German Legislation on Azo Dyes

Environmental protection and product safety are becoming increasingly important criteria in the purchase of textiles, due to the emotive nature of the debate and greater consumer concern.

This publication provides general information about azo dyes to help put the issue on a more factual basis. Here you will find some background notes about the German Consumer Goods Ordinance, together with a list of the amines and dyestuffs involved. Information is also provided about the test methods used for textiles, as well as an overview of other national regulations relating to azo dyes. DyStar's products are continuously monitored to make sure they meet statutory requirements throughout the world. DyStar

DyStar sets standards in environmental responsibility. DyStar has not had to make any changes to its product range to comply with the amendments to the German Consumer Goods Ordinance. What better evidence could there be that

with DyStar products you're on the safe side.

By buying and using dyes and pigment preparations from DyStar, you can be sure you comply with the German Consumer Goods Ordinance and other statutory regulations. None of our azo dyes generate banned amines following azo bond cleavage. So consumers can be confident that textiles dyed and printed correctly with DyStar products are safe.

Contact us if you would like further information. Your local DyStar representative or our central ecology team will be happy to help you.

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Amendments to the German Consumer Goods Ordinance

In 1994, the German Consumer Goods Ordinance (Bedarfsgegenständeverordnung) was amended to ban specific azo dyes, triggering widespread discussion about textile ecology. The German amendment also had an international impact, with headlines such as "German Azo Ban". Textile finishers and the trade were confronted overnight with a ban on azo dyes which *"release specific amines as a result of reductive cleavage of azo bonds"*.

This definition was only understood by dye chemists initially, as only these experts had a concrete idea which dyestuffs would be affected by the ban. But even the experts could not agree about the details of the law, because some single regulations and phrases were rather vague.

Toxicological background

MAK amines

The first serious reports about an increased risk of cancer of the bladder for people working in dyestuff production were published in trade journals as long as 100 years previously. The cause of these malignant diseases was soon thought to be certain aromatic amines widely used in the production of synthetic dyes in those days.





¹⁾ The MAK list was set up by the German Senate Committee for Testing of Occupational Hazardous Substances, and is updated annually (MAK = maximum workplace concentration). Group III of the MAK list summarizes carcinogenic chemicals (for carc. cat. 1 and 2 substances no max. tolerable workplace concentration is specified, though). The earlier divisions A1 and A2 of Group III have been renamed Category 1 and Category 2 in 1998, in keeping with the EU classification system for carcinogenic substances.



In particular, benzidine (basis of benzidine dyes) was thought to play a leading role.

Today scientifically based epidemiological evidence shows that four aromatic amines have a carcinogenic effect in humans:

- benzidine
- 2-naphthylamine
- 4-aminodiphenyl
- 4-chloro-o-toluidine

These four compounds are listed as "substances definitely known to be carcinogenic in humans" in Category 1, Section III of the MAK¹⁾ list.

Animal studies have shown that other aromatic amines are also carcinogenic under conditions, such as would indicate a carcinogenic potential for humans too. These substances make up Category 2, Section III of the MAK list.

Azo dyes

Azo dyes are synthesized by the diazotization of aromatic amines, followed by coupling to a further aromatic compound (known as the coupling component). This results in the formation of the so-called azo group – two nitrogen atoms joined by a double bond — N = N — (see Figure 1).

Azo groups in dyestuffs can be easily clea-ved using a reducing agent, which results in the decolorization of the azo dye. As a result of this azo cleavage, the aromatic amine that had been used as a diazo component in the dyestuff synthesis is set free again; also the coupling component is released, but now substituted with an additional amino group (see Figure 2). This reaction can be technically useful elsewhere.

Over the last 40 years, additional evidence has accumulated that azo dyes can also be metabolically cleaved by bacteria in the human digestive tract or by enzymatic reduction in some organs. Several studies carried out with textile workers handling benzidine dyes showed the presence of traces of free benzidine in the urine. MAK amines released in the human organism from azo dyestuffs can have a carcinogenic effect there. Epidemiological studies exist which describe an increased incidence of carcinomas of the bladder among painters and dye factory workers who had never had contact with free MAK amines, but only with the related azo dyes. It should be emphasized here that benzidine dyes and "MAK-dyes" in general can only have a carcinogenic effect where there is sufficient exposure, i.e., when these dyes actually enter the human organism as a result of improper handling or low occupational safety standards.

