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Benzidine-based dyes

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The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.

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1 Introduction

Benzidine is an aromatic amine that has been used as an intermediate of azo dyes since the late 19th century. The Colour Index lists 171 benzidine dyes, and the European Inventory of Existing Chemical Substances lists 58 benzidine dyes. It is estimated that about 45-50 benzidine dyes are currently in commerce worldwide./1/.

The azo dyes are organic compounds that contain the colour-giving azo group (-N=N-) and can be broken down into arylamines. This can be done both chemically by means of reductive cleavage, and by the body's own enzyme system. Some azo dyes can also be broken down to arylamines during storage due to light and high temperature. /2/.

Dyestuffs were among the first products of the developing chemical industry, and aromatic amines were the first synthetic chemicals found to cause cancer in humans. Originally, only benzidine was considered to be carcinogenic. However, studies found that dyes derived from benzidine release free benzidine via metabolic routes. The dyes were predicted to be carcinogens based on these findings./3/. In light of this, voluntary cessation of manufacture in Europe and US was effectuated in the early 1970s /1/.

IARC classifies benzidine as a Group 1 carcinogen and benzidine-based dyes as Group 2A carcinogens.

The chronology of key developments with respect to benzidine and the benzidine-based dyes is summarised by OCDE /1/ and is referred in table 1. The table is updated (1993/1994-) based on information given in a report recently published by the Swedish National Chemicals Inspectorate /2/.

1906	Reported correlation between benzidine exposure and bladder cancer in humans.
1940	Suspicion that benzidine induces bladder cancer in workers.
1954	Elevated bladder cancer incidence in workers exposed to benzidine.
1957	Voluntary code of practice for carcinogenic amines set up by Association of British Chemical Manufacturers
1967	Carcinogenic Substances Regulations (UK) prohibit use of benzidine.
Early 1970s	Germany prohibits occupational handling of 20 arylamines, covered by bans on imported goods. Among these are 2-Napthylamine, 4-Aminobiphenyl and Benzidine. (This
1971	Bayer ceases to manufacture benzidine.
1971-72	Major European dye manufacturers cease manufacturing of benzidine dyes.
1972	IARC Monographs Vol. 1 concludes benzidine is bladder carcinogen in man.

1975	Metabolism of benzidine dyes to benzidine in monkeys.
1978	NCI 90-day sub-chronic studies on three benzidine dyes.
1980	OSHA/NIOSH health hazard alert on benzidine and some benzidine congener dyes.
1987	IARC Monographs Suppl.7 classifies benzidine dyes in Group 2A.
1993	German TRGS 614, September 1993, recommends that benzidine and certain other carcinogenic azo dyes are not used.
1993	India bans the use of 42 benzidine dyes in textiles and leather.
1994	German Consumer Goods Ordinance ban certain dyes (including benzidine dyes) in certain consumer goods.
1996	Netherlands ban certain dyes that can form certain amines (including benzidine-based dyes). Test methods are established in the regulation.
1996	France ban azo dyes in textiles, leather goods and similar consumer goods.
1996	Germany also include pigments containing azo dyes that can degrade to carcinogenic arylamines. This part of the ban will enter force during 1998. Forbidden arylamines must not be present in higher concentrations than 30 mg/kg. Test method is specified.
1996	The Indian Government notified a proposed ban on the manufacture, sale and use of 74 azo dyes found to be carcinogenic.
1996	The Swedish National Board of Occupational Safety and Health banned occupational handling of three arylamines, while handling of seven other arylamines require

Table 1 *Chronology of concern about benzidine and benzidine dyes.*

This report has been prepared by COWI Consulting Engineers and Planners on behalf of the Danish Environmental Protection Agency as part of the project "Identification of substances of concern for which global initiatives are necessary".

2 General Description

2.1 Global Production

According to /1/, the following countries are presently manufacturers of benzidine dyes:

- Argentina
- Brazil
- China
- India
- Republic of Korea
- Mexico
- Taiwan

Additionally, manufacturers in Romania and Greece might exist according to unconfirmed reports /1/.

No information has been found reporting the yearly production of benzidine-based dyestuffs.

2.2 Uses

Benzidine-based dyes are largely classified as direct dyes, since they may be applied directly to fabrics or other substrates without pre-treatment or without subsequent processes that firmly attach the dye to the substrate /4/. Table 2 lists the benzidine-based azo dyestuffs which are still available on the world market /2/. The list is gathered from a list compiled by the German Chemical Industry's Trade Organisation.

The uses of the specific benzidine-based dyes given in Table 2, are referred from a review conducted by NIOSH in 1980 /4/ and it should be stressed that some of the listed uses may no longer be relevant or new uses may have been introduced.

C.I.-No.	Name/synonym	Uses
30 334	Acid Black 232	-
30 336	Acid Black 94	-
22 195	Acid Orange 45	Dyeing of cotton, silk, nylon and leather; heavy metal salts used as pigments.
22 245	Acid Red 85	Dyeing of cotton, wool, silk, nylon and viscose; Viqoureux printing.

