

**DETOX Program**  
**Hazardous Substances Fact Sheet**

**Amines from azo dyes and  
carcinogenic dyes**

**Content**

1	Background.....	3
2	Definition .....	3
3	Legal Aspects.....	5
4	Hazardous Properties and Exposure .....	6
4.1	Hazardous Properties.....	6
4.2	Exposure.....	6
5	Sources for amines and carcinogenic dyes in production of textiles .....	7
6	Alternative and Substitute Substances .....	7

## 1 Background

Most of the colorants used in the textile industry are soluble dyestuffs, and 70-80 % of them are azo dyes. Also most of the (insoluble) pigments on the market are azo pigments. Azo dyes are broadly used as colorants in the apparel, home textile, leather industry and other industrial sectors. In textiles dyeing up to 50 % of the azo dyes can be washed out. With the factory discharges they often end up in water bodies as they can be hardly removed by standard waste water treatment processes.

Some azo dyes can break down in dangerous aromatic amines which can cause serious sicknesses like cancer, but also environmental damages. Furthermore, there are several dyes from other substance groups that may cause cancer and are of equal concern. For this reason several azo and other dyes are prohibited by EU legislation as well as in many other countries. Under certain conditions colorants may be absorbed through the skin of consumers wearing dyed textiles on the skin. They may also be orally ingested by babies and young children due to sucking of textiles. In 2016, REWE Group will initiate an investigation into the status of phase out of restricted azo amines in the production of textiles.

The latest list of hazardous substances that shall be phased out in the production including limit values can be found in the REWE Groups MRSL (Manufacturers Restricted Substance List).

REWE Group MRSL: <https://www.rewe-group.com/dam/jcr:b9c63a3f-6e2b-416b-9541-7da6a1bc63d9/REWE%20Group%20MRSL%202.0.pdf>

## 2 Definition

- Thousands of azo dyes exist<sup>1</sup>. Chemically azo compounds are marked by the functional group R-N=N-R<sup>2</sup>. Azo dyes and other carcinogenic dyes can be found in the REWE Group MRSL.
- Some azo dyes may cleave into amines which often are more toxic than the original dye. Amino compounds with their CAS number are:

No.	CAS Number	Name
	92-67-1	4-Aminodiphenyl
	92-87-5	Benzidine
	95-69-2	4-Chloro-o-Toluidine
	91-59-8	2-Naphthylamine
	97-56-3	o-Aminoazotoluene
	99-55-8	2-Amino-4-Nitrotoluene
	106-47-8	p-Chloroaniline
	615-05-4	2,4-Diaminoanisole
	101-77-9	4,4'-Diaminodiphenylmethane
	91-94-1	3,3'-Dichlorobenzidine
	119-90-4	3,3'-Dimethoxybenzidine
	119-93-7	3,3'-Dimethylbenzidine

<sup>1</sup> AFIRM (Apparel & Footwear International RSL Management Working Group) 2011. AFIRM Supplier Toolkit. Online available: [www.afirm-group.com/toolkit](http://www.afirm-group.com/toolkit)

<sup>2</sup> <http://goldbook.iupac.org/A00560.html>

838-88-0	3,3'-Dimethyl- 4,4'diaminodiphenylmethane
120-71-8	p-Cresidine
101-14-4	4,4'-Methylene-Bis(2-Chloroaniline)
101-80-4	4,4'-Oxydianiline
139-65-1	4,4'-Thiodianiline
95-53-4	o-Toluidine
95-80-7	2,4-Toluylenediamine
137-17-7	2,4,5-Trimethylaniline
90-04-0	o-Anisidine
60-09-3	p-Aminoazobenzene
95-68-1	2,4-Xylidine
87-62-7	2,6-Xylidine

- Benzidine (CAS Number 92-87-5) serves also as example of a hazardous amine:

The predominant use for benzidine is in the production of dyes, especially azo dyes in the leather, textile, and paper industries.

Benzidine has been detected in soil and water near industrial sources. It is considered to be acutely toxic to humans when ingested. Dermal exposure may cause skin rashes and irritation. Chronic exposure to benzidine in humans may affect the bladder. Epidemiological studies have shown occupational exposure to benzidine to result in an increased risk of bladder cancer. Animal studies have reported various tumor types at multiple sites from benzidine exposure via oral, inhalation, and injection exposure.<sup>3</sup> Animal studies showed also effects on blood, liver, kidney, and the central nervous system.

