

# TFL WHITE LINE SYSTEM



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## In harmony with the skin

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### Summary

Leather in the form of shoes, upholstery, clothing and merchandise offer their wearers and users enormous advantages, though these are scarcely still perceived as such. Against the numerous undisputed benefits, discussion has recently focussed on the risk of unwanted chemical uptake by the human body. Governments, such as that of Germany and the legislators of the European Union (EU), protect consumers by legislation and directives, although in the past there has been little evidence of harm caused by leather.

In order to protect the high reputation of leather and goods made from it, TFL has decided to introduce "WHITE LINE". This is leather based on scientific investigation and research which offers the consumer major assurances in health terms. There are also tannery guidelines for the production of this customized leather.

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## **Introduction**

Interest in the impact of leather and textiles on the consumer's health and sense of well being are progressively increasing. There has been discussion about hazardous chemicals in consumer goods made of leather and textiles. The purchaser and the public are paying increasing attention to this phenomenon, which is prompting the introduction of relevant regulations by authorities and new labels by private organizations. Keeping in mind that leather provides their wearers and users enormous advantages, though these are scarcely still perceived as such.

## **1. Regulations**

This paper cannot cover the whole field in detail, one reason being that regulations are highly complex and can change fast and often. In principle, the following legal regulations govern the production, import and sale of textile and leather products in Germany, the leading country, the European Union and selected other countries in respect of hazardous substances present in these products.

### **1.1 Unwanted dyes**

#### *1.1. Prohibited azo dyes*

An update of the German "Bedarfsgegenständeverordnung" (Consumer Goods Ordinance) was published on 07.01.98. Under the terms of § 3 of the valid Consumer Goods Ordinance, it is forbidden to use certain azo dyes for the production or treatment of the following specific consumer goods, which are defined as having direct skin contact, see Table 1

1. Clothing and materials for the production of clothing
2. Bed linen, blankets, pillows, sleeping bags
3. Towels, beach towels, airbeds
4. Masks, hairpieces, wigs, false eyelashes
5. Items of jewellery worn on the skin, bracelets
6. Money bags worn round the neck, rucksacks
7. Crawling rugs, covers for reclining chairs and seats for babies and small children
8. Nappies, sanitary towels, panty pads, tampons

**Table 1**

The annex of the Ordinance states that prohibited azo dyes are dyes, which, as a result of the splitting of one or more azo-groups, can release one of the amines listed in table 2. These amines are considered as having high carcinogenic potentials for human and animals.

No.	Substance	CAS number
1	4-aminodiphenyl	92-67-1
2	benzidine	92-87-5
3	4-chloro-o-toluidine	95-69-2
4	2-naphthylamine	91-59-8
5 *	4-amino-2',3-dimethylazobenzene	97-56-3
6 *	2-amino-4-nitrotoluene	99-55-8
7	4-chloroaniline	106-47-8
8	2,4-diaminoanisole	615-05-4
9	4,4'-diaminodiphenylmethane	101-77-9
10	3,3'-dichlorobenzidine	91-94-1
11	3,3'-dimethoxybenzidine	119-90-4
12	3,3'-dimethylbenzidine	119-93-7
13	3,3'-dimethyl-4,4'-diaminodiphenylmethane	838-88-0
14	4-cresidine	120-71-8
15	4,4'-methylene-bis-(2-chloroaniline)	101-14-4
16	4,4'-oxydianiline	101-80-4
17	4,4'-thiodianiline	139-65-1
18	2-aminotoluene	95-53-4
19	2,4-diaminotoluene	95-80-7
20	2,4,5-trimethylaniline	137-17-7
21	2-methoxyaniline	90-04-0
22 **	4-aminoazobenzene	60-09-3

**Table 2** \* amines 5 and 6 are analysed indirectly via reduction to the amines 18 and 19 respectively  
\*\* no analytical procedure is currently available for 4-aminoazobenzene

On September 9th, 2003, the regulation on banned azo dyes became EU legislation adding two new amines. Many countries have enacted similar ordinances as shown in Table 3. In the past some of these dyes were used for leather, but serious illness caused by leather dyes was not statistically recorded because the incidence was very low or non-existent.