37 225	Azoic Diazo Component 112	-
22 580	Direct Black 29	-
30 235	Direct Black 38	Dyeing of leather, plastics, cotton, wool and silk; aqueous inks, biological stain; wood flour used as a resin filler, wood stain; typewriter ribbons.
30 245	Direct Black 4	Dyeing of cotton, wool, silk, nylon, leather and paper.
22 590	Direct Blue 2	Dyeing of cotton, leather and paper.
22 610	Direct Blue 6	Dyeing of leather, cotton, silk, paper; aqueous writing inks, biological stains.
30 045	Direct Brown 1	Dyeing of leather, paper, silk, nylon, wool, and cotton.
30 110	Direct Brown 1:2	-
22 311	Direct Brown 2	Dyeing of leather, paper, silk, nylon, wool, and cotton; heavy metal salts used as pigments.
30 140	Direct Brown 6	Dyeing of leather, paper, silk, wool, and cotton.
36 030	Direct Brown 25	-
31 725	Direct Brown 27	-
35 660	Direct Brown 31	Dyeing of leather and paper; heavy metal salts used as pigments; printing on cellulose (concentrated dye only).
35 520	Direct Brown 33	-
31 710	Direct Brown 51	-
22 345	Direct Brown 59	Dyeing of cotton, wool, and silk; leather; occasional use on chrome and vegetable tannages.
36 300	Direct Brown 74	Dyeing on cotton, wool, silk, leather, chrome tannages (occasional).
30 050	Direct Brown 79	-
30 145	Direct Brown 95	Dyeing of cotton, wool, silk, paper, plastics and leather; heavy metal salts used as pigments.
31 740	Direct Brown 101	-
30 120	Direct Brown 154	Dyeing of cotton, wool, silk, leather and paper; direct printing on cellulose weave and silk fabrics.

21 060	Direct Dye	-
30 280	Direct Green 1	Dyeing of cotton, wool, silk, nylon, leather and paper; aqueous inks; direct printing on cellulose, silk and nylon fabrics.
30 295	Direct Green 6	Dyeing of cotton, wool, silk, and nylon; aqueous inks, pigments, leather, paper, and soap; direct printing on nylon.
30 315	Direct Green 8	Dyeing of cotton, wool, silk, nylon, leather and paper.
-	Direct Green 8:1	_
22 370	Direct Orange 1	Dyeing of cotton, wool, silk, nylon, paper; and leather; direct printing on cellulose and nylon.
22 130	Direct Orange 8	Dyeing of cotton, wool, silk, nylon, and paper.
22 310	Direct Red 1	Dyeing of cotton, wool, silk, nylon, paper, and leather.
22 145	Direct Red 10	Dyeing of cotton, wool, silk, and leather; biological stain.
22 155	Direct Red 13	Dyeing of cotton, wool, nylon, paper and leather (chrome tennage); printing of cellulose.
22 150	Direct Red 17	-
22 120	Direct Red 28	Dyeing of cotton, wool, silk, and paper; biological stain and indicator; (first synthetic direct cellulose dye).
22 240	Direct Red 37	Dyeing of cotton, wool, silk, leather, and paper; direct and discharge printing of cellulose and nylon.
22 500	Direct Red 44	-
22 570	Direct Violet 1	Dyeing of cotton, wool, silk, leather, and paper; biological stain.
22 555	Direct Violet 4	-
22 550	Direct Violet 12	-
22 480	Direct Violet 22	Dyeing of cotton, wool, silk, nylon, leather.
22 250	Direct Yellow 1	-
22 010	Direct Yellow 24	-
22 310	Mordant Red 57	-

***Table 2** Azo dyes based on benzidine, available on the world market.*

2.3 International and National Trade

No data has been found showing the international trade of benzidine-based dyes.

Benzidine-based dyes may be imported with textile and clothing imported from countries still using those kind of dyes. No data has been found documenting the quantity of benzidine-based dyes per garment/textile[1], the share of textiles dyed with benzidine-based dyes or the trade of those textiles. Therefore, no estimates can be given on the quantity of benzidine-based dyestuffs imported with dyed textile and clothing. However, statistics from the European Apparel and Textile Trade Organization, EURATEX show, that the import to the EU of clothing is nearly five times greater than export from EU (based on data from 1994 and 1995) /2/. As an example, the total quantity of textiles sold on the Swedish market, only perhaps 10-20% are Swedish-made[2]. When it comes to clothing, the figure is even lower, 5-10%. Primarily, the textile goods are dominated by import from EU/EFTA countries, while the imported clothing for the most part comes from countries outside EU/EFTA. A large part of the Swedish import came from China (more than 32,000 tonnes in 1994). Also regarding clothing, the main portion came from China, together, the China and Hong Kong share comprised 44% of the Swedish imported clothing. /2/. Even though some differences may exist due to traditional and cultural factors, the situation in the other EU countries, Portugal excepted, is believed to be similar to the Swedish. Thus, the numbers indicate the relevance of identifying to what extent primarily the Asian countries use benzidine-based dyes. This has further relevance knowing that the majority of dyes used in the textile industry in China, Hong Kong and India are azo dyes /2/.

Based on data from EURATEX /5/, the 1996 top-10 suppliers of textile and clothing to the fifteen EU member states were:

Textile suppliers		**Clothing suppliers**	
Country	Approx. Mill. ECU	Country	Approx. Mill. ECU
India	1,400	China	3,300
Switzerland	1,100	Turkey	3,100
Turkey	1,050	Hong Kong	2,400
China	1,000	Tunisia	1,700
USA	980	Morocco	1,600
Pakistan	810	Poland	1,550

[1] A broad range is given in /2/: The quantity of dye naturally differs between textiles with strong colours and those in paler hues. The concentrations lie between 0.05 and 3%, depending on dye type, fibre material and the structure of the textile.
[2] Sweden imported 252,000 tonnes of textile goods in 1994 coming from more than 100 different countries.

Indonesia	450	India	1,500
Ex-Czechoslov.	420	Ex-Yugoslavia	1,000
Iran	380	Romania	980
South Korea	350	Bangladesh	950

Relevant associations in India, China, Turkey, Hong Kong, Bangladesh, Korea and Thailand have been contacted and asked about manufacture and export of benzidine, benzidine salts, benzidine-based dyestuffs and export of textiles and/or clothes dyed with benzidine-based dyes. Additionally, the same questions have been forwarded to the Far East Importers Association (VIVO) in the Netherlands.