Several azo dyes are based on benzidine, for example the following<sup>4</sup>:

No.	CAS Number	Name
	3701-40-4	Acid Red 99
	6459-94-5	Acid Red 114
	68318-35-4	Acid Black 209
	6470-20-8	Acid Orange 56
	6548-30-7	Acid Red 128
	10169-02-5	Acid Red 97
	72-57-1	Direct Blue 14
	992-59-6	Direct Red 2
	573-58-0	Direct Red 28
	2150-54-1	Direct Blue 25
	2429-71-2	Direct Blue 8
	2429-74-5	Direct Blue 15
	6449-35-0	Direct Blue 151
	6548-29-4	Direct Red 46
	6655-95-4	Direct Blue 158
	16071-86-6	Direct Brown 95

<sup>3</sup> United States Environmental Protection Agency 2000. Benzidine. Online available: <http://www.epa.gov/ttn/atw/hlthef/benzidin.html>

<sup>4</sup> Government of Canada 2014. Chemical Substances. Certain Benzidine-based Dyes and Related Substances of the Aromatic Azo and Benzidine-based Substance Grouping. Online available: (<http://www.chemicalsubstanceschimiques.gc.ca/fact-fait/glance-bref/colorants-eng.php>)

### 3 Legal Aspects

The European Commission has laid out its stance on azo dyes in the so called REACH legislation (Section 43 of Annex XVII of REACH, Azo dyes and Azocolourants). Azo dyes, which, by cleavage of their azo groups, produce one or more of the known carcinogenic aromatic amines in detectable concentrations, defined as 30ppm, may not be used in the following articles<sup>5</sup>:

- clothing, bedding, towels, hairpieces, wigs, hats, nappies and other sanitary items, sleeping bags.
- footwear, gloves, wristwatch straps, handbags.
- textile or leather toys and toys which include textile or leather garments.
- purses/wallets, briefcases, chair covers, purses worn round the neck.
- yarn and fabrics intended for use by the final consumer.

EU Directive 2002/61/EC and 2003/3/EC accessories lists 24 harmful aromatic amines<sup>6</sup>:

No.	CAS Number	Name
1	92-67-1	4-Aninobiphenyl
2	92-87-5	Benzidine
3	95-69-2	4-Chloro-o-toluidine
4	91-59-8	2-Naphthylamine
5	97-56-3	o-Aminoazotoluene
6	99-55-8	2-Amino-4-nitrotoluene
7	106-47-8	p-Chloroaniline
8	615-05-4	2,4-Diaminoanisole
9	101-77-9	4,4'-Diaminobiphenylmethane
10	91-94-1	3,3'-Dichlorobenzidine
11	119-90-4	3,3'-Dimethoxybenzidine
12	119-93-7	3,3'-Dimethylbenzidine
13	838-88-0	3,3'-Dimethyl-4, 4- diaminobiphenylmethane
14	120-71-8	p-Cresidine
15	101-214-4	4,4'-Methylene-bis-(2-chloroaniline)
16	101-80-4	4,4'-Oxydianiline
17	139-65-1	4,4'-Thiodianiline
18	95-53-4	o-Toluidine
19	95-80-7	2, 4-Toluenediamine
20	137-17-7	2,4,5-Trimethylaniline
21	90-04-0	o-Anisidine
22	95-68-1	2,4-Xylidine
23	87-62-7	2,6-Xylidine
24	60-09-3	4-Aminoazobenzene

<sup>5</sup> UK Houses of Parliament. Parliamentary office of science and technology, undated. The Environmental, Health and Economic Impacts of Textile Azo Dyes. Online available: [http://2014.igem.org/wiki/images/2/29/Goodbye\\_Azo\\_Dye\\_POSTnote.pdf](http://2014.igem.org/wiki/images/2/29/Goodbye_Azo_Dye_POSTnote.pdf)

<sup>6</sup> Consumer Product Testing services 2012. Azo dyes testing. Online available: <http://www.cpssc-lab.com/en/RSLTesting.asp?id=184&cid=94>

Annex XVII\_to REACH Regulation (EC) No 1907/2006, entry 43 lists 22 carcinogenic aromatic amines. The EU directive does not have any restriction on azo pigments. The solubility of pigments is expected to be low and so they are not thought to pose a risk to human health.<sup>7</sup>