The German Law on Hazardous Substances classifies those azo dves as carcinogenic where a carcinogenic arylamine can be formed following reductive azo cleavage. The strict workplace protection rules which apply when handling carcinogenic substances apply to these dyes, too. The MAK Committee recommends that all azo dyes which can form MAK amines following cleavage should be avoided in general. German legislation has adopted this recommendation in TRGS 614²⁾ "Technical Regulation for Hazardous Substances", thereby putting this into effect. This recommendation is widely followed in Germany. DyStar as well as its parent companies stopped producing and marketing benzidine dyes in 1971. Marketing of other dyes based on Cat. 1 or 2 amines of the MAK list also ceased several years ago. However, numerous non-traditionals still produce and market these dyes worldwide and even in Europe today.

²⁾ TRGS: Technische Regeln für Gefahrstoffe (= Technical Regulation for Hazardous Substances). Up to May 1999, the TRGS 614 contained a list of 20 carcinogenic amines (identical with the German Consumer Goods Ordinance list, see Table 1). From May 1999, four further amines were added to the TRGS list: 6-amino-2-ethoxy-naphthaline; 4-amino-3-fluorophenol; 2-methoxyanaline (o-anisidine): p-amino azobenzene. Only the last two mentioned amines, already classified by the EU as carcinogenic since years, are relevant to dyes.



The German Consumer Goods Ordinance

Implementation of the recommendations of the MAK Committee and the TRGS 614 not to use dyestuffs based on MAK amines, together with the strict workplace protection rules of the Hazardous Substances Law and corresponding EU Directives, offers an effective protection to dye factory workers from health risks which could result from inhalation of dust-forming "MAK dyes" or from direct skin contact with these dyes where they are still in use.

After textiles have been dyed, azo dyestuffs based on MAK amines do not represent a real health risk to the consumer. In order to enter the consumer's organism, the dye must migrate from the textile to the skin, and must then be absorbed by the body through the skin. This risk is negligible where the fastness of the dye is high enough.

A genuine risk may exist where babies or infants suck on textiles or soft toys so that traces of the dye can enter the body with the saliva.

Amendments to the Consumer Goods Ordinance

Nevertheless, with preventative consumer protection in mind, the German Consumer Goods Ordinance was amended in 1994 to prevent any potential health risk from textiles dyed with dyestuffs based on cleavable carcinogenic amines. The amendment to the regulations then read:

"Textiles and other articles with prolonged skin contact shall not be dyed with azo dyestuffs which, by cleavage of one or more azo bonds, can release any of 20 listed aromatic amines. Furthermore, such textiles may not be imported or brought into circulation."

The regulations were re-amended several times over the next few years due to problems with the wording of the regulation, and other difficulties in the enforcement of the statutory transition periods.

As of April 18, 1997 the current 5th amendment to the Consumer Goods Ordinance came into force:

Annex 1, No. 7 column 3 of the German Consumer Goods Ordinance, as of 18. 4. 1997 presp. 23. 12. 1997 (abbreviated):

"The following may not be used in the commercial production or treatment of consumer goods: Azo dyestuffs which, on cleavage of one or more azo groups, release any of twenty listed amines (see list in Table 1).

Pigments are exempted from this regulation, provided none of the following amines (see list in Table 1) can be detected after cleavage of one or several azo groups (using the analysis method described in Annex 10, No. 7).

Consumer goods which do not comply with these regulations may not be imported or brought into circulation."



Table 1

Listed amines

The following 20 aromatic amines are listed in the German Consumer Goods Ordinance. All are also listed in Group III of the MAK list under Category 1 or 2:

Aromatic amines	CAS No.	MAK Group III under
2-naphthylamine	91-59-8	Cat. 1
4-aminodiphenyl	92-67-1	Cat. 1
4-chloro-o-toluidine	95-69-2	Cat. 1
benzidine	92-87-5	Cat. 1
2,4,5-trimethylaniline	137-17-7	Cat. 2
2,4-diaminoanisol	615-05-4	Cat. 2
2,4-toluenediamine	95-80-7	Cat. 2
2-amino-4-nitrotoluene	99-55-8	Cat. 2
3,3'-dichlorobenzidine	91-94-1	Cat. 2
3,3'-dimethoxybenzidine [3,3'-dianisidine]	119-90-4	Cat. 2
3,3'-dimethyl-4,4'-diaminodiphenylmethane	838-88-0	Cat. 2
3,3'-dimethylbenzidine [o-tolidine]	119-93-7	Cat. 2
4,4'-diaminodiphenylmethane	101-77-9	Cat. 2
4,4'-methylene-bis-(2-chloroaniline)	101-14-4	Cat. 2
4,4'-oxydianiline	101-80-4	Cat. 2
4,4'-thiodianiline	139-65-1	Cat. 2
o-aminoazotoluene	97-56-3	Cat. 2
o-toluidine	95-53-4	Cat. 2
p-chloroaniline	106-47-8	Cat. 2
p-cresidine	120-71-8	Cat. 2

On December 23rd, 1997 the Consumer Goods Ordinance was re-published including all the five amendments enacted until that date. On March 8th, 2000 the 6th amendment was enacted. It contains no essential dyestuff-related regulations.