No response has been received from the associations so far. However, it was assumed to be difficult to gather such information. Other consultants /2/ recent attempts to gather information indicated that azo dyes are used by many producers, and that use is very difficult to check in countries such as China, India and Thailand. The latter is said to be true even when national control has been introduced in the producing country. As an example, the ban on using certain benzidine-based dyes in India is mentioned. Even though the ban is effectuated, compliance, and monitoring of the same is low. /2/.

Asian manufacture and trade

A qualitative and descriptive study of the manufacture of textile in Hong Kong and China has recently been published by the Swedish Chemical Inspectorate /6/. Below relevant information is referred:

China produced 160,000 tonnes of dye in 1995 (including benzidine-based dyes). The majority is of low quality. When using dyes for textiles or cloths to be exported, the Chinese manufacturers are using dyes of higher quality than when manufacturing for the local market. Harmful chemicals are primarily used by the national textile manufacturers, which have more difficulties buying raw materials from abroad.

The majority of the dye works in Hong Kong buy their dyes from Asian dye manufacturers, primarily from China, Taiwan, India, Thailand and Southern Korea. The main reason is the price differential between Western and Asian dyes, where the latter is approximately half-price. Because of the higher quality of Chinese export goods, the dye works in Hong Kong prefer to buy Chinese dyes through agents in Hong Kong rather than directly from the manufacturers in China.

Samples from textile manufactures in Hong Kong and China, tested for content of aryl amines which are banned in Germany and the Netherlands, show a decreasing number of samples with banned amines above 30 ppm. Benzidine is a frequently detected amine. The proportion of samples with an amine content exceeding 30 ppm is of same magnitude whether the samples come from a Chinese or a Hong Kong manufacturer. 5-30% of the samples tested in 1995 contained more than 30 ppm amines (for leather the percent was approximately 30%). However, the proportion may be biased,

as manufacturers with high quality products have their textiles tested more often than others (the percent might not reflect the overall percent of textile with amines above 30 ppm, because the manufacturers sending samples for testing might not be representative, as it is primary manufacturers with high quality products who have their textiles tested).

The cost of the dye is minor compared to the total production cost of a garment and it might not seem worth it for the exporting manufacturer to take the risk of using dyes, which can be broken down into the banned aryl amines. However, for the dye works, the cost of the dyes amount to approximately 30% of the total production cost and buying cheap dyes will therefore be tempting. If local dyes can be bought at half-price, it might be worth taking the risk of later failing an azo-colour test, even if the client demands compensation. In addition it can be difficult to document whether the banned amine originated from the used sewing thread, the yarn or the possible print.

Besides exporting dyes, China also is a giant exporter of dyed textile. 17% of the clothes sold in US is imported from China. In Europe the figure is 14% and in Japan 52%. Approximately 70% of the clothes sewed in Bangladesh comes from China (the remaining part comes from Thailand and Southern Korea). This means that figures showing the import of clothes, not always indicate the origins of the textile or the dyes used.

3 Environmental Exposure and Effects

3.1 Sources

From an environmental point of view, the major route for possible environmental impact of colorants is through the waste water and solid waste from dye-houses.

Regarding textiles coloured with dyes which can degrade to carcinogenic aryl-amines, for instance benzidine, it is primarily the content of these amines that is of environmental interest[1]. The content of benzidine in the benzidine-based dyes vary between the different dyes and even within dyes with the same colour. For instance older analyses show great variations of benzidine content in the colour Direct Black 38: "The benzidine content of domestically produced Direct Black 38 has been found to range from 2 to 20 mg/kg; benzidine content of imported samples ranged from 2 to 1,254 mg/kg. Another product was found to contain < 0.1 mg/kg benzidine, 150 mg/kg 4-aminobiphenyl, and 9,200 mg/kg 2,4-diaminoazobenzene. The composition of commercial Direct Black 38 varies in order to meet individual shade and intensity requirements.", /7/. No updated data has been found giving an average value of benzidine content in the benzidine-based dyes. In /8/ the content of benzidine in commercial benzidine-based dyes is mentioned as "containing small amounts of benzidine".

The following paragraphs will focus on which influence benzidine, released from the benzidine-based dyes, will cause on the environment.

Waste waters and sludge and solid waste containing benzidine-based dyes appear to be the major release routes of benzidine to the environment. Relatively high benzidine levels have been detected in soils and water near industrial sources as a result of the improper disposal of benzidine solid wastes. Because benzidine will absorb to soil particles, it may persist for considerable periods around such disposal sites. /9/. In contrast analyses of wash water after laundering of textiles show only low concentrations (microgram/kg) of the substances that are leached out of the textile during the laundering process /2/, and can therefore be regarded as a less important source.

[1] Apart from potential hazards to the envoronment posed by the dyestuffs, coloration of waste water due to discharge of these substances is an environmental problem of its own. Even low concentrations of colorants discharged into receiving water give "shadow effects" in the aquatic environment which cause reduced photo synthesis. /11/.

3.2 Emissions to the Environment

The present-day knowledge of the environmental properties of dyes is limited. In general, however, most dyes and pigments can be judged to have poor biodegradability and to degrade slowly. However, the majority of azo dyes are water-soluble and are therefore considered to have high bioavailability. /2/.

Air

In the atmosphere, benzidine primarily exists as an aerosol, subject to dispersion, gravitational setting, and washout by rain /9/. Benzidine's half-life period in air is roughly estimated at 1 day /10/.

Due to its function, most of the dyestuff is not photochemically degradable /2/.