## 4 Hazardous Properties and Exposure

### 4.1 Hazardous Properties

Some azo dyes pose serious health risks to humans if they are used in textiles with skin contact or if they get into food or drinking water supplies.<sup>8</sup> Under certain (reductive) conditions the azo group can break down, building potentially dangerous substances known as aromatic amines. Such conditions are typical for the digestive tracts and some other organs of animals and humans<sup>9</sup>. 24 aromatic amines have been proven as being carcinogenic for humans. Up to five percent of the known azo dyes can cleave to form these dangerous compounds.<sup>10</sup>

Several soluble azo dyes also can cause allergic skin reactions<sup>11</sup>. The German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) recommends that consumers should not get in contact with hazardous azo dyes<sup>12</sup>.

Azo dyes are often persistent and hardly degrade under natural environmental conditions. In addition they can tend to bioaccumulate in the food chain.<sup>13</sup>

Many Azo dyes are highly toxic to ecosystems and mutagens, meaning they can have acute and chronic effects upon organisms. For example, dye effluent has been connected to growth reduction, neurosensory damage, metabolic stress and death in fish, and impairing growth and productivity in plants<sup>14</sup>.

### 4.2 Exposure

The risk of a chemical for human health and the environment is not only determined by its toxicity but by the degree of exposure, too.

#### a) Workers

The main causes of workers exposure to azo dyes are dermal absorption and inhalation. This is the case for workers in dye production and factories where such dyes are used.

<sup>7</sup> UK Houses of Parliament. Parliamentary office of science and technology, undated. The Environmental, Health and Economic Impacts of Textile Azo Dyes. Online available: [http://2014.igem.org/wiki/images/2/29/Goodbye\\_Azo\\_Dye\\_POSTnote.pdf](http://2014.igem.org/wiki/images/2/29/Goodbye_Azo_Dye_POSTnote.pdf)

<sup>8</sup> Khan et al. (2005) Managing and Monitoring Effluent Treatment Plants. Department for International Development, UK under the Asia Pro Eco Programme. In: UK Houses of Parliament. Parliamentary office of science and technology, undated.

<sup>9</sup> F.M.D. Chequer et al. (2013). Textile Dyes: Dyeing Process and Environmental Impact. In: UK Houses of Parliament. Parliamentary office of science and technology, undated.

<sup>10</sup> A. Puntener, C. Page (2004) European Ban on Certain Azo Dyes. Quality and Environment. In: UK Houses of Parliament. Parliamentary office of science and technology, undated. Impacts of Textile Azo Dyes. Online available: [http://2014.igem.org/wiki/images/2/29/Goodbye\\_Azo\\_Dye\\_POSTnote.pdf](http://2014.igem.org/wiki/images/2/29/Goodbye_Azo_Dye_POSTnote.pdf)

<sup>11</sup> Forschungsinstitut für Arbeitsmedizin der Deutschen Gesetzlichen Unfallversicherung Institut der Ruhr-Universität Bochum 2009. Azofarbstoffe und deren Hautgängigkeit beim Menschen. Online available: [http://www.ipa.ruhr-uni-bochum.de/pdf/09-02-27\\_BGFA-Report2\\_Azofarbstoffe.pdf](http://www.ipa.ruhr-uni-bochum.de/pdf/09-02-27_BGFA-Report2_Azofarbstoffe.pdf)

<sup>12</sup> Stellungnahme Nr. 021/2014 des Bundesinstituts für Risiko-bewertung vom 24. Juli 2013, veröffentlicht unter [http://www.bfr.bund.de/de/a-z\\_index/aromatische\\_amine-4779.html](http://www.bfr.bund.de/de/a-z_index/aromatische_amine-4779.html)

<sup>13</sup> Gudelj I, Hrenović J, Dragičević TL, Delaš F, Soljan V, Gudelj H. 2011. Azo dyes, their environmental effects, and defining a strategy for their biodegradation and detoxification. Abstract online available: <http://www.ncbi.nlm.nih.gov/pubmed/21421537>

<sup>14</sup> UK Houses of Parliament. Parliamentary office of science and technology, undated. The Environmental, Health and Economic Impacts of Textile Azo Dyes. Online available: [http://2014.igem.org/wiki/images/2/29/Goodbye\\_Azo\\_Dye\\_POSTnote.pdf](http://2014.igem.org/wiki/images/2/29/Goodbye_Azo_Dye_POSTnote.pdf)

Also workers in the textile industry and in retail who handle dyed products may be exposed.<sup>15</sup>

#### **b) Environment**

The major source of dye-loss corresponds to the incomplete fixation of the dyes during textile dyeing. Colorant loss during dyeing can be as high as 50%. The remaining dyestuff poses a challenge for wastewater treatment due to poor degradability of many azo compounds. The dyes often end up in the water bodies because standard waste water treatment with activated sludge is ineffective in removing them. If improperly treated effluents are discharged into the environment they can cause significant damages.

