

# IUE – 10: DOCUMENT ON RESTRICTED PRODUCTS IN LEATHER

2007 Draft document **DRAFT**

## Introduction

Regulations to prevent the presence of some restricted products are set up in various countries. These regulations are not necessarily based on risk assessments but are precautionary measures. The presence of these chemicals in the leather results from their inclusion in commercial products used at various stages of the tannery's operations.

## 1. Pentachlorophenol

This preservative was widely applied before the nineties, for improving the biocidal activity on raw hides and skins. Due to the risk of transformation into dioxin, it is now completely forbidden to use PCP in leather manufacture in Europe. However it can be found in wood used for the storage of raw hide, leather or leathersgoods. It is also possible to find it in some speciality chemicals to prevent bacterial growth. PCP traces can remain in the leather, at amounts higher than the 5 mg/kg limit. Care should be taken to prevent any risk of controlled or uncontrolled addition of PCP into leather. Up to now, Germany is the only country with a regulation for PCP in leather, where it should not exceed 5 mg/kg.

## 2. Forbidden amines

Azo dyes or pigments used for leather dyeing and finishing can produce some aryl amines considered as carcinogenic or potentially carcinogenic under reductive conditions. The restricted amines are listed below in the table:

CAS No.*	European Union No.	name	Synonym	Classification CE 76/769	German No.
92-67-1	202-177-1	4-amino diphenyl and salts		carcinogenic cat. 1	1
92-87-5	202-199-1	4,4'-diamino diphenyl and salts	benzidine and salts	carcinogenic cat. 1	2
95-69-2	202-441-6	4-chloro 2-methyl aniline	4-chloro-o-toluidine	IARC 2A**	3
91-59-8	202-080-4	2-naphthylamine and salts		carcinogenic cat. 1	4
106-47-8	203-401-0	4-chloro aniline	p-chloroaniline	IARC 2B**	5
615-05-4	210-406-1	4-methoxy-1,3-phenyl diamine	2,4-diaminoanisole	IARC 2B**	6
101-77-9	202-974-4	4,4'-diamino diphenyl methane		carcinogenic cat. 2	7
91-94-1	202-109-0	3,3'-dichloro benzidine		carcinogenic cat. 2	8

CAS No.	European Union No.	Name	Synonym	Classification CE 76/769	German No.
119-90-4	204-355-4	3,3'-dimethoxy benzidine	o-dianisidine and salts	carcinogenic cat. 2	9
119-93-7	204-358-0	3,3'-dimethyl benzidine	4,4'-bi-o-toluidine	carcinogenic cat. 2	10
838-88-0	212-658-8	3,3'-dimethyl-4,4'-diamino diphenyl methane	4,4'-methylene di-o-toluidine	carcinogenic cat. 2	11
120-71-8	204-419-1	2-methoxy-5-methylaniline	p-cresidine	IARC 2B**	12
101-14-4	202-918-9	4,4'-methylene-bis-(2-chloroaniline)	2,2'-dichloro-4,4'-methylene dianiline	carcinogenic cat. 2	13
101-80-4	202-977-0	4,4'-diamino diphenyl ether	4,4'-oxydianiline		14
139-65-1	205-370-9	4,4'-diamino diphenyl sulfide	4,4'-thiodianiline	IARC 2B**	15
95-53-4	202-429-0	2-aminotoluene	o-toluidine	carcinogenic cat. 2	16
95-80-7	202-453-1	2,4-diaminotoluene	2,4-toluene diamine	carcinogenic cat. 2	17
137-17-7	205-282-0	2,4,5-trimethyl aniline			18
97-56-3	202-591-2	4-amino-2',3-dimethyl azobenzene	o-amino azotoluene	carcinogenic cat. 2	F
60-09-3	200-453-6	4-aminoazobenzene		carcinogenic cat. 2	F
90-04-0	201-963-1	o-anisidine	2-methoxyaniline	carcinogenic cat. 2	F
99-55-8	202-765-8	2-amino-4 nitrotoluene			
92-93-3		4-nitro biphenyl		carcinogenic cat. 2	

\*CAS : Chemical Abstract Services

\*\*IARC 2A : probably carcinogenic, 2B : possibly carcinogenic)

All the dyes and pigments used for leather production must not contain or must not produce during their use any of the restricted amines (below detection limit of 30 mg/kg for carcinogenic compounds).

This regulation is enforced in Germany and the Netherlands and a EU directive has been proposed.

### 3. Hexavalent chromium

Regulations limiting the Cr(VI) content in leather are in place in certain countries. The detection limit is currently 10 mg/kg (IUC 18). Some hexavalent chromium *is alleged to* occur under strong oxidative conditions, especially when vegetable and animal fats, containing unsaturated fatty acids, are used for fatliquoring.

*The reducing effect of* vegetable tanning agents, synthetic fatliquors and dyes can prevent the oxidation effect of trivalent chromium even under ageing conditions.

### 4. Formaldehyde

Formaldehyde can be used in the tanning, retanning and finishing of leather. It is classified as toxic and with possible carcinogenic effect (cat. 3 in 67/548/CEE modified in 98). In the European Union, restricting limits on the concentration of free

formaldehyde in leather may vary from 20 ppm for leather used for young children to 100 ppm when the leather is in contact with the skin, 150 ppm for shoe uppers and 400 ppm for leather without permanent contact with the skin. Formaldehyde vapour permissible in the workplace has also been restricted in many countries, up to a level of 0.6 mg/m<sup>3</sup> or 0.5 ppm.

For the tanning process, formaldehyde alone can be used for tanning gloving leather, sportswear and white military leather. It can be used as a pretanning agent, followed by oil tanning with unsaturated animal oil (usually cod liver oil), for chamois leather. It can also be used to prevent wool loosening in the early stages of wool-on sheepskin processing, by tanning the protein at the base of the follicle, conferring resistance to microbial attack. Today it is quite possible to replace most of these uses with safer products.

In retanning operations, it is recommended to use formaldehyde free syntans or combination of syntans giving formaldehyde free leather.

New aldehydic crosslinking products can replace formaldehyde for the fixation of protein finish and give the same gloss for box calf leather.

## **5. Other restricted chemicals**

This list here is not exhaustive. Discussions are pending to include other chemicals: such as trichloro phenol (TCP) and tributyl tin (TBT), both used as biocidal and antifungal agents .

IUE Commission

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