Water

In water, benzidine does not significantly volatilize or hydrolyze, but it may slowly oxidise. It is uncertain whether it photodegrades in solution. Based on calculation of benzidine's carbon/water partition coefficient (K_{oc}), benzidine is assessed to be very highly mobile in saturated soil-water systems. However, benzidine is a weak base in solution and exists in both neutral and cationic forms and experiments have shown an adsorption magnitude greater than that predicted by K_{oc} values because of the contribution of cationic benzidine to the total amount of benzidine adsorbed. /9/. Benzidine's half-life period in water is roughly estimated at 100 days /10/.

Soil

Benzidine may be strongly adsorbed from solution by soils, sediments, and clays, depending on the acidity or alkalinity of the soil-water system. It may be oxidized at clay surfaces and held in a reversible form while it is strongly bound by soil organic matter. Benzidine does not seem to be readily biodegradable in soil, but it does degrade at low concentrations in acclimated sludge. /9/.

3.3 Environmental Effects

Benzidine may be bio-concentrated by aquatic organisms, but it appears that the extent of concentration is not significant and that it will not be transferred through the food chain to higher levels /9/.

The following values are referred in the literature and indicate the bioaccumulation potential of benzidine: /10/

- Oedogenium (alga), BCF: 2,620
- Daphnia, BCF: 290
- Physa (snail), BCF: 650
- Gambusia (fish), BCF: 55
- Lepomis, 42 days, BCF: 38-44

The following concentrations are referred as being acute toxic: /10/

- Alga-test, EC_{50} (72H) 26 mg/l
- Alga-test, EC_{10} (72H) 4,5 mg/l

Evertebrater:

- Daphinia, EC_{50} (24H) 1,1 mg/l
- Gammarus, LC_{50} (96H) >20 mg/l

Fish:

- Leuciscus, LC_{50} (96H) 94 mg/l
- Pimephales, LC_{50} (96H) >20 mg/l
- Salmo gairdneri, LC_{50} (96H) 7,4 mg/l

Additionally, the following concentrations are referred as being subacute-chronic toxic: /10/

- Daphnia, LOEC (21 days) 0,1 mg/l
- Daphinia, NOEC (21 days) 0,032 mg/l

4 Human Exposure and Health Effects

The use of dyestuffs may cause a number of adverse effects to the human health. The health effects may be exerted directly at the site of application (affecting the workers) and later in the life cycle (affecting the consumers) /11/. The main concern related to benzidine-based dyes is the risk of causing cancer, due to the release of free benzidine. A recent published review report /9/ shows that urinary bladder cancer is the most common form of cancer caused by exposure to benzidine. The stomach, kidneys, brain, mouth, esophagus, liver, and gallbladder might also be targets /9/. The risk is of primary concern for occupational handling of benzidine-based dyes. Numerous epidemiological studies have clearly established that occupational exposure to benzidine induces bladder cancer /9/. Further, oral exposure to benzidine-based dyes has been reported to increase the risk of bladder cancer in Japanese kimono painters /12/. For the users of clothes dyed with benzidine-based dyes, the skin-contact will be the potential exposure route. In general, only low concentrations are analysed in textile and clothes. Concentrations which have been shown to cause effects in animals are higher than these analysed concentrations. /2/. However, higher concentrations have been found leading researchers to conclude that the risk for the users of getting cancer from exposure to azo-dyed textiles is small, but existing /13/.

The following paragraphs will focus on benzidine, as the main cause for health concern from using benzidine-based dyestuffs.

Benzidine

The following information on benzidine is referred from EPA[1] /14/.

- No information is available on the acute (short-term) effects of benzidine in humans by inhalation exposure. Benzidine is considered to be very acutely toxic to humans by ingestion, with an estimated oral lethal dose of between 50 and 500 mg/kg in a 70-kg person.

- Chronic (long-term) exposure to benzidine in humans may result in bladder injury. Animal studies have reported effects on the blood, liver, kidney, and central nervous system from chronic, oral exposure to benzidine.

[1] Please Note: The main sources of information for this fact sheet are EPA's Integrated Risk Information System (IRIS), which contains information on oral chronic toxicity of benzidine and the RfD, and the carcinogenic effects of benzidine including the unit cancer risk for inhalation exposure, and the Agency for Toxic Substances and Disease Registry's (ATSDR's)Toxicological Profile for Benzidine. Other secondary sources include the Hazardous Substances Data Bank (HSDB), a database of summaries of peer-reviewed literature, and the Registry of Toxic Effects of Chemical Substances (RTECS), a database of toxic effects that are not peer reviewed.

- The Reference Dose (RfD) for benzidine is 0.003 mg/kg/d[1]. The U.S. Environmental Protection Agency (EPA) estimates that consumption of this dose or less, over a lifetime, would not likely result in the occurrence of chronic, non-cancer effects[2].

- EPA has determined that the data are inadequate to establish a Reference Concentration (RfC) for benzidine.

- No information is available on the reproductive or developmental effects of benzidine in humans. Benzidine has been reported to be teratogenic (cause birth defects) in chickens when injected into eggs.

- Epidemiological studies have shown occupational exposure to benzidine to result in an increased risk of bladder cancer. Animal studies have reported various tumour types at multiple sites from benzidine exposure via oral, inhalation, and injection exposure. EPA has classified benzidine as a Group A, human carcinogen of high carcinogenic hazard, with a 1/ED10 value of 2,200 per (mg/kg)/d[3] and an inhalation unit risk estimate of 6.7×10^{-2} $(\mu g/m3)^{-1}$.

Benzidine-based dyes

In general, low concentrations (few milligrams/kg of textile) of hazardous substances are found in textiles that are analysed. The analysed concentrations are lower than the concentrations that have given effects in animal tests. /2/. In a Danish survey, benzidine or isomers hereof were found at a level of 300 mg/kg. Based on this, the authors conclude, that the risk of getting cancer from exposure to azo-dyed textiles is small, but existing. /13/.

