

The restrictions on the marketing and use of azo colourants according to the European legislation following the Directive 2002/61/EC (19th Amendment of Council Directive 76/769/EEC)

ETAD Information Notice No. 6

(Revised February 2008)

DISCLAIMER

Although every effort has been made to check the correctness of the information provided, ETAD cannot accept responsibility for any errors which exist.

All recipients are advised to seek legal advice on their specific obligations under the described regulations and any future amendments.

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1. INTRODUCTION

This updates Information Notice No 6 (originally issued in November 1995¹ and last revised in October 1998²) to include developments subsequent to the enactment of the Directive 2002/61/EC (19th Amendment of the Council Directive 76/769/EEC³, specially dealing with azo colourants) as well as further amendments⁴.

2. WHAT WERE THE MAIN CHANGES AFTER THE 19TH AMENDMENT?

- The original restrictions on azo colourants, formerly issued by the German authorities and known as the “German ban”⁵, were superseded by the introduction of a corresponding section in the European regulation on the restrictions on the marketing and use of certain dangerous substances and preparations;
- Two new members have been added to the list of carcinogenic amines:
 - o-Anisidine (CAS 90-04-0)
 - 4-Aminoazobenzene (CAS 60-09-3)
- Azo pigments, which were mostly exempted from the “German ban” under the 5th Amendment of the Consumer Goods Ordinance, are not regulated in this Directive;
- The examples list of affected consumer goods has been expanded in order to further clarify the scope of the regulation.

3. WHAT CONSUMER GOODS ARE AFFECTED?

The latest amendment to the affected consumer goods⁶ refers to all “textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity”. The following examples are listed:

- 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.

4. WHAT AZO DYES AND AZO PIGMENTS FALL WITHIN THE SCOPE OF THE REGULATION?

Many lists have been compiled and any list should be used with caution as there are likely to be errors and omissions. This applies also to the list of azo pigments included in this Information Note, in spite of the considerable effort expended in its compilation.

A) Azo dyes

Those azo dyes are banned, which through cleavage of one or more azo bonds could form any of the twenty-two aromatic amines listed in Table 1⁷ in concentrations above 30 ppm in the finished articles or in their dyed parts. Azo dyes are the most important chemical class of dyes, representing 60 - 70 % of all dyes used. This Directive restricts the use of only about 5 % of azo dyes.

Table 1

List of the specified amines	CAS-No
4-Aminobiphenyl	92-67-1
Benzidine	92-87-5
4-Chloro-o-toluidine	95-69-2
2-Naphthylamine	91-59-8
o-Aminoazotoluene	97-56-3
5-Nitro-o-toluidine	99-55-8
p-Chloroaniline	106-47-8
4-Methoxy-m-phenylenediamine	615-05-4
4,4'-Methylenedianiline	101-77-9
3,3'-Dichlorobenzidine	91-94-1
3,3'-Dimethoxybenzidine	119-90-4
3,3'-Dimethylbenzidine	119-93-7
4,4'-Methylenedi-o-toluidine	838-88-0
6-Methoxy-m-toluidine	120-71-8
4,4'-Methylenebis(2-chloroaniline)	101-14-4
4,4'-Oxydianiline	101-80-4

4,4'-Thiodianiline	139-65-1
o-Toluidine	95-53-4
4-Methyl-m-phenylenediamine	95-80-7
2,4,5-Trimethylaniline	137-17-7
o-Anisidine	90-04-0
4-Aminoazobenzene	60-09-3

Additionally, the following dye

Component 1:	CAS-No.: 118685-33-9	$C_{39}H_{23}ClCrN_7O_{12}S_2Na$
Component 2:		$C_{46}H_{30}CrN_{10}O_{20}S_2 \cdot 3Na$

may not be placed on the market or used for coloring textile and leather articles as a substance or constituent of preparations in concentrations higher than 0,1 % by mass⁷.

B) Azo pigments

The EU Directive does not contain any restrictions on azo pigments, and it is acknowledged that, due to their generally extremely low solubility, they do not pose a risk to consumer health. However, some azo pigments are sufficiently soluble under the analytical test conditions to yield detectable amounts of a listed amine (i.e. greater than 30 mg/kg consumer good). For this reason ETAD members have screened many of the azo pigments involved and Appendix 1 indicates the results obtained as regards their detectable content of carcinogenic aromatic amines.

ETAD recommends to its members a responsible approach to pigments belonging to the category B in Appendix 1 (amine content above 30 mg/Kg consumer good) even though they are not officially restricted by the Directive.

