

In order that both people and the environment are protected against substances that can damage either health or the environment, directives have been issued by the EU which now form the basis of national regulations in EU Member States. Any materials used in footwear destined for EU countries must therefore be tested and this can be more complex than many of us realise.

Testing for hazardous materials

Dr. Kerstin Schulte, PFI, Germany

EU Directive 76/769/EEC forms the basis for the laws, regulations and administrative provisions of Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations. It is repeatedly updated by numerous alterations and amendments; and a series of substances—the adverse effects of which, on people and the environment, have been scientifically proven—have been regulated accordingly.

For example, the following EU directives apply to azo colourants, which are used to dye leather, textiles, greases, straw, wood, paper and some foodstuffs:

- 76/796/EEC
- 2002/61/EC (19th amendment of EU Directive 76/796/EEC)
- 2004/21/EC (13th adaptation of EU Directive 76/769/EEC)

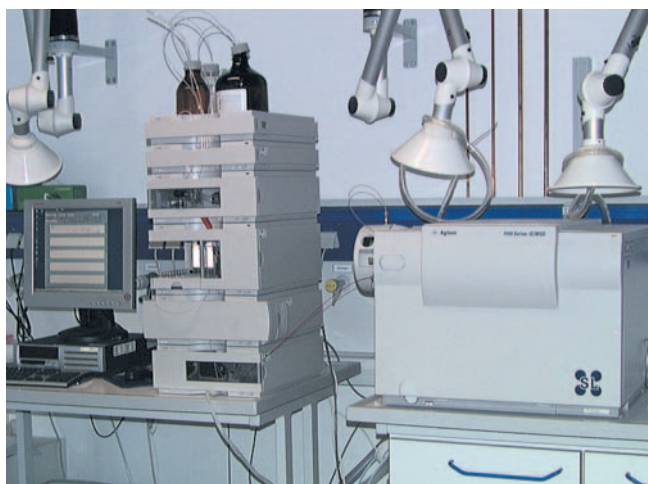
Annex I of Directives 76/769/EEC and 2002/61/EC contains the precise wording for the regulation of azo colourants and Directive 2004/21/EC contains test methods that may be used to identify the dyes.

What are azos?

Azo colourants is the largest group of dyes and are characterised by the azo group ($-N=N-$) which provides the colour. They can contain one or more of this azo group, combining the various aromatic residues with one another. The advantages of these dyes are their lightfastness, their stable, powerful colour and good intermixing in order to create new shades.

The great disadvantage of this class of substances is that the dyes decompose to form aromatic amines under reductive conditions, some of them manifesting a carcinogenic or toxic potential. For example, a reductive fission can come about in clothing dyed with azo colourants as a result of sweat, the aromatic amines caused by this easily penetrating through the skin. Likewise, a reductive fission can be initiated by the consumption of foodstuffs through the saliva, with toxic aromatic amines being released into the body.

The following table (*Table 1*) contains some examples of azo colourants which are used for dyeing clothing made of leather