Regarding Carcinogenicity of azo-dyestuffs, there are two aspects of concern:

1. The carcinogenicity of the colorant as is.
2. The carcinogenicity of the aromatic amines which may occur as degradation products upon reductive cleavage of the azo group.

The formation of carcinogenic amines is regarded to be the major causative factor of the carcinogenity of a given dye. Benzidine-based dyes are typical examples, thus they are metabolized to the known human carcinogen benzidine. /13/.

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[1] Milligrams per kilogram per day is one way to measure the amount of the contaminant that is consumed in food.

[2] The RfD is not a direct estimator of risk but rather a reference point to gauge the potential effects. Exceedance of the RfD does not imply that an adverse health effect would necessarily occur. As the amount and frequency of exposures exceeding the RfD increase, the probability of adverse health effects also increases.

[3] The 1/ED10 value is a measure of the carcinogenic potency of a chemical. The value reported here has been proposed in the hazard ranking of hazardous air pollutants in EPA's proposed rulemaking (Section 112(g) of the Clean Air Act, April 1994).

Far from all azo dyestuffs have been tested sufficiently to determine whether they should be regarded as carcinogens or not. However, it should be stressed that all benzidine-based dyes are classified in group 2A by IARC[1].

Of the benzidine-based dyestuffs which are listed in table 2 as dyestuffs still present on the world market, the following are classified specifically by IARC as agents which are probably carcinogenic to humans (Group 2A): /8/.

CI-No.	CAS-no.	Name	Chemical name
30 235	1937-37-7	Direct Black 38	2,7-Naphthalenedisulfonic acid, 4-amino-3-[[4'-[(2, 4-diaminophenyl)azo][1,1'-biphenyl]-4-yl]azo]-5- hydroxy-6-(phenylazo)-, disodium salt
22 610	2602-46-2	Direct Blue 6	2,7-Naphthalenedisulfonic acid, 3,3'-[[1,1'-biphenyl] -4,4'-diylbis(azo)]bis[5-amino-4-hydroxy-. tetrasodium salt
30 145	16071-86-6	Direct Brown 95	Cuprate(2-), [5-[[4'-[[2,6-dihydroxy-3-[(2-hydroxy-5-sulfophenyl)azo]phenyl]azo] [1.1'-biphenyl]-4yl]azo]-2-hydroxybenzoato(4-)]-, disodiumsalt

Table 3
Benzidine-based dyestuffs specific mentioned by IARC as probably carcinogenic to humans.

IARC states that the epidemiological data were inadequate to evaluate the carcinogenicity of these dyes to humans. However, indications are given that exposure is strongly associated with the occurrence of bladder cancer. /8/.

Further, IARC states that sufficient evidence is given that the three mentioned dyes (technical grades) are carcinogenic to animals /8/.

Another concern given is the risk of teratogenic effects. Although some azo dyes have teratogenic effects, such effects have not generally been observed across the universe of azo dyes. Out of the benzidine-based dyestuffs still on the world market, the following benzidine-based dyes are referred to as teratogenic in animals in an unpublished Danish report reviewing health and environmental effects of azo-colorants /13/:

CI-No.	CAS-no.	Name	Chemical name
22 610	2602-46-2	Direct Blue 6	2,7-Naphthalenedisulfonic acid, 3,3'-[[1,1'-biphenyl] -4,4'-diylbis(azo)]bis[5-amino-4-hydroxy-. tetrasodium salt
22 120	573-58-0	Direct Red 28	1-Naphthalenesulfonic acid, 3,3'-[[1,1'-biphenyl]-4,4'-diylbis(azo)]bis[4-amino-, disodium salt

Table 4 *Benzidine-based dyestuffs found teratogenic in animals.*

[1] IARC category group 2A: The agent is probably carcinogenic to humans. The exposure circumstances entails exposures that are probably carcinogenic to humans.

It should be stressed, that the Danish report mainly focuses on allergy and carcinogenicity, and it only refers one single source with regard to teratogenicity.

Regarding allergy, none of the reviewed reports brings data on allergy caused by benzidine-based dyestuffs. In /13/ it is noted, that most allergy cases are due to the use of disperse dyes on synthetic fabrics which do not provide sufficient dye fastness. According to /2/, none of the benzidine-based dyes are classified as disperse dyes. However, other dyes such as reactive and acid dyes are also judged to be skin-sensitizing /2/. None of the acid benzidine-based dyestuffs listed as still available on the world market, are among those mentioned as sensitizing /2/.

5 International Regulations

5.1 Legislation and Other Regulations

In table 5, relevant legislation/regulation in different countries are listed.

Country	Legislation/Regulation
USA	In 1973, Occupational Health Association (OSHA) regulations banned United States production of benzidine. In addition, benzidine is no longer imported into the United States; however, benzidine-based dyes may be imported /15/. EPA has promulgated a rule that requires persons to notify EPA at least 90 days before commencing the manufacture, import or processing of certain benzidine-based chemicals for any significant new use. The rule became effective on November 20, 1996. The benzidine-based chemical substances covered by the rule are listed in appendix 1. EPA determined that in 1995 there was no ongoing manufacture, import or processing of the covered benzidine-based chemical substances, except for use in small amounts as a reagent to test for hydrogen peroxide in milk; a reagent to test for hydrogen sulphate, hydrogen cyanide, and nicotine; a strain in microscopy; a reagent for detecting blood; an analytical standard; and also for C.I. Direct Red 28 as an indicator dye. Significant new use will therefore be assessed as any other uses./16/. In the United States, a list is biennially published covering all substances to which a significant number of persons resident in US are exposed, and which are known to be human carcinogens or may reasonably be anticipated to be human carcinogens. Dyes metabolized to benzidine are listed as "Known to be a Human Carcinogen".
Canada	Benzidine is included on the list of Priority Substances to be assessed under the Canadian Environmental Protection Act (CEPA) /17/.
Japan	Production of benzidine and its salts is prohibited in Japan /18/.
Former USSR	Also in the former Soviet Union, production of benzidine is stopped /18/.
EEC	Regulations are given by the Council Directive 76/769/EEC with amendment. The directive's purpose is to approximate the laws, regulations and administrative provisions of the member states relating to restrictions on the marketing and use of certain dangerous substances and preparations. In the Directive, it is stated that marketing and use of benzidine and its salts should be limited. Further, suggestions have been proposed within the 18th modification of the directive, that benzidine based azo dyes should not be legal-contents in substances and preparations sold to private users.