5. WHY IS IT IMPORTANT TO KNOW THE AROMATIC AMINE CONTENT OF AZO PIGMENTS?

Even though the number of azo pigments that could release relevant amounts of carcinogenic amines is extremely low, ETAD considers the gathering and communication of information on this issue as a part of its duty of responsible care.

A recent finding has stressed the importance of a constant screening and of the commitment of industry on this topic. In November 2007 an ETAD member noticed that particular combinations

of Pigment Black 7 with Pigment Orange 13 or Pigment Orange 34 release the carcinogenic amine 3,3'-dichlorobenzidine under the conditions of textile printing, whereas the single pigments are known not to undergo the same process. The amount of amine seems to depend on the quality and quantity of the applied Pigment Black 7.

The information was immediately communicated to the clients, to the authorities [among others to the Bundesinstitut für Risikobewertung (BfR)] and to ETAD. Other manufacturers of the pigment combinations also included a warning about the affected application in their SDS.

6. WHAT OFFICIAL TEST METHODS ARE AVAILABLE?

The official analytical methods for textiles and leather reported in the Council Directive⁶ are the following:

- CEN ISO/TS 17234:2003: Determination of certain azo colorants in dyed leathers
- EN 14362-1:2003: Textiles — Methods for the determination of certain aromatic amines derived from azo colorants — Part 1: Detection of the use of certain azo colorants accessible without extraction
- EN 14362-2:2003: Textiles — Methods for the determination of certain aromatic amines derived from azo colorants — Part 2: Detection of the use of certain azo colorants accessible by extracting the fibres

To determine the compliance with the EU Directive it is very important to ensure that an official method is used as many of the more aggressive test conditions applied by some contract laboratories tend to produce false positive results.

7. WHAT IS MEANT BY A FALSE POSITIVE RESULT?

This is simply when a listed amine is detected under the conditions of the analytical test but no banned azo dye or azo pigment is present in the consumer good. The amine is an artifact of the test procedure, resulting from chemical reactions other than azo cleavage. Numerous examples⁸ have been reported:

1. Detection of 4-aminobiphenyl from e.g. C.I. Acid Red 1, C.I. Solvent Yellow 7. **The detection of 4-aminobiphenyl should always be treated with suspicion** as no known azo dyes or pigments would form this amine by cleavage of one or more azo bonds.

2. Detection of 4-methoxy-m-phenylenediamine from textiles printed with C.I. Pigment Red 23. C.I. Pigment Red 23 is not restricted under the EU Directive as it would not form a listed amine through azo bond cleavage. Under the test conditions the expected cleavage product, 2-methoxy-5-nitroaniline, is further reduced to 4-methoxy-m-phenylenediamine (a listed amine).

Furthermore a study⁹ indicates that C.I. Pigment Red 23 does not metabolise to this amine in the presence of intestinal bacteria.

3. Detection of 2-naphthylamine from dyes based on Tobias acid. Although the official method yields smaller amounts of 2-naphthylamine than detected under more aggressive test conditions, the results are false positive as the responsible dyes do not fall within the scope of the EU Directive.

The above mentioned examples of false positive results have been observed with the currently available official methods. It must, however, be acknowledged that these official methods are very much better than the early test procedures. It is not surprising that any indirect analytical procedure of this type, when applied to such a wide variety of dyed or printed substrates, yield some false positive results.

8. HOW CAN A RETAILER BEST ENSURE COMPLIANCE?

Whereas the dye or pigment manufacturer is in a position to know which products are affected by these restrictions, it is the retailer or importer who is responsible for compliance. A textile finisher in Europe must also ensure that he does not use a banned azo compound for the manufacture of a regulated consumer item. The European Directive does not require any analytical testing. If the retailer can ensure by a certification procedure that banned azo colorants are not present, he can avoid substantial analytical costs.

A prudent importer or retailer should:

1. Seek to exclude banned azo colorants from the manufacturing chain by establishing a formal certification procedure with his suppliers. A possible format, developed by agreement of Euratex and ETAD, is illustrated in Appendix 2.
2. Ensure that suppliers of colorants to his manufacturing chain are fully conversant with the current regulatory requirements, and can be relied upon to provide accurate information on their products.
3. Establish a formal system for checking compliance by testing an appropriate sample of affected consumer goods. The extent of this testing can be reduced as confidence is established.

9. WHAT ARE THE OBLIGATIONS OF ETAD MEMBERS?

ETAD members no longer supply any of the restricted azo dyes for the applications as defined in the Directive 76/769/EEC and reported under paragraph 3 of this Notice.

All ETAD members are aware of the European restrictions and have specifically agreed to provide their customers with reliable information on the regulatory status of their products. Failure to provide correct information would be a serious breach of the ETAD Code of Ethics,

which is binding on all members. The list of ETAD members as in January 2008 is given in Appendix 3.