The following two aromatic amines, which can also be used in dyestuff production, have been classified by the European Union as carcinogenic (see also footnote 2 on page 3)

Aromatic amines	CAS No.	EC Canc. cat.
o-anisidine	90-04-0	2
azobenzene	60-09-3	2

Dyestuffs based on either of these two amines have not yet been banned by the German Consumer Goods Ordinance to date. However, o-anisidine was included in the MAK list in 1996.

Many textile traders now prohibit their suppliers from using dyes based on the last two mentioned amines.



Draft for 6th Amendment to German Consumer Goods Ordinance

In March 1999 a draft 6th Amendment to the German Consumer Goods Ordinance was published, that proposed the following new regulations for dyestuffs:

- The list of 20 carcinogenic amines (Table 1) was to be expanded by 4 further amines: o-anisidine, p-amino azobenzene and two xylidine isomers.
- 2. The prohibition on using azo dyes by the German Consumer Goods Ordinance was to be extended to cover children's toys (children's toys were previously not considered to be consumer goods under the Ordinance).
- 3. The transition period within which consumer goods based on used or recycled fibers which do not meet with the Ordinance requirements may be manufactured, imported and marketed was to be extended to 31. 12. 2000.

However, this draft has been completely withdrawn following objections by the trade associations against the incorporation of p-amino azobenzene (current testing technology cannot detect the corresponding dyes with certainty) and xylidine isomers (insufficient evidence of carcinogenic potential) in the Ordinance. On the 4th of August, 1999 a second draft was presented which, in terms of its relevance to dyestuffs, now only mentions the extension of the transition period for recycling materials which do not comply with the Ordinance (see #3 above).

The withdrawal of the first draft was expressively made in view of current prepa-

rations for a EU-wide regulation which will restrict the usage of dyes based on aromatic amines suspected of being carcinogenic. This new EU regulation is designed to prevent individual member states from introducing their own (differing) national regulations again (see below).

Detection of banned azo dyestuffs

Following several years of analytical experimentation, a team of experts set up by the Federal Institute for Health, Consumer Protection and Veterinary Medicine (BgVV) adopted a set of test procedures in 1996 which ensures reliable analysis of goods covered by the German Consumer Goods Ordinance. The analytical method has been published in the "Official Archives of Test Methods in accordance with §35 LMBG" under the following catalogue numbers:

Method B 82.02-2

Detection of "banned" azo colourants on consumer articles, in particular those made of cellulose and proteinbased fibers (cotton, viscose, wool, silk).

Method B 82.02-4

Detection of "banned" azo colourants on consumer articles made of polyester.

These analytical methods are now referenced in Annex 10, No. 7 of the Consumer Goods Ordinance and have thus been given full legal recognition.

Detection of banned azo dyestuffs in textiles is performed indirectly by extracting a dyed textile specimen in a chemical reduction media, followed by chromatographic identification of the amines released. With polyester articles, the disperse dyes (which are not water-soluble) are first extracted from the textile specimen using an organic solvent, and then transferred into the reduction media.



⁰ An analytical method to detect "banned" azo dyestuffs in leather goods has been published under Catalogue No. B82.02-2 in the Official Archives of Test Methods in accordance with §35 LMBG (identical to the German DIN 53316).

Testing for "banned azo dyestuffs" based on Method B82.02-2:

- **1.** 1.0 g textile test sample is treated in 17 ml of a 0.06 molar citrate-buffered aqueous solution.
- 2. The sample is stored for 30 min. at 70 °C.
- **3.** 3.0 ml of an aqueous sodium dithionite solution (200 g/L) is added and the sample stored for a further 30 min. at 70 °C.
- **4**. After cooling, the extract is passed over a silica column and eluted with 80 ml of t-butyl methyl ether.
- **5.** The ether solution is carefully concentrated to around 1 ml and dissolved to 2.0 ml with methanol.
- 6. The extract is analyzed for the 20 listed amines using one of the following methods:
 - thin layer chromatography (TLC)
 - high-performance liquid chromatography (HPLC)
 - gas capillary chromatography (GC)
 - capillary electrophoresis (CE).