	Further, regulations are given by Council Directive 793/93/EEC dealing with evaluation and control of the risks of existing substances.
Great Britain	The use (for research purposes) of prohibited substances, such as benzidine and its salts, is only possible if special permission obtained for work in completely closed systems or if the benzidine, in the form of a hydrochloride, is always kept moist with at least one part water to two parts benzidine hydrochloride /19/.
Germany	A ban on azo dyestuffs was introduced in Germany in 1996, forbidding import or sale of textile coloured with azo dyes that can split into one or more of twenty specified carcinogenic or suspected carcinogenic arylamines, including benzidine. The ban is applicable to all products which are in contact with the skin for prolonged periods, like textile garments (even if it is outerwear) and bath towels /20/. A test method associated with the ban puts limit for arylamine at 30 ppm. Pigments will be covered by the ban in 1998 /2/. The import of textile garments containing the banned pigments is permitted up to 31 March 1998 /20/. The ban will be extended to cover working clothes, protective clothing, uniforms and commodity goods made from recycled fibres by 31 December 1999 /23/. The ban has had an effect on the textile manufacturers in exporting countries. Thus, in Hong Kong where Germany is the second largest export market, action has been taken to establish voluntary registration schemes for harmless dyestuffs. The purpose of the registration schemes are to provide the manufacturers and the exporters with knowledge on which dyestuffs do not conflict with the German ban. /21/. Also regarding working environment, Germany has regulations affecting the use of materials containing benzidine and its salts. Important diphenyl bases are included among the regulated dangerous working substances. Benzidine and its salts are regarded as carcinogenic hazards in concentrations above 0,01% by weight in the working material. When working with these substances, all the necessary measures relating to safety, industrial medicine, and occupational hygiene should be taken to protect employees from the effects of these substances and to keep their health under constant medical check. Equipment in which benzidine or its salts may be present, must be operated in such a way that breakdowns are prevented and the harmful effects are kept to a minimum. In many other countries, i.e. Belgium and Japan, there are similar regulations for handling of benzidine and its derivates. /19/.
Netherlands	Per August 1996, a ban has been placed on marketing and use of a number of specified carcinogenic aromatic amines (the same list of twenty amines as in Germany). A list of 117 prohibited azo dyes is issued. Clothes coloured with pigments, protective textiles like work gloves, commodity goods made from recycled fibres and second hand clothing are expected to be banned from 31 December 1999 /20/.
Sweden	In Sweden, benzidine and it salts are, among a number of other substances, subject to regulation due to an ordinance focusing on reduce sale and use of hazard chemical substances and products to specific purposes /12/. It is stated that sale of chemical products containing 0.1% or more of benzidine or its salts are prohibited. Further, occupational handling of benzidine and

	its salts are banned /12/. Also limits are given for the content of certain benzidine-based dyes in products /12/.
Denmark	In Denmark, benzidine and it salts are, among a number of other substances, subject to regulation due to an ordinance focusing on reduced sale and use of hazardous chemical substances and products to specific purposes /22/. It is stated that sale of chemical substances or products containing 0.1% or more of benzidine or its salts are prohibited. However, the prohibition does not cover waste containing these substances, as sale of waste is covered by other restrictions.

***Table 5** Legislation/regulation of benzidine and benzidine-based dyes.*

6 Substitution/Alternatives

Dye type

Textile material can be dyed with a variety of different dyeing methods and techniques. Which methods and chemicals can be used depends largely on the fibre or textile material to be dyed. In table 6 different dye type are listed regarding effectiveness for different textile types. /2/.

Dye type	Cotton and Viscose	Silk	Wool	Polyester	Polyamid	Acrylic
Direct	x	x	x			
Reactive	x	x	x		x	
Sulphur	x	x				
Vat	x					
Azoic	x			x	x	
Disperse				x	x	x
Acid		x	x		x	
Mordant		x	x		x	
Basic						x

***Table 6** Applicable dyes for different textile types.*

Sulphonated aromatic amines

As an alternative to using the aromatic amines in manufacture of colorants for some textiles (cotton, viscose, silk and wool), the sulphonated aromatic amines could be used instead. In /13/ a comparison of genotoxicity and carcinogenicity on sulphonated aromatic amines and their unsulphonated analogues are referred. The comparison shows that the sulphonated aromatic amines generally have no or very low genotoxic effects.

Dyes derived from plants

Dyes derived from plants (C.I.-No. 75 000 - 75 999) are reported to be safe from an environmental perspective /20/.

