

European Ban on Certain Azo Dyes



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Introduction

In the European Parliament Directive 2002/61/EC of July 2002, the European Union (EU) has decided that by 11th September 2003 the harmonised legislation regarding azo dyes in consumer goods has to be enacted. This has led to numerous misleading and often totally false media statements by interested lay people along the lines that “azo dyes can no longer be used after September 2003”. This is simply wrong! In this publication we attempt to put clearly the actual status and what this new legislation will mean for tanners. In most cases it will mean no changes for the tanner but rather a continuation of what they have already been undertaking for the German Consumer Goods Ordinance.

What is the correct situation?

Following the introduction in 1994 of the German Consumer Goods Ordinance that restricted the use of certain azo dyes in consumer goods, several other EU member states introduced similar but different regulations. In the interests of transparency and the maintenance of the single market, the European Parliament accepted the 19th amendment of the Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azo colorants). In order to protect human health, those azo dyes, which can break down under reductive conditions to release any of a group of defined aromatic amines, are prohibited from being used in those consumer goods which are considered to have regular skin contact. The EU Directive was published in September 2002 and all EU member states have until 11th September 2003 to enact appropriate legal restrictions in their countries.

In simple words, this means that from September 2003 all EU countries will be required to prohibit the manufacture and sale of those defined consumer goods, which on chemical analysis are found to contain the listed aromatic amines originating from a small number of azo dyes. Articles coloured with all other azo dyes will be able to be manufactured and sold without restriction. Since most coloured textile and leather articles are treated with azo dyes and pigments, it is an important basic point to realise that only very few azo dyes will be affected. It has been estimated that less than 4 % of known azo dye structures would release the corresponding amines. Additionally over the last years all reputable dye manufacturers have stopped manufacturing such azo dyes and test institutes report the vast majority of samples tested today do comply with the EU Directive.

Frequently asked questions

There are still questions that are commonly asked about this azo dye restriction:

1) *The directive refers to azo colorants?*

Azo colorants are the most important class of synthetic dyes and pigments, representing 60 - 80% of all organic colorants. They are used widely in substrates such as textile fibres, leather, plastics, papers, hair, mineral oils, waxes, foodstuffs and cosmetics.

Hence azo colorants are part of our everyday colourful life, they are all around us and we could not do without them.

The English term colorant includes both pigments and dyes. These 2 groups can be conveniently classified as follows; dyes are soluble in the medium of application and pigments are not. In the English version of the Directive the terminology clearly distinguishes between parent term "colorants" and the sub-category "dyes".

2) *Which articles are included in the EU Directive?*

Consumer goods, which often come into **contact with the skin.** Examples of consumer goods covered by the restrictions are:

Clothing, bedding, towels, hairpieces, wigs, hats, nappies and other sanitary items, sleeping bags,

Footwear, gloves, wristwatch straps, handbags, purses/wallets, briefcases, chair covers, purses worn round the neck,

Textile or leather toys and toys which include textile or leather garments,

Yarn and fabrics intended for use by the final consumer.

3) *Why do azo dyes contain amines?*

Azo dyes contain one or more nitrogen-nitrogen double bonds called azo groups in their chemical structure, see Fig. 1.

- N=N -

Fig. 1. Azo group

Under reductive conditions using sodium dithionite these azo groups can be cleaved to form 2 amines, which can be schematically shown as in Fig. 2.

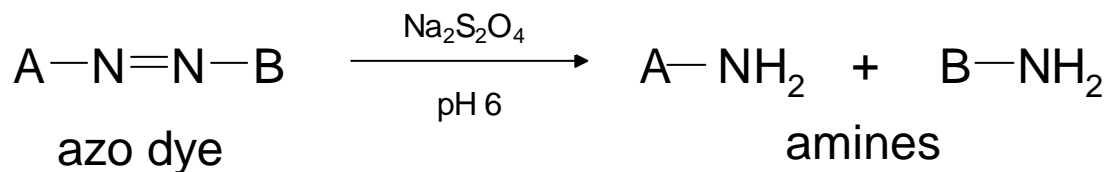


Fig. 2. Reductive cleavage of the azo dye to form amines

The chemical groups A and B are aromatic or aryl species in order to stabilise the electron structure and absorb light in the visible range, so the amines formed by cleavage of the azo group will obviously be aromatic amines. A small number of the aromatic amines are classified as being carcinogenic or potentially carcinogenic to humans. Only those few azo dyes that can release these amines upon reductive cleavage are affected.