A positive finding must be confirmed using two different separation methods. (o-aminoazotoluene and 2-amino-4-nitrotoluene are detected from their cleavage products o-toluidine and 2,4-toluenediamine.)

- 7. Quantification of amines where present is performed using HPLC/DAD or GC-MS (with internal standard).
 (DAD = diode array detector;
 - GC-MS = gas chromatograph with mass spectrometer)

Compared to earlier methods, the validated analytical method differs as follows:

- Only azo colourants and certain susceptible pigments are cleaved. The following are not cleaved:
 - polyurethanes
 - amine or amide compounds in non-azo dyestuffs
 - non-bioavailable azo pigments.

False positive findings, therefore, can be practically discounted.

 Only the analytical detection of more than 30 mg of a listed amine per kg of tested textile is regarded as a safe indication that a "banned" azo colourant has been used to dye the analyzed fabric (recognition threshold value: 30 mg/kg = 30 ppm).

List of "banned" azo dyestuffs

The German Consumer Goods Ordinance does not list individual azo colourants, but only the aromatic amines which may



not be cleaved from the colourant. The chemical structure of a dyestuff gives a clear indication whether it is affected or not. However, this information is frequently not known to the textile finisher. Textile finishers therefore generally need a written confirmation from suppliers that the dyestuffs they intend to use comply to the requirements of the Consumer Goods Ordinance (see DyStar Statement on *Annex 1, see page 11*).

The German Chemical Industry Association (VCI) has made up a list of commonly marketed dyestuffs (generic names) which release listed amines following reductive azo cleavage. These individuals should not be present in dyestuff preparations used for the dyeing of consumer goods.

The list of prohibited dyestuffs issued by the VCI is provided in *Annex 2a (see page 12)* of this article. Dyestuffs whose chemical structure is not published in the Color Index, or whose existence on the world market is unknown, are naturally not included in the list.

Annex 2b (see page 14) shows a list of azo dyestuffs which contain either azobonded o-anisidine or p-amino azo-benzene. While these dyestuffs are not subject to the German Consumer Goods Law yet, a large number of textile companies and eco standards prohibit their use.

Azo pigments

The 5th amendment of the Consumer Goods Ordinance states clearly that azo pigments based on MAK amines such as 3,3'-dichlorobenzidine (DCB) do not fall under the ban, *provided* they cannot be cleaved under conditions laid down by the validated test methods, i.e., no MAK amines can be detected above the 30 ppm recognition threshold. (These pigments are regarded as being also non-bioavailable and hence not posing a cancer risk.) DCB- based pigments used in textile printing fulfil these conditions and can therefore be used in future.

However, under official testing conditions some low molecular weight pigments can cleave to form MAK amines in quantities clearly higher than the 30 ppm recognition threshold value. These pigments are prohibited under the Consumer Goods Ordinance.

Those azo pigments which fall within the prohibition and those which are not affected are summarized based on material from an ETAD publication, and are listed in *Annexes 2c* and *2d* at the end of this brochure.

Consumer Goods

According to Section 5, No. 6 of the German Food and Consumer Goods *Law* from September 9, 1997, textile consumer goods are defined as "articles which have more than a passing contact with the human skin". The Consumer Goods *Ordinance*, defines this more precisely:

- 1. Garments; fabrics and yarn used to produce garments
- 2. Bedding; bed linen and blankets; pillows; sleeping bags
- 3. Towels; beach mats
- 4. Masks; hairpieces; artificial eyelashes
- 5. Jewelry worn against the skin; bracelets
- 6. Neck purses; rucksacks
- 7. Items on which babies and small children lie or sit
- 8. Diapers; sanitary towels; panty liners; tampons

Source: Consumer Goods Ordinance, 5th amendment



Time limits

Several transition periods have been set up for enforcing the amended Consumer Goods Ordinance:

- Consumer goods containing "banned azo dyestuffs":
 - could be produced and imported until March 31, 1996
 - could be sold
 - until December 31, 1996
- 2. Consumer goods containing "banned/ cleavable azo pigments":
 - could be produced and imported until March 31, 1998
 could be
 - sold until October 31, 1998
- Used consumer goods like uniforms, protective clothing, boilersuits and similar workwear which have been dyed with "banned" dyestuffs or pigments can be re-sold even after December 31, 2000.
- Consumer goods made of used, recycled yarn may be produced, imported and sold until December 31, 1999³.