Mineral dyes

Among the dyes reported to be safe from an environmental perspective, some mineral dyes could be found, thus colours with the following C.I.-No.: /20/

- 75 000 - 75 019 (Al)
- 75 220 - 75 250 (Ca)
- 75 265 - 75 268
- 75 485 - 75 543 (Fe)
- 75 711 - 75 718 (Mg)
- 75 726 - 75 755 (Mn)

Specific alternatives

In table 7, specific alternatives for some benzidine-based dyes are given. The alternatives are recommended in a report from 1996 /20/, where environmental issues relevant for manufacturers and exporters of textile are discussed. The authors stress that the alternatives are considered safer, but that no guarantee can be given.

Benzidine-based dyes		**Alternative dyes**	
C.I.-No.	**Name/synonym**	**C.I.-No.**	**Name/synonym**
30 336	Acid Black 94	26 370	Acid Black 24
22 195	Acid Orange 45	14 690	Acid Orange 19
22 580	Direct Black 29	27 720	Direct Black 51
22 311	Direct Brown 2	29 166	Direct Brown 112
22 130	Direct Orange 8	29 156	Direct Orange 19
22 145	Direct Red 10	25 275	Direct Red 120
22 570	Direct Violet 1	29 120	Direct Violet 66

Table 7 *Recommended alternatives to some benzidine-based azo dyes.*

7 Conclusion

A number of countries have national regulations focusing on benzidine-based dyes, either as bans for marketing and use of the dyes or restrictions on the content in leather, textile, clothing or similar consumer goods market in the countries (i.e. Germany, Netherlands, France, and India). Within the EEC, it is proposed that private use of benzidine-based dyes should be banned (18th amendment of 76/769/EEC).

Studies show strong evidence that benzidine-based dyes are carcinogenic, and in 1987, IARC grouped benzidine-based dyes in Group 2A.

Benzidine-based dyes are able to cleavage to benzidine. Older studies (reported in1975) found that dyes derived from benzidine, release free benzidine via metabolic routes. The dyes were predicted to be carcinogens based on these findings. Regarding benzidine, the most common form of cancer caused by exposure to benzidine is urinary bladder cancer. However, the stomach, kidneys, brain, mouth, esophagus, liver, and gallbladder might also be targets /9/.

The risk of getting cancer is primarily related to occupational handling of benzidine and benzidine-based dyes. However, exposure due to skin contact with shoes and clothes dyed with benzidine-based dyestuff, might reach critical levels. Danish tests have shown concentrations in textile where a cancer risk is assessed as small, but existing /13/.

Keeping track on the trade and the spread of benzidine-based dyes is very difficult. Within the Asian countries, which are assessed to be the major manufacturers of textile and clothing dyed with benzidine-based dyes, an intensive trade with both dyes and dyed textile takes place. For instance, the dyes might be bought in China, the textile dyed in Hong Kong, the textile sewn in Poland and at last sold in Sweden. In such cases, the origin of the dye might be very difficult to track. Tests to determine the content of benzidine-based dyes in textile (azo-tests) are carried out, as random check. However, manufacturers might be tempted to use benzidine-based dyes since the benzidine-based dyes are cheaper (approximately half-price). For the dye works, this price difference might weigh out the risk of failing an azo-test, even if the client demands compensation. All together this leads to a conclusion that benzidine-based dyes might be spread and found globally.

It is however possible to find alternatives to the benzidine-based dyes. For a number of specific benzidine-based dyes, specific alternatives exists. As more general recommendations, dyes derived from plants might be used as alternatives and so can sulphonated aromatic amine dyes.

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Appendix 1

Benzidine-Based Chemical Substances covered by the US notification rule /3/, /16/.