Country	Legislation	Limit
EU	Directive 76/769 EWG, update 2002/61vom 19.07.2002 valid of 09.11.2003	30 mg/kg
France	Office Gazette of the French Republic Notification 97/0141/F	30 mg/kg
Netherlands	"Warenwetregeling Azo-kleurstoffen" (Commodity Legislation, Azo dyes), 24.07.96	30 mg/kg
Austria	"Azoverordnung" (Azo Ordinance), BGBl II No. 241/1998	30 mg/kg
Switzerland	Verordnung über Gebrauchsgegenstände Art. 26a	30 mg/kg
Turkey	List of banned dyes	may not be used
Scandinavia	planned	expected 30 mg/kg
USA, Canada, other countries of the EU, Eastern Europe	according to our information	no regulations

**Table 3**

Harmonised testing methods are necessary for the application of this EU Directive. For leather the appropriate European analytical method is the newly approved CEN ISO/TS 17234. It is very similar to the German DIN 53316 and the IUC 20 analytical methods.

Special rules apply to the amines 2-naphthylamine and 4-aminodiphenyl due to the possibility of false positives. Further it should be noted that no current analytical procedures are suitable to detect 4-aminoazobenzene.

### 1.1.2 Sensitizing disperse dyes

A sensitizer is a chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to it. Some organic dyes are classified as having an allergenic potential.

Sensitizing dyes belong mainly to the disperse dye class, which is not applied on leather but found in some textiles (e.g. polyamide fabrics) and fur articles. Today, there are no special regulations for these dyes, but self-regulation in Europe does indicate that the suspected dyes shown in Table 4 are scarcely present in consumer goods.

Dispersion blue 1	Dispersion yellow 3
Dispersion blue 35	Dispersion orange 3
Dispersion blue 106	Dispersion orange 37/76
Dispersion blue 124	Dispersion red 1

**Table 4**

## 1.2 Organic biocides

Biocides are under discussion for investigation in the European Union: Directive 98/8/EC concerning the placing of biocidal products on the market.

### 1.2.1 Pentachlorophenol (PCP)

Country	Legislation	Limit
Germany	"Chemikaliengesetz" (Chemicals Law), Article 15, Annex to § 1, Valid for all products, materials	5 mg/kg
France	Official gazette of the French Republic Notification 97/0141/F, not yet valid according to our information	5 mg/kg without skin contact 0.5 mg/kg direct skin contact
Netherlands	Act on PCP, 18.02.94	5 mg/kg
Austria	Verbot von PCP, BGBL Nr. 58/1991	5 mg/kg
Switzerland	Stoffverordnung, Anhang 3.1 PCP und TeCP" (Ordinance on Substances posing a Hazard to the Environment, PCP and TeCP and other pesticides) Valid for all products, materials	10 mg/kg
other countries of the EU		1000 mg/kg
USA, Canada, Eastern Europe	according to our information	no regulations

**Table 5**

PCP has been in the past applied as a transport preservative against mould for chemicals but chiefly for wood conservation. Previously it was also used to treat cotton tenting and outdoor goods, paper, and occasionally leather goods coming from humid and warm countries to prevent mould growth. Today's regulations are shown in Table 5.

The basic standard method for determining of PCP in leather is the newly approved CEN /TS 14494, which is similar to DIN 53313.

### 1.2.2 Formaldehyde

Another preservative, especially for chemicals and for cosmetics, is formaldehyde. It is also found as a non-reacted chemical in wood glue (formaldehyde condensates occur as resins) and is therefore present in fibreboards. Formaldehyde can also be found in textiles and leather for the same reason or possibly owing to the use of agents containing residual levels of formaldehyde, which can continue to release trace levels of formaldehyde under suitable conditions.

Annex III, No. 9 of the German "Gefahrstoffverordnung" (Hazardous Substances Ordinance) of 26.10.1993 states that textiles containing more than 1500 mg/kg of formaldehyde have to be marked with the following statement: "Contains formaldehyde; to avoid sensitive or allergic skin reactions, it is recommended that the garment should be washed before wear".