Dutch regulations: "Warenwetregeling Azo-Kleurstoffen"

On August 1, 1996 similar Dutch regulations came into force under the "Warenwetregeling Azo-Kleurstoffen". These regulations are almost identical to the 5th amendment of the German Consumer Goods Ordinance:

"Garments, shoes and bedding may not contain azo dyestuffs from which one of 20 listed aromatic amines can be cleaved (see Table 1)." The Dutch rules differ from the German regulations in the following points:

- The *Warenwetregeling* refers explicitly to (soluble) azo dyestuffs only; azo pigments (which are practically insoluble in the application medium) are not affected.
- Garments, shoes and bedding produced or ordered before August 1, 1996, which had been dyed with "banned" azo dyestuffs, could still be sold until September 1, 1997.
- Second-hand articles, protective clothing and items produced with recycled yarn containing "banned" azo dyestuffs could still be sold until December 31, 1999.
- The Dutch regulations for determining "banned" azo dyestuffs in consumer goods (textiles, leather) are similar to the German rules for detecting "banned" azo dyestuffs in textiles:

After extracting the test article in a dithionite/citrate-buffered solution, screening for aromatic amines is performed using HPLC/DAD. Positive findings are confirmed by derivatizing the amine using heptafluorobutyric acid anhydride, followed by identification via GC-MS.

The detection threshold for screening with HPLC/DAD is 30 mg amine/kg test article, and 3 mg/kg for selective identification following derivatization. The German analytical methods are considered to be equivalent.

Textiles which comply to the German Consumer Goods Ordinance also fulfil the requirements of the Dutch *Warenwetregeling*.



Turkey

The following rules apply under Turkish law from March 1, 1995:

- Dyestuffs based on MAK III cat. 1 or cat. 2 amines may not be used, produced or imported into Turkey.
- MAK cat. 1 or cat. 2 amines may not be used to produce dyestuffs in Turkey.

The Turkish regulations contain a list of 119 C.I. generic names of dyestuffs which following chemical reduction can release any of the 20 arylamines (see Table 1), as well as o-anisidine or p-amino benzene. Where dyestuffs are imported, Turkish customs require documentation stating the Color Index type of the dyestuff. This information is checked randomly by spot testing the color development reaction as specified in the Color Index.

Further spot checks include analytical sampling of dyed textiles to ensure compliance with the regulations.

India

As from January 30, 1993 the manufacture, processing, storage, consumption and sale of dyestuffs based on benzidine and its congeners is prohibited by law. An accompanying publication refers to 42 benzidine dyestuffs affected (generic types).

A corresponding ban was imposed on June 26, 1997 on 70 other azo dyestuffs which can release carcinogenic arylamines (including o-anisidine and p-amino azobenzene) following reductive azo cleavage.



France

The French Government is planning to promulgate extensive textile regulations

(« Décret relatif à la prévention des risques liés au comportement à l'usage des produits textiles, produits en cuir et similaires du cuir, produits en fourrure et similaires de la fourrure.»)

The most recent draft is dated January 21, 1997 and includes among others, a ban on using azo dyestuffs which can cleave one of 20 aromatic amines listed in Table 1.

European Union

The European Union is planning to adopt EU-wide restrictions on the use of dyestuffs which release carcinogenic amines following reductive cleavage in order to prevent other countries from promulgating their own national restrictions. Currently a *draft* directive is under discussion:

Proposal for a European Parliament and Council Directive amending for the 19th time Directive 76/769/EEC 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 (azo dyes).

The planned European regulation is based in terms of content on the German Consumer Goods Ordinance in the version of December 23, 1997 (including the 5th Ordinance Amendment). Changes are planned in the following areas:

- o-Anisidine will be added to the list of aromatic amines classified as carcinogenic (see Table 1).
- Dyestuffs based on p-amino azobenzene will not be affected by the prohibition on use *initially*. However, they are to be included as soon as a validated analysis method to detect these dyestuffs on dyed consumer goods is available (the testing procedure de-

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scribed on page 7 is not suitable as the p-amino azobenzene released following azo cleavage is further cleaved into aniline and p-phenylendiamine. These two amines, which are not classified as carcinogenic, are contained in many dyestuffs as individual azo components. They can be released from various dyestuffs during testing and thus (wrongly) indicate the presence of a p-amino azobenzene based dyestuff in a textile).

 The wording of the draft is such that azo pigments do not fall under the EU prohibition. When testing for "prohibited" azo dyestuffs no differentiation can be made between azo dyestuffs on the one hand, and azo pigments with "weakly" bonded amines on the other. Where testing is positive, further tests or studies need to be performed in order to prove that the MAK amine detected did not originate from a dyestuff, but rather from a pigment.