4) Which aromatic amines are concerned?

Those consumer goods containing azo dyes that, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in the Table are forbidden. The detectable concentrations of any amine should not exceed 30 ppm in the finished articles or in the dyed parts thereof.

The list has been up-dated since 1994 and now includes 22 aromatic amines. It should be noted that two of these amines are analysed by breaking down to form other amines on the list. Further one of the most recent amines added to the list is 4-aminoazobenzene, which in itself contains an azo group. Currently no analytical procedure exists for this amine since it breaks down to form amines that are not listed. As with many of the amines in the list, no commercially available leather dyes are known to be based on the amine, 4-aminoazobenzene.

Table: List of aromatic amines according to the EU Directive 2002/61/EC.

| 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

5) Which analytical method should be used for testing dyed leather?

Harmonised testing methods are necessary for the application of this EU Directive. For leather the appropriate European analytical method is the newly approved CEN/TS 17234. It is very similar to the German DIN 53316 and the IUC 20 analytical methods. To avoid mistaken identification the amines must be identified by means of at least two different chromatographic separation methods. Quantification of the amines is required to be made by the high performance liquid chromatograph with UV detector, the so called HPLC / DAD procedure.

To minimise the possibility of false positive results it is important that the official extraction and analytical procedures are followed carefully.

6) What is meant by false positive results?

For certain dyed goods a listed amine is detected under the conditions of the analytical test even though no banned azo dye is present in the consumer good. The amine is an artefact of the test procedure, resulting from a chemical reaction other than azo cleavage. Numerous examples have been reported. For example, cleavages carried out at too high pH can release restricted amines from non-biologically accessible pigments, dyes without azo groups or non-banned azo dyes. Side reactions forming 2-naphthylamine and 4-aminodiphenyl are well known. Further false positive results are also known from polyurethane binders and by reduction of nitro groups to form amines, an example is shown in Fig. 3:

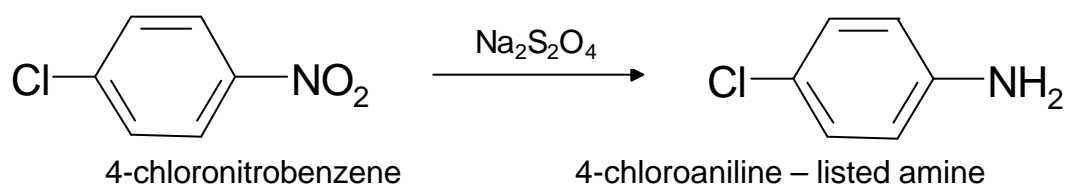


Fig. 3. Nitro group reduction to form amine

Further work to improve the analytical procedures is continuing in the EU-funded AALARM project co-ordinated by BLC Leather Technology Centre Ltd.

7) How can the tanner best ensure compliance?

Since this regulation applies to consumer goods manufactured or traded within the EU, one can expect that for azo dyes manufactured within the EU the Material Safety Data Sheet (MSDS) will be sufficient. No azo dyes which release banned amines are available within the EU. Additionally all dyes and pigments supplied by members of the Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers (ETAD) comply with the EU Directive.

For consumer goods coloured with azo dyes, which come from outside the EU, routine checking of the dyed leather should be undertaken to ensure compliance with the EU Directive.

It would be optimistic to believe that the current discussion on azo dyes will not persist for the foreseeable future. Hopefully scientific investigation and control will standardise and regulate this colorant matter on a world-wide basis.

Acknowledgements

We thank ETAD for providing information, Dr. H. Motschi for discussion.

Further information

www.etad.com

www.euroleather.com

www.tfl.com

updated 5.Jan.2004/AP