The regulation applies whether the garment has direct skin contact or not. Baby clothes receive special attention as shown in Table 6.

Country	Legislation	Limit
Germany	Bedarfsgegenständeverordnung, 26.06.2002, (last update) Anlage 9 zu §10 Abs.6, Lfd.Nr. 1.2.	above 1500 mg/kg must be marked
France	Official gazette of the French Republic, Notification 97/0141/F, not yet valid according to our information	400 mg/kg without skin contact 200 mg/kg direct skin contact 20 mg/kg < 36 months, baby
Netherlands	regulations dated 29 July 1998	120 mg/kg
Austria	Formaldehydverordnung, BGBl Nr. 194/1990	above 1500 mg/kg must be marked
USA, Canada, Eastern Europe, Switzerland	according to our information	no regulations
Japan	LAW 112	depending on product 20 - 300 mg/kg

**Table 6**

There are several methods for quantitative analysis of formaldehyde in leather and care must be taken in determining which method is being used, what limits are required and in interpreting the results. The 2 main methods used.

1) For the analysis of leather

- Free-formaldehyde and releasable formaldehyde by water extraction method: newly approved CEN ISO/TS 17226, which is equivalent to IUC 19 and similar to DIN 53315.

2) For the analysis of automotive interior articles

- Free-formaldehyde by gas phase method: VDA 275 and PV 3925 - VW/Audi (they are similar to EN 717-3 procedure used for wood articles).

**1.3 Metal and metal compounds**

*1.3.1 Nickel*

EC Directive 94/27 prohibits nickel metal items that come into repeated and prolonged contact with the skin. Many users obtain an allergic reaction with them. Pure metallic nickel is not used for manufacturing leather, but it is sometimes worn as accessories to leather articles.



### 1.3.2 Cadmium and cadmium compounds

Cadmium is an extremely toxic metal sometimes found in industrial workplaces. The cadmium compound substances are mostly applied as pigments and used as stabilizers for PVC. They are therefore found in coatings on textiles and very seldom on leather. Cadmium compound coloured pigments do not have any adverse effects on skin and mucous membranes. They have a very low solubility except in diluted hydrochloric acid, concentration equivalent to that in the stomach concentration. Some inhalation studies on animals indicated a significant increase of lung cancer. The limit value for cadmium is shown in Table 7.

Country	Legislation	Limit
EU	76/769/EEC, Annex I, 12.07.'91	100 mg/kg
Netherlands	"Cadmiumbesluit" 01.06.99	100 mg/kg
Switzerland	Stoffverordnung, Annex 4.11 limit 10 mg/kg until 1991	100 mg/kg
USA, Canada, Eastern Europe	according to our information	no regulations

**Table 7**

### 1.3.3 Chromium (VI)

Chromium (VI) is a typical leather issue. Chromium (III) tanning (with basic chrome sulphate) is the standard tanning procedure. However, it must be clearly pointed out that chromium (VI) is not used for tanning and does not form organic complexes. Chromium (VI) ions are known to be strong reducing agents and may occur in trace amounts as a result of non-optimised tanning procedures, faulty after treatment like softening or less often by the finishing process, when Cr (III) is accidentally oxidized to Cr (VI). Regulations are shown in Table 8.

Country	Legislation	Limit
Germany	Objections on the basis of §30, 31 LMBG, ban on toxic ingredients	Not detectable*
Switzerland	"Verordnung über Gebrauchsgegenstände" (Commodities Ordinance), Art. 2, 24 ban on health hazards Assessment still not clear	not specified
USA, Canada, Eastern Europe, other countries of the EU, Scandinavia	according to our information	no regulations

**Table 8** \* detection limit for the newly approved CEN/TS 14495 is 10 ppm, whereas the older DIN method, which is not suitable for many dyed leathers giving incorrect results, is 3 ppm.