Our opinion: Even if expensive and time-consuming tests and studies do show that an analytically detected amine has been cleaved from a pigment, rather than from a dyestuff, no textile producer is likely to want to expose himself to the risk of image loss (blacklisting), not to mention delayed deliveries due to time-consuming analytical work and possible infringements against stricter national regulations.

Instead the textile producer is more likely to simply refrain from using such cleavable pigments, even if not necessarily obliged to under the precise wording of the EU draft.

Annex 1

Statement by DyStar on the prohibition of certain azo dyestuffs

DyStar Textilfarben GmbH does not produce or market azo dyestuffs which, following reductive cleavage¹⁾ of azo bonds release any of the 20 aromatic amines as listed in the 2nd amendment to the German Consumer Goods Ordinance.

In addition, DyStar refrains from marketing dyestuffs which reductively split off o-anisidine or p-amino azo-benzene, although these amines do not yet fall under the legal ban in Germany.

All dyestuffs and pigments marketed by DyStar comply to the 5^{th} amendment of the German Consumer Goods Ordinance as promulgated on April 18, 1997 (re-published on December 23, 1997) and the 6^{th} amendment of March 8, 2000.



Annex 2a

Azo dyestuffs which can be cleaved to release carcinogenic amines as defined by the German Consumer Goods Ordinance Only dyestuffs still available on the world market are listed.*

No guarantee for the accuracy of this list is given.

No.	C.I. No.	Name / Synonym	Diazo component
1	-	Acid Black 29	benzidine
2	-	Acid Black 209	3,3'-dimethylbenzidine (o-tolidine)
3	30 334	Acid Black 232	benzidine
4	30 336	Acid Black 94	benzidine
5	22 195	Acid Orange 45	benzidine
6	26 420	Acid Red 104	o-aminoazotoluene, o-toluidine
7	23 635	Acid Red 114	3,3'-dimethylbenzidine (o-tolidine)
8	27 200	Acid Red 115	o-aminoazotoluene, o-toluidine
9	-	Acid Red 119:1	p-chloroaniline
10	24 125	Acid Red 128	3,3'-dimethoxybenzidine (o-dianisidine)
11	26 665	Acid Red 148	o-aminoazotoluene, o-toluidine
12	20 530	Acid Red 158	o-toluidine
13	-	Acid Red 167	3,3'-dimethylbenzidine (o-tolidine)
14	16 140	Acid Red 24	o-toluidine
15	18 129	Acid Red 265	o-toluidine
16	18 065	Acid Red 35	o-toluidine
17	22 245	Acid Red 85	benzidine
18	37 085	Azoic Diazo Component 11	4-chloro-o-toluidine
19	37 105	Azoic Diazo Component 12	2-amino-4-nitrotoluene
20	37 235	Azoic Diazo Component 48	3,3'-dimethoxybenzidine (o-dianisidine)
21	37 225	Azoic Diazo Component 112	benzidine
22	-	Azoic Diazo Component 113	3,3'-dimethylbenzidine (o-tolidine)
23	21 010	Basic Brown 4	2,4-toluenediamine
24	-	Basic Yellow 103	4,4'-diaminodiphenylmethane
25	76 035	Developer 14	
		= Oxidation Base 20	2,4-toluenediamine
26	-	Direct Black 154	3,3'-dimethylbenzidine (o-tolidine)
27	22 580	Direct Black 29	benzidine
28	30 235	Direct Black 38	benzidine
29	30 245	Direct Black 4	benzidine
30	24 410	Direct Blue 1	3,3'-dimethoxybenzidine (o-dianisidine)
31	22 590	Direct Blue 2	benzidine
32	23 705	Direct Blue 3	3,3'-dimethylbenzidine (o-tolidine)
33	22 610	Direct Blue 6	benzidine
34	24 140	Direct Blue 8	3,3'-dimethoxybenzidine (o-dianisidine)
35	24 155	Direct Blue 9	3,3'-dimethoxybenzidine (o-dianisidine)
36	24 340	Direct Blue 10	3,3'-dimethoxybenzidine (o-dianisidine)
37	23 850	Direct Blue 14	3,3'-dimethylbenzidine (o-tolidine)
38	24 400	Direct Blue 15	3,3'-dimethoxybenzidine (o-dianisidine)
39	23 710	Direct Blue 21	3,3'-dimethylbenzidine (o-tolidine)
40	24 280	Direct Blue 22	3,3'-dimethoxybenzidine (o-dianisidine)
41	23 790	Direct Blue 25	3,3'-dimethylbenzidine (o-tolidine)
42	24 145	Direct Blue 35	3,3'-dimethoxybenzidine (o-dianisidine)
43	24 175	Direct Blue 151	3,3'-dimethoxybenzidine (o-dianisidine)
44	-	Direct Blue 160	3,3'-dimethoxybenzidine (o-dianisidine)
45	-	Direct Blue 173	3,3 -dimethoxybenzidine (o-dianisidine)
46	-	Direct Blue 192	3,3 -dimethoxybenzidine (o-dianisidine)
47	24 415	Direct Blue 215	3,3 -dimethoxybenzidine (o-dianisidine)
48	23 820	Direct Blue 295	3,3 -dimethylbenzidine (o-tolidine)
49	24 203	Direct Blue 306	3,3 -dimethoxybenzidine (o-dianisidine)
50	30 045	Direct Brown 1	Denzidine
51	30 110	Direct Brown 1:2	Denzidine
5Z	22 311	Direct Brown 2	Denzidine
53	30 140	Direct Brown 6	Denzidine