10. REFERENCES

1. ETAD Information Notice No 6 "German Ban of use of certain azo compounds in some consumer goods", November 1995.
2. ETAD Information Notice No 6 "German Ban of use of certain azo compounds in some consumer goods", July 1997.
3. DIRECTIVE 2002/61/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL relating to restrictions on the marketing and use of certain dangerous substances and preparations (azo colourants) of 19 July 2002.
4. The reference for the information contained in this document is the consolidated version of the Council Directive on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations, of 27 July 1976 (76/769/EEC), including all amendments and corrections published till January 2008.
5. See consolidated version of Consumer Goods Ordinance, Bundesgesetzblatt, 1998, Teil 1 Nr. 1, pp. 5-36.
6. Commission Directive 2004/21/EC of 24 February 2004.
7. Latest amendment: Commission Directive 2003/3/EC of 6 January 2003.
8. Schneider G., "Verwendungsverbot bestimmter Azofarbstoffe für Bedarfsgegenstände: Analytik und Bewertung von Analyseergebnissen", Deutsche Lebensmittel-Rundschau, 93, Heft 3, pp. 69 - 74 (1997).
9. Weideli H.J., "C.I. Pigment Red 23 - zu Unrecht gebrandmarkt", Farbe + Lack 1998, 104(5), 126.

AZO PIGMENTS CATEGORIZED BY ETAD AS REGARDS THEIR CONTENT IN AROMATIC CARCINOGENIC AMINES

(A) Pigments with C.I Generic Name ^{a)}

<i>C.I. Name</i>	<i>C.I. No.</i>	<i>EINECS No.</i>	<i>CAS No.</i>	<i>Amine content</i>
Pigment Yellow 12	21090	228-787-8	6358-85-6	A
Pigment Yellow 13	21100	225-822-9	5102-83-0	A
Pigment Yellow 14	21095	226-789-3	5468-75-7	A
Pigment Yellow 14	-	-	7621-06-9	A
Pigment Yellow 17	21105	224-867-1	4531-49-1	A
Pigment Yellow 49	11765	220-802-6	2904-04-3	C
Pigment Yellow 55	21096	228-771-0	6358-37-8	A
Pigment Yellow 63		238-611-1	14569-54-1	C
Pigment Yellow 83	21108	226-939-8	5567-15-7	A
Pigment Yellow 87	21107:1	239-160-3	15110-84-6	C
Pigment Yellow 114	21092	271-879-8	68610-87-7	C
Pigment Yellow 121	See Pigment Yellow 63			
Pigment Yellow 124	21107	267-243-4	67828-22-2	C
Pigment Yellow 126	21101	290-823-3	90268-23-8	A
Pigment Yellow 127	21102	271-878-2	68610-86-6	A
Pigment Yellow 152	21111	250-799-7	31775-20-9	C
Pigment Yellow 170	21104	250-797-6	31775-16-3	C
Pigment Yellow 171	-	-	53815-04-6	C
Pigment Yellow 172	21109	-	76233-80-2	C
Pigment Yellow 174	21098	279-017-2	78952-72-4	A

Pigment Yellow 176	21103	290-824-9	90268-24-9	A
Pigment Orange 3	12105	-	6410-15-7	C
Pigment Orange 13	21110	222-530-3	3520-72-7	A
Pigment Orange 14	21165	229-920-2	6837-37-2	C
Pigment Orange 15	21130	228-789-9	6358-88-9	C
Pigment Orange 16	21160	229-388-1	6505-28-8	A
Pigment Orange 34	21115	239-898-6	15793-73-4	A
Pigment Orange 35	See Pigment Orange 34			
Pigment Orange 37	See Pigment Orange 34			
Pigment Orange 44	21162	241-469-3	17453-73-5	C
Pigment Orange 63	-	-	76233-79-9	C
Pigment Red 7	12420	229-315-3	6471-51-8	C
Pigment Red 8	12335	229-100-4	6410-30-6	B
Pigment Red 17	12390	229-681-4	6655-84-1	C
Pigment Red 22	12315	229-245-3	6448-95-9	B
Pigment Red 37	21205	229-986-2	6883-91-6	C
Pigment Red 38	21120	228-788-3	6358-87-8	B
Pigment Red 41	21200	229-389-7	6505-29-9	C
Pigment Red 42	21210	228-790-4	6358-90-3	C
Pigment Red 114	12351	228-774-7	6358-47-0	C
Pigment Blue 25	21180	233-354-1	10127-03-4	C
Pigment Blue 26	21185	226-614-0	5437-88-7	C
Pigment Green 10	12775	262-934-7	61725-51-7	C

