

White Line – harmony with the skin

In recent years, a number of regulations have come into force to protect the consumer against leather containing heavy metals, PCPs, azo dyes, formaldehyde, nonylphenol ethoxylates and others. Leather chemical producers, TFL have devised a new system known as White Line which produces leathers which avoid potentially harmful substances in the final product. By Dr Alois Püntener, TFL

SUMMARY

Leather in the form of shoes, upholstery, clothing and other merchandise offers wearers and users enormous advantages. Against the numerous undisputed benefits of leather, discussion has recently focused on the risks of unwanted chemical uptake by the human body. Governments, such as that of Germany and the legislators of the European Union, 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 the products made from it, TFL have 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 customised leather.

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 of new labelling from private organisations.

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 in the EU and selected other countries in respect of hazardous substances present in these products.

1.1 Unwanted dyes

1.1.1 Prohibited azo dyes
An update of the German 'Bedarfsgegenständeverordnung' (consumer goods act) was published on 07/01/98. Under the terms of paragraph 3 of the valid consumer goods act, it is forbidden to use certain azo dyes for the production or treatment of the following specific consumer goods, which are

Table 1

- Clothing and materials for the production of clothing
- Bed linen, blankets, pillows, sleeping bags
- Towels, beach towels, airbeds
- Masks, hairpieces, false eyelashes
- Items of jewellery worn on the skin
- Money bags worn round the neck, rucksacks
- Crawling rugs, covers for reclining chairs and seats for babies and small children
- Nappies, sanitary towels, panty pads, tampons

Table 2

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

* 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

defined as having direct skin contact (Table 1).

The annexe of the act 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 humans and animals.

The regulation on banned azo dyes became EU legislation, adding two new amines on September 9, 2003. Many countries have enacted similar limits 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.

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.

Table 3

Country	Legislation	Limit
EU	Directive 76/769 EWG, update 2002/61 on 19/07/02 valid of 09.11.2003	30mg/kg
France	Office Gazette of the French Republic Notification 97/0141/F	30mg/kg
Netherlands	'Warenwetregeling Azo-kleurstoffen' (commodity legislation, azo dyes), 24/07/96	30mg/kg
Austria	'Azoverordnung' (azo act), BGBl II No. 241/1998	30mg/kg
Switzerland	Verordnung über Gebrauchsgegenstände Art. 26a (consumer products act, article 26a)	30mg/kg
Türkiye	List of banned dyes	may not be used
Scandinavia	Planned	expected to be 30mg/kg
USA, Canada, other countries of the EU, eastern Europe	According to our information	no regulations

Table 5

Country	Legislation	Limit
Germany	'Chemikaliengesetz' (Chemicals law), Article 15, Annex to para 1. Valid for all products, materials	5mg/kg
France	Official gazette of the French Republic Notification 97/0141/F, not yet valid according to our information	5mg/kg without skin contact 0.5mg/kg direct skin contact
Netherlands	Act on PCP, 18.02.94	5mg/kg
Austria	Forbidden PCP, BGBl regs Nr. 58/1991	5mg/kg
Switzerland	Stoffverordnung, Anhang 3.1 PCP und TeCP (including substances posing a hazard to the environment, PCP and TeCP and other pesticides). Valid for all products, materials	10mg/kg
Other countries of the EU		1000mg/kg
USA, Canada, eastern Europe	According to our information	no regulations

1.1.2 Sensitising 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.

Sensitising dyes belong mainly to the disperse dye class, which is not applied on leather but found in some textiles (eg 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.

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)

PCP has been applied as a transport preservative against mould for chemicals but chiefly for wood conservation. 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 PCP

in leather is the newly-approved CEN/TS, which is similar to DIN 53313.

1.2.2 Formaldehyde

Another preservative for chemicals and 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 fibre boards. 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 formaldehyde under suitable conditions.

Annexe III, No 9 of the German 'Gefahrstoffverordnung' (Hazardous Substances Act) of 26/10/93 states that textiles containing more than 1500mg/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 displayed in 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 two main methods used are as follows:

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 used for wood articles).

1.3 Metal and metal compounds

1.3.1 Nickel

EC Directive 94/27 prohibits nickel 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 worn as leather accessories.

1.3.2 Cadmium and cadmium compounds

These cadmium containing substances are mostly applied as pigments and used as stabilisers for pvc.

They are, therefore, found in coatings on textiles and very seldom on leather. Cadmium is an extremely toxic metal sometimes found in industrial workplaces.

Cadmium-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 in lung cancer. The limit value for cadmium is shown in Table 7.