*) Compiled by the German TEGEWA association based on internal investigation and Color Index 3rd Edition, 1994



No.	C.I. No.	Name / Synonym	Diazo component
54	36 030	Direct Brown 25	benzidine
55	31 725	Direct Brown 27	benzidine
56	35 660	Direct Brown 31	benzidine
57	35 520	Direct Brown 33	benzidine
58	31 710	Direct Brown 51	benzidine
59	22 345	Direct Brown 59	benzidine
60	36 300	Direct Brown 74	benzidine
61	30 050	Direct Brown 79	benzidine
62	30 145	Direct Brown 95	benzidine
63	31 740	Direct Brown 101	benzidine
64	30 120	Direct Brown 154	benzidine
65	30 368	Direct Brown 222	3,3'-dimethylbenzidine (o-tolidine)
66	-	Direct Brown 223	3,3'-dimethylbenzidine (o-tolidine)
67	21 060	Direct Dye	benzidine
68	30 280	Direct Green 1	benzidine
69	30 295	Direct Green 6	benzidine
70	30 315	Direct Green 8	benzidine
71	-	Direct Green 8:1	benzidine
72	30 387	Direct Green 85	3,3'-dimethylbenzidine (o-tolidine)
73	22 370	Direct Orange 1	benzidine
74	23 375	Direct Orange 6, di sodium salt	3,3'-dimethylbenzidine (o-tolidine)
75	23 380	Direct Orange 7	3,3'-dimethylbenzidine (o-tolidine)
76	22 130	Direct Orange 8	benzidine
77	23 370	Direct Orange 10	3,3'-dimethylbenzidine (o-tolidine)
78	29 173	Direct Orange 108	o-toluidine
79	22 310	Direct Red 1	benzidine
80	23 500	Direct Red 2	3,3'-dimethylbenzidine (o-tolidine)
81	24 100	Direct Red 7	3,3'-dimethoxybenzidine (o-dianisidine)
82	22 145	Direct Red 10	benzidine
83	22 155	Direct Red 13	benzidine
84	22 150	Direct Red 17	benzidine
85	23 560	Direct Red 21	3,3'-dimethylbenzidine (o-tolidine)
86	23 565	Direct Red 22	3,3'-dimethylbenzidine (o-tolidine)
87	22 120	Direct Red 28	benzidine
88	22 240	Direct Red 37	benzidine
89	23 630	Direct Red 39	3,3'-dimethylbenzidine (o-tolidine)
90	22 500	Direct Red 44	benzidine
91	23 050	Direct Red 46	dichlorobenzidine
92	29 175	Direct Red 62	o-toluidine
93	23 505	Direct Red 67	3,3'-dimethylbenzidine (o-tolidine)
94	22 570	Direct Violet 1	benzidine
95	22 555	Direct Violet 4	benzidine
96	22 550	Direct Violet 12	benzidine
97	24 080	Direct Violet 13	3,3'-dimethoxybenzidine (o-dianisidine)
98	23 520	Direct Violet 21	3,3'-dimethylbenzidine (o-tolidine)
99	22 480	Direct Violet 22	benzidine
100	22 250	Direct Yellow 1	benzidine
101	22 010	Direct Yellow 24	benzidine
102	23 660	Direct Yellow 48	3,3'-dimethylbenzidine (o-tolidine)
103	-	Disperse Orange 60	dichlorobenzidine
104	-	Disperse Red 221	p-chloroaniline
105	-	Disperse Yellow 218	p-chloroaniline
106	22 310	Mordant Red 57	benzidine
107	25 100	Mordant Yellow 16	4,4'-thiodianiline
108	-	Solvent Red 19 (similar)	o-toluidine
109	26 105	Solvent Red 24	o-aminoazotoluene, o-toluidine
110	26 120	Solvent Red 26	o-toluidine
111	-	Solvent Red 164	o-toluidine
112	-	Solvent Red 215	o-aminoazotoluene, o-toluidine