#### **c) Consumers**

The main routes of consumer's exposure to azo dyes are oral ingestion, mainly caused by the sucking of textiles by babies and young children, and dermal absorption, the route of primary concern for consumers wearing azo compound-dyed products.

Furthermore, contamination of food can contribute to the intake of such compounds. Soluble azo dyes can be absorbed by lung, skin and gastrointestinal tract.<sup>16</sup> Insoluble azo pigments can be absorbed rather by lung and gastrointestinal tract but hardly by skin.<sup>17</sup>

## **5 Sources for amines and carcinogenic dyes in production of textiles**

Most of the colorants used in the textile industry are soluble dyestuffs. The clear majority of these are azo dyes (70-80%). Also most of the (insoluble) pigments on the market are azo pigments, followed next by phthalocyanines<sup>1</sup>. Azo colorants are frequently used to dye textile fibers, leather, plastics, paper, and other consumer products. Many have vivid colors, especially reds, oranges, and yellows. Azo dyes are the most important class of synthetic dyes and pigments for the textile industry representing in total 70% of all organic colorants<sup>18</sup>. Dyes are applied to textile goods by dyeing from dye solutions and by printing from dye pastes. Methods include direct application and yarn dyeing.

## **6 Alternative and Substitute Substances**

All alternatives used as substitutes for hazardous substances must be free of hazardous properties. Some tools to identify hazardous properties of chemicals and to find safer alternatives are listed the factsheet about hazardous substances.

Dyestuffs, which are not synthesized based on restricted aromatic amines or cannot cleave such under reductive conditions, can be used as substitute. There are a variety of alternative dyestuffs for every dyestuff class available on the market.

<sup>15</sup> European Commission 1999. Opinion on Risk of cancer caused by textiles and leather goods coloured with azo-dyes. Online available: [http://ec.europa.eu/health/scientific\\_committees/environmental\\_risks/opinions/sctee/sct\\_out27\\_en.htm](http://ec.europa.eu/health/scientific_committees/environmental_risks/opinions/sctee/sct_out27_en.htm)

<sup>16</sup> European Commission 1999. Opinion on Risk of cancer caused by textiles and leather goods coloured with azo-dyes. Online available: [http://ec.europa.eu/health/scientific\\_committees/environmental\\_risks/opinions/sctee/sct\\_out27\\_en.htm](http://ec.europa.eu/health/scientific_committees/environmental_risks/opinions/sctee/sct_out27_en.htm)

<sup>17</sup> Forschungsinstitut für Arbeitsmedizin der Deutschen Gesetzlichen Unfallversicherung Institut der Ruhr-Universität Bochum . 2009. Azofarbstoffe und deren Hautgängigkeit beim Menschen. Online available: [http://www.ipa.ruhr-uni-bochum.de/pdf/09-02-27\\_BGFA-Report2\\_Azofarbstoffe.pdf](http://www.ipa.ruhr-uni-bochum.de/pdf/09-02-27_BGFA-Report2_Azofarbstoffe.pdf)

<sup>18</sup> UK Houses of Parliament. Parliamentary office of science and technology, undated. The Environmental, Health and Economic Impacts of Textile Azo Dyes. Online available: [http://2014.igem.org/wiki/images/2/29/Goodbye\\_Azo\\_Dye\\_POSTnote.pdf](http://2014.igem.org/wiki/images/2/29/Goodbye_Azo_Dye_POSTnote.pdf)

In order to minimize environmental and health effects and to use resources efficiently the use of best available technology (BAT<sup>19</sup>) in textiles industry is a standard requirement.

Please refer to the factsheet about hazardous substances for further information on alternatives. In addition the Chemsec Textile Guide offers access to a list of hazardous and safer dyes and should be taken into account when a chemical inventory is assessed<sup>20</sup>.

---

<sup>19</sup> European Commission: Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry July 2003

<sup>20</sup> <http://textileguide.chemsec.org/find/textiles-come-with-a-toxic-footprint/>