N:B: there are no registered manufacturers of these pigments

(B) Pigments without C.I. Generic Name^{a)}

<i>EINECS No.</i>	<i>CAS No</i>	<i>Amine content</i>
-	171091-00-2	C
-	169873-88-5	C
-	169873-87-4	C
-	169798-13-4	C
-	169798-12-3	C
-	169798-08-7	C
-	169873-87-4	C
-	160611-26-7	C
-	124236-34-6	C
-	103621-95-0	C
-	103621-93-8	C
-	103621-94-9	C
304-380-1	94249-03-3	C
300-272-3	93924-77-7	C
288-428-6	85721-17-1	C
280-397-7	83399-84-2	C
279-221-1	79665-33-1	C
-	78952-70-2	C
-	78245-94-0	C
-	76822-91-8	C
276-461-9	72207-62-6	C
-	71130-18-2	C
272-732-0	68910-13-4	C
255-508-7	41709-76-6	C
250-798-1	31775-17-4	C

-	30496-22-1	C
-	26841-50-9	C
-	5629-79-8	C

Key: A = amine content ^{b)} below the 30 mg/kg ^{a)}

B = amine content ^{b)} above the 30 mg/kg ^{a)}

C = test data not available

a) the listed pigments and the carcinogenic amine limits are based on the requirements of the now superseded 5th amendment to the German Ordinance and are only reported as information.

b) only the carcinogenic aromatic amines listed in Table 1 are considered.

Important explanatory notes

This appendix indicates the carcinogenic amine content of azo pigments which, even though not directly addressed in the Directive text, are sufficiently soluble to be included in the mentioned concentration range. The reported information is based on the results of tests conducted by ETAD members.

The aim of this appendix is to promote information by downstream processors about the range of pigments they may use for certain consumer goods to be marketed in Europe. As the quality of pigments varies between suppliers all downstream processors are advised to obtain a certification of compliance from their pigment suppliers.

For many of the pigments listed the amine content is unknown as no test data have been made available. The absence of test data may indicate that the pigment is not sold by ETAD members, or is not used to manufacture affected consumer goods.

Although efforts have been made to achieve completeness, other non-listed pigments could be in use, especially in non-EU countries. No pigments are included which have not been assigned a CAS No.

**MODEL DECLARATION OF COMPLIANCE WITH
THE COUNCIL DIRECTIVE 76/769/EEC
AS REGARDS AZO COLORANTS**

The undersigned, duly authorised representative of (name of dye / pigment supplier)

.....

hereby certifies that the textile dyes or pigments listed below, which have been supplied to
(name of textile dyeing and finishing company)

.....

on

are not restricted under the Council Directive 76/769/EEC

List of dyes or pigments (state "all" or specify):

.....

.....

.....

.....

The undersigned further certifies that the following dyes or pigments supplied on the date and to
the company described above are restricted under the Council Directive 76/769/EEC referred to
above:

List of azo dyes or azo pigments (state "none" or specify):

.....

.....

.....

.....

This company is / is not a member of ETAD (delete as appropriate).

Place:

Name:

Function:

Signature:

Date:

LIST OF ETAD MEMBERS (effective January, 2008)

Albion Colours Ltd.

ATUL Limited

BASF AG

BEZEMA AG

Cappelle Pigments n.v.

Ciba Specialty Chemicals Inc.

Clariant Products (Switzerland) Ltd.

Colourtex Industries Pvt. Ltd.

Dainichiseika

Dainippon Ink & Chemicals, Inc.

DyStar Textilfarben GmbH

EC Pigments

Everlight Chem. Ind. Corp.

Farbchemie Braun KG

Francolor Pigments SA

FUJIFILM Imaging Colorants Limited

Heubach GmbH

Hodogaya Chemical Co. Ltd.

Huntsman Advanced Materials

Jay Chemical Industries Ltd.

Jiangsu Taifeng Chemical Industrial Co., Ltd.

Kemira Germany GmbH

Kyung-In Synthetic Corporation

M. Dohmen GmbH

Mitsubishi Chemical Corporation
Nippon Kayaku Co., LTD
Oh Young Ind. Co. Ltd.
Oriental Giant Dyes & Chemical Ind. Corp
Sanyo Color Works Ltd.
Sensient Colors Inc.
Setas Kimya Sanayi A.S.
SunChemical A/S
Synthesia, a.s.
T&T Industries Corp.
Tennants Textile Colours Limited
TFL Ledertechnik GmbH & Co. KG
Thai Ambica Chemicals Co., Ltd.
Toyo Ink Mfg. Co. Ltd.
United Color Manufacturing, Inc.

The latest membership list is available on our Internet homepage

<http://www.etad.com>

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