The analytical procedures for Cr (VI) in a complex matrix like leather are currently under re-investigation. It has been shown that the current analytical procedure is subject to interference from other organic substances like dyes and vegetable tanning agents. The latest procedure is the European method, CEN/TS 14495, which includes a clean-up step. The detection limit

is now fixed at 10 ppm since interlab trials show this is the limit for quantification for this test method.

#### 1.3.4. Organic tin compounds

Organic tin components have been extensively used for anti-microbial finishing, coating agents and paints, mostly as anti-fouling agents for ship's hulls. They are also used as catalysts for some polymerization reactions. These substances are considered highly toxic and can be taken up via the skin and may affect the nervous system. As inorganic biocides they also fall also under EU Directive 98/8/EC concerning the placing of biocidal products on the market. The most important tin components with regard to textiles are shown in Table 9.

TeBT	Tetrabutyltin compounds	DOT	Diocetyl tin compounds
TBT	Tributyltin compounds	MOT	Monooctyltin compounds
DBT	Dibutyltin compounds	TCyT	Tricyclohexyltin compounds
MBT	Monobutyltin compounds	TPhT	Triphenyltin compounds

**Table 9** For marketing and use of tin, PCP and cadmium see also EU Directive 1999/51/EC.

### 1.4 Plasticizers or softeners, flame retardants, and others

#### 1.4.1 Phthalic acid esters

Phthalic acid esters are technically used as plasticizers for polyvinyl chloride, polyvinyl acetate, rubbers, cellulose plastics and polyurethane. End applications include PVC floorings and wall coverings, PVC foams, leather finishing, films, sealing and adhesive systems based on polyurethane or polysulphide. It is argued that they act as hormone mimics. For the time being, regulations do not apply to clothing, but to toys and other goods that are typically taken into the mouth; see Table 10

Country	Legislation	Limit
EU	Entscheidung der Kommission vom 19.02.2002 1999/815/EG - wird ggf. verlängert	0.1 % for 8 Phthalates
Germany	Bedarfsgegenständeverordnung 07. März 2000 (7.VO),	0.1 % all Phthalates
Danemark	statutory order No. 151 15.03.1999	0.05 % all Phthalate

**Table 10**

#### 1.4.2 Softeners

Chlorinated paraffins (CPs) are very complex mixtures, and are often divided into several groups depending on the chain length of the starting material and the amount of chlorine in the final product. Three major groups are short, medium and long chain chlorinated paraffins. Fat liquors for leather use long chain chlorinated paraffins. Some could contain trace levels of short chain chlorinated paraffins (SCCPs) as residual by-products.

The restrictions regarding SCCPs, introduced by European Union Directive 2002/45/EC, and extended by 2003/549/EC, were directed towards their use in metal working fluids and leather products, as being responsible for unacceptable sources of emissions to the aquatic environment.

#### *1.4.3 Flame-retarding substances*

These are found in plastic, but are also used with textile items such as soft toys, furniture coverings, cotton fleece and bed sheets. When used incorrectly some of them can cause serious health and environmental problems. The German Consumer Goods Ordinance classifies the flame retardants in Table 11, mostly used on cotton or polyester textiles, as unwanted in consumer goods. Leather goods as such can be considered as sparingly flammable and flame-retarding substances would only be used for special articles like aircraft leather.

- Tri-(2,3-dibromopropyl)- phosphate (TRIS),
- Tris - (aziridiny)- phosphineoxide (TEPA),
- Polybrominated diphenyls (PBB)

**Table 11**

EU directive 2003/11/EG specified the PBB as Pentabromodiphenyl ether and Octabromodiphenyl ether derivatives, which may not be placed on the market in concentration higher than 0.1 %.

#### *1.4.1 Nonylphenol ethoxylate (NPE) and Nonyl phenol (NP) products*

The EU Directive, 2003/53/EC, will restrict the marketing and use of products and product formulations that contain more than 0.1% of NPE or NP. This applies to many industries including the textile and leather industries, except in the case of closed application systems where no releases into waste water occurs. For NP the risk assessment showed that the main concern is the high aquatic toxicity and that it did not break down readily in eco-systems. No adverse human exposure risks were identified but are discussed. The EU European countries have until January 2005 to implement in their own country the necessary legislation to make this EU directive into law.