1.3.3 Chromium VI

Chromium VI is a typical leather issue. Chromium III tanning (with basic chrome sulfate) is the standard tanning procedure.

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 such as softening or less often by the finishing process, whereby Cr III is

Table 6

Country	Legislation	Limit
Germany	Bedarfsgegenständeverordnung, (consumer goods act) 26/06/2002 (last update). Anlage 9 zu §10 Abs.6, Lfd.Nr. 1.2.	as of 1500mg/kg must be marked
France	Official gazette of the French republic, Notification 97/0141/F, not yet valid according to our information	400mg/kg without skin contact 200mg/kg direct skin contact 20mg/kg <36 months, baby
Netherlands	Regulations dated 29 July 1998	120mg/kg
Austria	Formaldehyde legislation, BGBl Nr. 194/1990	as of 1500mg/kg must be marked
USA, Canada, eastern Europe, Switzerland	According to our information	no regulations
Japan	LAW 112	depending on product 20-300mg/kg

Table 4

- 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 7

Country	Legislation	Limit
EU	76/769/EEC, Annexe I, 12/07/91	100mg/kg
Netherlands	Cadmium limits 01/06/99	100mg/kg
Switzerland	Cadmium limits, Annexe 4.11 limit 10mg/kg until 1991	100mg/kg
USA, Canada, eastern Europe	According to our information	no regulations

Table 8

Country	Legislation	Limit
Germany	Objections on the basis of para 30, 31 LMBG, ban on toxic ingredients	Not detectable*
Switzerland	'Verordnung über Gebrauchsgegenstände' (Commodities act), 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

* 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, is 3 ppm

accidentally oxidised to Cr VI. Regulations are shown in Table 8.

The analytical procedures for Cr VI in a complex matrix such as leather are currently under re-investigation.

It has been shown that the current analytical procedure is subject to interference from other organic substances such as 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 10ppm since inter-laboratory trials show this is the most reliable detection limit.

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 ships hulls.

They are also used as catalysts for some polymerisation reactions. These substances are considered

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

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

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.

1.4 Plasticisers or softeners, flame retardants, and others

1.4.1 Phthalic acid esters

Phthalic acid esters are technically used as plasticisers for polyvinyl chloride, polyvinyl acetate, rubbers, cellulose plastics and polyurethane. End applications include pvc floorings and wall coverings, leather finishing, pvc foams, films, sealing and adhesive systems based on polyurethane or polysulfide. 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 from which can be put into the mouth (see 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.

Fatliquors for leather use long chain chlorinated paraffin. Some could contain trace levels of short

Table 11

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

chain chlorinated paraffin (SCCPs) as residual byproducts.

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 and textile items such as soft toys, cotton fleece and bed sheets. Some of them can cause serious health and environmental problems. Leathergoods as such can be considered as sparingly flammable. The German consumer goods act classifies the flame retardants in Table 11, mostly used on cotton or polyester textiles, as unwanted in consumer goods.

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 nonylphenol (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 release into wastewater 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 ecosystems. No adverse human exposure risks were identified but are discussed (poisonous to hormones).

The EU European countries have until January 2005 to implement the necessary in their own

country legislation to make this EU directive into law.

1.4.5 Other chemicals

Similar or, very often, similar regulations apply to other chemicals. EU regulation 2037/2000/EC covers substances that deplete the ozone layer based on the Montreal Protocol 1987.

Other regulation addresses some unnecessary metals such as 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 = carcinogenic, 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 very often occur in leather made in developing countries, which are not subject to the strict regulations of for example the EU.

However, end-user loss of product confidence has motivated the introduction of product labels giving health and safety 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 below:



TFL sees the White Line system as a pro leather concept. Numerous

Table 10

Country	Legislation	Limit
EU	EU decision due 19/02/02 1999/815/EG - but delayed	0.1% for 8 Phthalates
Germany	Consumer goods act 07 March 2000 (7.VO)	0.1% all Phthalates
Denmark	Statutory order No. 151 15.03.1999	0.05% all Phthalates

Table 12

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

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.

The White Line system is a certified leather system that fits the TÜV no-harmful-substance 'Schadstoffgeprüft' (SG) criteria (see Figure 2 below):



The consumer can be sure that during the manufacture of White Line leathers, exceptional care was taken as shown in 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 specialised in the treatment of allergic skin reactions. An epicutaneous patch test was performed under especially tough conditions. In the 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, leathersgoods 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 emphasise that leather is still the best material for the production of shoes and leathersgoods (including watch straps) from the consumer's point of view. ■

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Above: Florian Döppert, TFL, with a range of leathers produced with the White Line system

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