*) Compiled by the German TEGEWA association based on internal investigation and Color Index 3rd Edition, 1994



Annex 2b

Azo dyestuffs which can be cleaved to release carcinogenic amines which are <u>not</u> listed in the German Consumer Goods Ordinance

Only dyestuffs still available on the world market are listed.* No guarantee for the accuracy of this list is given.

No.	C.I. No.	Name / Synonym	Diazo component
1	-	Acid Black 131	o-anisidine
2	-	Acid Black 132	o-anisidine
3	-	Acid Brown 415	o-anisidine
4	14 710	Acid Red 4	o-anisidine
5	14 905	Acid Red 5	o-anisidine
6	27 290	Acid Red 73	p-aminoazobenzene
7	26 660	Acid Red 116	p-aminoazobenzene
8	27 190	Acid Red 150	p-aminoazobenzene
9	18 133	Acid Red 264	o-anisidine
10	-	Acid Red 420	p-aminoazobenzene
11	18 075	Acid Violet 12	o-anisidine
12	-	Basic Red 42	o-anisidine
13	12 245	Basic Red 76	o-anisidine
14	-	Basic Red 111	p-aminoazobenzene
15	-	Basic Red 114	o-anisidine
16	-	Basic Yellow 82	p-aminoazobenzene
17	29 185	Direct Red 24	o-anisidine
18	29 190	Direct Red 26	o-anisidine
19	29 200	Direct Red 72	o-anisidine
20	-	Disperse Orange 149	p-aminoazobenzene
21	26 130	Disperse Red 151	p-aminoazobenzene
22	26 090	Disperse Yellow 7	p-aminoazobenzene
23	26 070	Disperse Yellow 23	p-aminoazobenzene
24	-	Disperse Yellow 56	p-aminoazobenzene
25	12 150	Solvent Red 1	o-anisidine
26	26 050	Solvent Red 19	p-aminoazobenzol
27	26 100	Solvent Red 23	p-aminoazobenzol
28	-	Solvent Red 68	p-aminoazobenzol
29	27 290	Solvent Red 69	p-aminoazobenzol
30	-	Solvent Yellow 72	o-anisidine

*) Compiled by the VCI association based on internal investigation and Color Index 3rd Edition, 1994



Annex 2c

Azo pigments which can be cleaved* to release carcinogenic amines as defined by the German Consumer Goods Ordinance ("Banned Azo Pigments")

Only pigments still available on the world market are listed.

No guarentee for the accuracy of this list is given.**

No.	C.INo.	Name / Synonym	Diazo component
1	12 335	Pigment Red 8	2-Amino-4-nitrotoluene
2	12 315	Pigment Red 22	2-Amino-4-nitrotoluene
3	21 120	Pigment Red 38	3,3'-Dichloro benzidine

Annex 2d

Azo pigments which cannot be cleaved* to release carcinogenic amines as defined by the German Consumer Goods Ordinance ("Acceptable Azo Pigments")

Only pigments still available on the world market are listed.

No guarentee for the accuracy of this list is given.**

No.	C.INo.	Name / Synonym
1	21 090	Pigment Yellow 12
2	21 100	Pigment Yellow 13
3	21 095	Pigment Yellow 14
4	21 105	Pigment Yellow 17
5	21 096	Pigment Yellow 55
6	21 108	Pigment Yellow 83
7	21 101	Pigment Yellow 126
8	21 102	Pigment Yellow 127
9	21 098	Pigment Yellow 174
10	21 103	Pigment Yellow 176
11	21 110	Pigment Orange 13
12	21 160	Pigment Yellow 16
13	21 115	Pigment Yellow 34

*) This assessment is based on the recognized official test method B82.02-2 published in the Official Archives of Test Methods in accordance with § 35 LMBG

**) Compiled from ETAD publications on the basis of experience/testing by ETAD member firms (see also ETAD Information No. 006).

The above assessments are based on high quality pigments from well-known manufacturers (e.g. members of ETAD).

No data is available on pigments not named in the above tables.



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