HPLC-MS Mass-specific detector

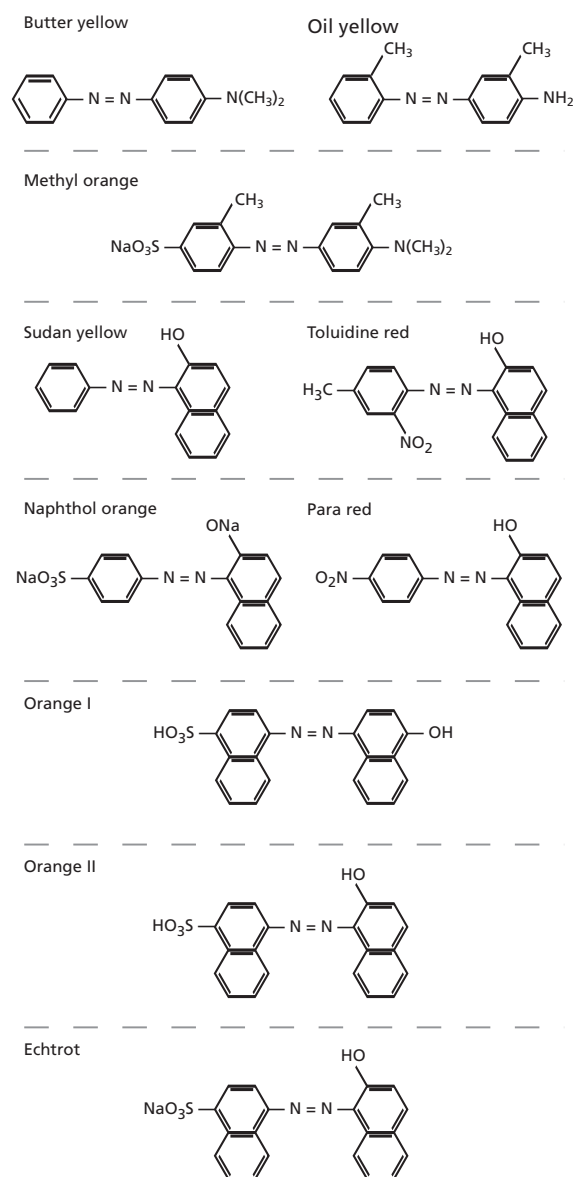
and textiles and are also used as foodstuff dyes.

EU Directive 2002/61/EC currently contains 22 aromatic amines in which a carcinogenic potential has been proven by scientific examinations (*Table 2*).

Test standards

In order to check compliance with these statutory regulations, products must be examined for the forbidden azo colourants to be able to detect their possible use. The European Committee for Standardisation (CEN) has developed test methods for this purpose, to examine textile and leather products in accordance with the provisos of Annex I Number 43 of Directive 76/769/EEC. The following test methods (Directive 2004/21/EC) are used:

- CEN ISO/TS 17234: 2003 Leather
Chemical tests for the determination of certain azo colourants in dyed leathers
- EN 14362-1:2003 Textiles
Methods for the determination of certain aromatic amines derived from azo colourants – Part 1 Detection of the use of certain azo colourants accessible without extraction
- EN 14362-2:2003: Textiles
Methods for the determination of certain aromatic amines derived from azo colourants – Part 2 Detection of

Table 1

the use of certain azo colourants by extracting fibres

All three methods describe a process for the detection of the use of certain azo colourants, which are not permitted in the manufacture or treatment of products on the basis of the statutory regulation by the EU Directives. Depending on the kind of material, whether it is leather or textile-based, one of these methods must be used to determine their presence—if any.

The use of forbidden azo colourants in the manufacture or treatment of a product such as a shoe is deemed to be detected if at least one of the listed aromatic amines is found under the conditions of the analysis method in question, and the share of a certain amine is above the detection threshold of 30 mg/kg.

Test methods

To do this, the materials to be tested are removed from the shoe, weighed (Figure 1) and processed according to the standard procedure in question. First, there is reductive

Table 2

	Amine	CAS no.
1	4-aminobiphenyl	92-67-1
2	Benzidine	92-87-5
3	4-chloro-o-toluidine	95-69-2
4	2-naphthylamine	91-59-8
5	o-aminoazotoluene	97-56-3
6	5-nitro-o-toluidine	99-55-8
7	4-chloroaniline	106-47-8
8	4-methoxy-m-phenylenediamine	615-05-4
9	4,4'-methylenedianiline	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	4,4'-methylenedi-o-toluidine	838-88-0
14	p-cresidine	120-71-8
15	4,4'-methylene-bis-(2-chloro-aniline)	101-14-4
16	4,4'-oxydianiline	101-80-4
17	4,4'-thiodianiline	139-65-1
18	o-toluidine	95-53-4
19	4-methyl-m-phenylenediamine	95-80-7
20	2,4,5-trimethylaniline	137-17-7
21	2-methoxyaniline	90-04-0
22	4-amino azobenzene	60-09-3

