halogenated flame retardants are involved in the formation of PCDD/PCDF when incinerated (European Commission 2003b).

If the dirt removal and grease recovery loop is combined with evaporation of the effluent and incineration of the sludge, with full recycling of the water and energy, additional environmental benefits are achieved in terms of water savings and reduced amount of solid waste to be disposed of. The temperature of the incinerator would be around 1,200°C in order to destroy PCDD/PCDF. Fly ashes would be removed in a bag filter. In the gaseous emissions of such an integrated dirt removal and grease recovery loop plant 0.02 ng I-TEQ/Nm<sup>3</sup> were detected (European Commission 2003b, p. 278).<sup>2</sup> However, this technology is complex and is reported to involve very high capital costs and high running costs.

An incinerator may also be present when sludge from flotation is dewatered and then thermally regenerated in a rotary kiln. The flue gas is burnt in an afterburner (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> (at 11% O<sub>2</sub>) were found (European Commission 2003b, p. 415–417).

Experiences in some countries for sludge from wastewater treatment of wool scouring effluent include:

- Use sludge in brick making (mixed with clay) or adopt any other appropriate recycling routes;
- Incinerate the sludge with heat recovery, provided that measures are taken to control or avoid emissions of PCDD/PCDF arising from organically bound chlorine from pesticides potentially contained in the sludge.

For further information, the guidance related to best available techniques and best environmental practices for industrial facility recovery boilers should be consulted (section VI.D of the present guidelines).

## **2. Leather refining**

### **2.1 Introduction**

The tannery industry, specifically leather refining, 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 that gives leather its stability and essential character. Tanneries very often are small enterprises (European Commission 2003a), including artisanal activities in developing countries.

### **2.2 Process description**

The tanning industry is a potentially pollution-intensive industry with relevant water discharges and uses of certain chemicals such 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.

### 2.3 Sources of chemicals listed in Annex C of the Stockholm Convention

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 processes identified in the textile industry are also responsible for the occurrence of PCDD/PCDF in leather products and in emissions (UNEP 2003).

The primary source of contamination seems to be pentachlorophenol. This assumption is underlined by the fact that since its ban in Germany in 1989<sup>3</sup> the PCDD/PCDF concentrations in leather goods have declined (European Commission 1996).

## 3. Concentrations of PCDD/PCDF in chemicals used in the textile and leather production chains

Table 1 summarizes the range of PCDD/PCDF concentrations reported in the literature for biocides and chemicals used in the production of dyestuffs. It should be noted that some of the information is quite old and may no longer apply to the present situation. Nevertheless, for historic evaluation and since the presence of some 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.

■ **Table 1. Concentrations of PCDD/PCDF in biocides and dye pigments/dyestuffs**

Chemical	Country or use	Concentration (ng I-TEQ/kg)	Remark
<b>Biocides</b>			
PCP Pentachlorophenol	China, Europe, USA	800,000–4,445,000	Different production processes
PCP-Na Sodium salt of pentachlorophenol	China, Europe, USA	500–3,374,000	Different production processes
CNP Chloronitrofen	Japan	400/300,000	Old/new technology
<b>Dye pigments/starting materials/dye</b>			
Chloranil	Starting material for production of dioxazine dyes	100–3,065,000	Different production processes
Carbazole violet	Dye pigment	211,000	
Blue 106	Dioxazine dye	19,502–56,428	

## 4. Best available techniques and best environmental practices

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

Knowledge about the textile raw materials is essential in managing pollution transfers. Raw wool fibres may be contaminated with pesticides, sometimes organochlorine pesticides, including pentachlorophenol and chloronitrofen. Effective washing and wool scouring, for example with perchloroethylene, will effectively remove all grease and pesticides that are typically found in the solvent phase.

For artisanal activities, responsible authorities should advocate improvement in basic housekeeping and occupational safety. Information and awareness programmes should be undertaken.

The primary sources of PCDD/PCDF contamination in textiles and leather goods are the chemicals applied in the respective production or finishing chains, such as fungicides and dyestuffs known to be contaminated with PCDD/PCDF.

The most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use these chemicals in the production chains. If any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals).

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation, the best available techniques should be applied. However, other environmentally sound techniques should also be explored.

## 5. Alternatives

Since the occurrence of PCDD/PCDF in the textile and leather industries is primarily linked to the use of dioxin-contaminated chemicals such as pentachlorophenol and certain dye pigments, substitution of these chemicals by dioxin-free chemicals would be the alternative. For example, in Germany after the phase-out of pentachlorophenol as a preservative, the following chemicals have been used:

- 2-(thiocyanomethylthio) benzothiazole (TCMTB; CAS Registry No. 21564-17-0);
- o-phenylphenol (oPP; CAS Registry No. 90-43-7);
- 4-chloro-3-methylphenol (CMK; CAS Registry No. 59-50-7);
- 2-*n*-octyl-4-isothiazolin-3-one (OIT; CAS Registry No. 26530-26-1).

The above-mentioned chemicals are assessed as less hazardous for the environment than pentachlorophenol but they are not inherently safe at all. Safer alternative chemicals should be explored. As much as possible, it is imperative to avoid burning textile, upholstery, leather products and carpet to prevent PCDD/PCDF formation.

## 6. Monitoring

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

National capacity should be built/strengthened for monitoring possible sources of PCDD/PCDF from the textile and leather industry, including imported supply. More guidance is needed on monitoring of pentachlorophenol in wastewater.

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- <sup>1</sup> Not in European Commission 2003b.
- <sup>2</sup> 1 ng (nanogram) =  $1 \times 10^{-12}$  kilogram ( $1 \times 10^{-9}$  gram); Nm<sup>3</sup> = normal cubic metre, dry gas volume measured at 0°C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.
- <sup>3</sup> Which sets a maximum concentration of 5 mg pentachlorophenol per kg in the final product.



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