#### *1.4.5 Other chemicals*

Similar regulations apply to quite a few other chemicals. For example, EU Regulation 2037/2000/EC covers substances that deplete the ozone layer based on the Montreal Protocol 1987. Other regulations address some unnecessary metals like mercury, traces of pesticides, volatile solvents, selected organic halogen compounds called Absorbable Organic Halogens (AOX) and other hazardous substances including the chemical weapons convention (CWC). Special attention has to be paid to the so-called CMT substances (C = cancerogenic, M = mutagenic, T = teratogenic): EU Directive 67/548/EWG.

## 2. WHITE LINE System

Today, as in the past, all these unwanted chemicals scarcely occur in leather. Additionally, it is very rarely reported that leather has caused any health problems and if any do occur they are often the result of inappropriate application of care and protection agents by retailers and consumers. Leather related complaints often occur in leather made in developing countries, which are not subject to the strict regulations of for example the EU countries. However, end user loss of product confidence has motivated the introduction of product labels giving safety and health hazard information.

### 2.1 WHITE LINE Label

WHITE LINE leathers are produced by appropriate technology, avoiding potentially harmful substances in the final product. Specially selected chemicals are required to produce the appropriate leather type for the WHITE LINE label, see figure 1.



Figure 1

TFL sees the WHITE LINE System as a pro leather concept. Numerous chemical tests and even a dermatological test have confirmed that the leathers produced with this system are skin friendly and meet stringent quality requirements. Appropriate application methods are available from experienced TFL technicians.

WHITE LINE producers are entitled to offer their customers, end product manufacturers and retailers a label which guarantees that WHITE LINE leathers comply with the test specifications of the TÜV (Technical Inspection Associations of Germany).

### 2.2 Testing procedure

The production process for WHITE LINE leathers gives the customer peace of mind knowing the leather complies with test procedures for harmful substances. WHITE LINE system is a certified leather system that fits the TÜV no-harmful-substance "schadstoffgeprüft" (SG) criteria.



## Figure 2

The consumer can be sure that during the manufacture of WHITE LINE leathers exceptional care was taken as displayed in Table 12 to ensure that:

1. carcinogenic products are not detectable
2. contents of free formaldehyde are below the declaration limit of cosmetics ordinances
3. contents of PCP and other chlorophenols are far below the propitiatory ordinance for chemicals
4. chromium VI is not detectable
5. allergenic substances are not present

**Table 12**

## 2.3 Skin compatibility

Goods made of WHITE LINE leathers are dermatologically tested. It can be stated WHITE LINE leathers are a skin friendly material, with which even people with sensitive skin may come into direct contact without any irritation.

For that reason and to make absolutely sure that this does not imply any danger for the consumers, a special dermatological test was conducted. The test was carried out at the Darmstadt Klinikum (Clinical Centre), which is specialized in the treatment of allergic skin reactions. An epicutaneous patch test was performed under especially tough conditions. In this test, all participants including people with sensitive skin tolerated the leather samples. There were no visible reactions.

## 3. Conclusion

The TFL/TÜV WHITE LINE label is intended to demonstrate the company's responsibility to the leather industry, leather goods manufacturers and end users, backed by the provision of an innovative system. Various tests are carried out and different types of leather are made and certified by the TÜV. The aim of this joint effort is to emphasize that leather is still the best material for the production of shoes and leather goods (including watch straps) from the consumer's point of view.

## Acknowledgments

This publication is based on several reports drawn up by TFL and TÜV. Special thanks are due to Dr. A. Wennemer (TÜV), F. Döppert (TFL) and the joint WHITE LINE team for their contribution.

For more information visit [www.tuv.com](http://www.tuv.com) or use the TFL WHITE LINE brochures/ CD and the "TÜV Produkt und Umwelt Information" or send e-mail to [white.paper@tfl.com](mailto:white.paper@tfl.com).

This is a translation of a paper originally presented in July 2003. Updated 20.4.2004/ap