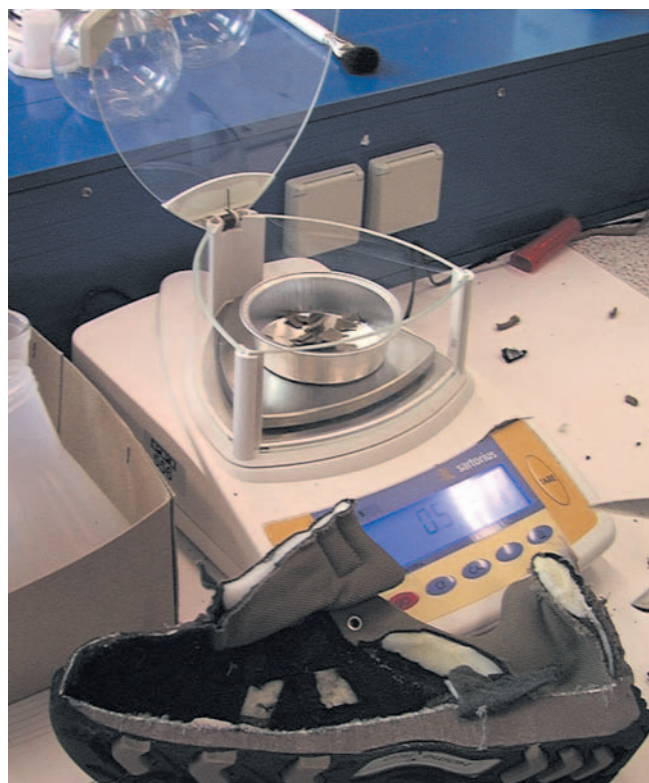


Figure 1: Weighing

fission of existing azo colourants into the corresponding amines (Figure 2), followed by column chromatography cleaning (Figure 3).

After further processes of analysis, detection of any amines present is undertaken by means of high-performance liquid chromatography. This employs a diode array or mass-specific detector (HPLC-DAD or HPLC-MS), thin-layer chromatography (TLC, HPTLC), gas chromatography with flame ionisation or mass-specific detector (GC-FID or GC-MS) or capillary ➤

WORLD FOOTWEAR



Figure 2: Reduction

electrophoresis with diode array detector (CE-DAD).

Any amines must be identified by at least two different separation processes in order to avoid possible misinterpretations from contaminating substances, leading to false results. HPLC-DAD or GC-MS procedures are exclusively used for this quantification.

It is essential to identify amines by means of two differing analysis machines, which makes the analysis of azo colourants complicated and therefore expensive.

We must also consider the further statutory regulations concerning contents in footwear with the potential to damage the health of the wearer such as PCP, formaldehyde, chromium VI, allergising dispersion paints, carcinogenic colourants or heavy metals. The detection of all these calls for further complicated methods of analysis which, in turn, have created further demands for substantial investment in testing facilities in order to protect people from health risks and the environment from further pollution. 🌍



Figure 3: Cleaning



TLC Thin-layer chromatography

...everything from one hand

Footbeds & Soles

ALSA-Sets

perfect fitting of the soles and comfort-footbeds

Anatomically shaped footbeds made of:
natural-cork, cork-latex, cork-EVA
and thermoplastic-foams
Product development -
Model- & mould department

Soles made of:
polyurethane, rubber,
rubber-PU, PU-TPU,
Compact-PU and
ALSA-Multicell®

Compact-PU

ALSA the solemaker®
Spitzenklasse für Schuhe made in Germany

ALSA GmbH, Uerzell, 36396 Steinau, Tel.: 0 66 67 - 81 0, Fax: 0 66 67 - 81 141, www.alsa.de

We exhibit: Lineapelle/Bologna 19-21 April 2006, Pav. 21-C 14/16/18, B 15/17/19 & PLW/Pirmasens 4-5 April 2006, Hall 6, Stand 6147