CAS number	C.I. Name	C.I. Number	Chemical Name
92-87-5	Benzidine	N/A	[1,1'-Biphenyl]-4,4'-diamine
531-85-1	Benzidine • 2HCL	N/A	[1,1'-Biphenyl]-4,4'-diamine,dihydrochloride
573-58-0	Direct Red 28	22120	1-Naphthalenesulfonic acid, 3,3'-[[1,1'-biphenyl]-4,4'-diylbis(azo)]bis[4-amino-, disodium salt
1937-37-7	Direct Black 38	30235	2,7-Naphthalenedisulfonic acid, 4-amino-3-[[4'-[(2, 4-diaminophenyl)azo] [1,1'-biphenyl]-4-yl]azo]-5- hydroxy-6-(phenylazo)-, disodium salt
2302-97-8	Direct Red 44	22500	1-Naphthalenesuifonic acid, 8,8'-[[1,1'-biphenyl]-4,4'-diyibis(azo)]bis[7-hydroxy-, disodium salt
2429-73-4	Direct Blue 2	22590	2,7-Naphthalenedisulfonic acid, 5-amino-3-[[4'-[(7-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo] [1,1'-biphenyl]-4-yl]azo]-4-hydroxy-, trisodium salt
2429-79-0	Direct Orange 8	22130	Benzoic acid. 5-{[4'-[(1-amino-4-sulfo-2- naphthalenyl)azo] [1,1'-biphenyl]-4yl]azol-2-hydroxy-, disodium salt
2429-81-4	Direct Brown 31	35660	Benzoic acid, 5-[[4'-[[2,6-diamino-3-[[8-hydroxy-3,6-disulfo-7-[(4-sulfo-1-naphthalenyl)azo] -2- naphthalenyllazol-5-methylphenyl]azo][1,1'-biphenyl]-4-yl]azo}-2-hydroxy-. tetrasodium salt
2429-82-5	Direct Brown 2	22311	Benzoic acid, 5-[[4'-[(7-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo] [1,1'-biphenyl]-4-yl]azo]-2- hydroxy-, disodium salt
2429-83-6	Direct Biack 4	30245	2,7-Naphthalenedisulfonic acid, 4-amino-3-[[4'-[(2,4-diamino-5-methylphenyl)azo] [1,1'- biphenyl]-4-yl]azo]-5-hydroxy-6-(phenylazo)-, disodium salt
2429--84-7	Direct Red 1	22310	Benzoic acid, 5-[[4'-[(2-amino-8-hydroxy-6-sulfo- 1-naphthalenyl)azo] [1,1'-biphenyl]-4-yl)azo}-2-hydroxy-, disodium salt
2586-58-5	Direct Brown 1:2	30110	Benzoic acid, 5-[[4'-[[2,6-diamino-3-methyl-5-[(4- sulfophenyl)azo]phenyl]azo] [1,1'-biphenyl]-4-yl]azo]-2-hydroxy-, disodium salt
2602-46-2	Direct Blue 6	22610	2,7-Naphthalenedisulfonic acid, 3,3'-[[1,1'-biphenyl] -4,4'-diylbis(azo)]bis[5-amino-4-hydroxy-. tetrasodium salt
2893-80-3	Direct Brown 6	30140	Benzoic acid, 5-[[4'-[[2,4-dihydroxy-3-[(4-sulfophenyl)azolphenyl]azo] [1.1'-biphenyl)-4-yl]azo]-2-hydroxy-, disodium salt
3530-19-6	Direct Red 37	22240	1,3-Naphthalenedisulfonic acid, 8-[[4'-[(4-ethoxy phenyl)azo] [1,1'-biphenyl]-4-yl]azo]-7-hydroxy-, disodium salt
3567-65-5	Acid Red 85	22245	1,3-Naphthaienedisuifonic acid, 7-hydroxy-8-[[4'-[[4-[[(4-methylphenyl)sulfonyl]oxy]phenyl] azo}[1,1'-biphenyl]-4-yl]azo]-. disodium salt
3626-28-6	Direct Green 1	30280	2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3-[[4'-[(4-hydroxyphenyl)azo] [1,1'-biphenyl]-4-yl]-6-(phenylzao)-, disodium salt
38111-71-0	Direct Brown 1	30045	Benzoic acid, 5-[[4'-[[2,4-diamino-5-[(4-sulfophenyl)azo]pehnyl]azo][1,1'-biphenyl]-4-yl]azo] -2-hydroxy-, disodium salt
4335-09-5	Direct Green 6	30295	2,7-Naphthalenedisuifonic acid, 4-amino-5-hydroxy-6-[[4'-[(4-hydroxyphenyl)azo] [1,1'-biphenyl]-4-yl]azo]-3-[(4-nitrophenyl)azo]-, disodium salt
6358-80-1	Acid Black 94	30336	2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3-[[4'-[[4-hydroxy-2-[(methylphenyl) amino]phenyl]azol] [1,1'-biphenyl]-4-yl]azo]-6-[(4-sulfophenyl)azo]-, trisodium salt

Benzidine-Based Chemical Substances covered by the US notification rule, continued.

CAS number	C.I. Name	C.I. Number	Chemical Name
6360-29-8	Direct Brown 27	31725	Benzoic acid, 5-[[4'-[[4-[(4-amino-7-sulfo-1-naphthalenyl)azo]-6-sulfo-1-naphthalenyl][1,1'-biphenyl]-4-yl]-2-hydroxy-, trisodium salt
6360-54-9	Direct Brown 154	30120	Benzoic acid, 5-[[4'-[[2,6-diamino-3-methyl-5-[(4-sulfophenyl)azo]phenyl]azo][1,1'-biphenyl]-4-yl]azo]-2-hydroxy-3-methyl-, disodium salt
8014-91-3	Direct Brown 74	36300	Benzoic acid, 3,3'-[(3,7-disulfo-1,5-naphthalenediyl)bis[azo(6-hydroxy-3,1-phenylene)azo[6(or7)-sulfo-4,1-naphthalenediyl]azo[1,1'-biphenyl]-4,4'-diylazo]]bis[6-hydroxy-, hexasodium salt
16071-86-6	Direct Brown 95	30145	Cuprate(2-), [5-[[4'-[[2,6-dihydroxy-3-[(2-hydroxy-5-sulfophenyl)azo]phenyl]azo][1,1'-biphenyl]-4yl]azo]-2-hydroxybenzoato(4-)]-, disodiumsalt

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Benzidinbaserede farvestoffer

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Petersen, Marchen Vinding

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Resumé:
Benzidin er en aromatisk amin, der anvendes som mellemprodukt ved fremstilling af azofarvestoffer. IARC klassificerer benzidinbaserede farvestoffer som gruppe 2Acarcinogener. Risikoen for kræft skyldes farvefrigivelse af fri benzidin. Den mest almindelige kræftform er kræft i urinblæren. Risikoen relateres især til erhvervsmæssig håndtering af benzidin og benzidinbaserede farvestoffer, som spredes med tekstil- og beklædningsprodukter fra asiatiske lande. En række lande har indført forbud mod markedsføring og anvendelse af visse azofarvestoffer eller begrænsninger af indholdet i farvede produkter. Der findes alternativer til benzidinbaserede farvestoffer.

Emneord:
benzidiner; farvestoffer; forbrug; stofvurdering; substitution; kræftfremkaldende stoffer; international lovgivning; forbud

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Abstract:
Benzidine is a aromatic amine used as an intermediate of azodyes. IARC classifies benzidine-based dyes in group 2A carcinogens. The cancer risk is due to release of free benzidine from the dyes. The most common form of cancer is urinary bladder cancer. The risk is primarily related to occupational handling of benzidine and benzidine-based dyes. Benzidine-based dyes are mainly spread with textile and clothing from Asia. A number of countries have bans for marketing and use of certain azodyes or restrictions on the content in coloured products. Alternatives to benzidine-based dyes do exist.

Terms:
benzidine-based dyes; substitution; human exposure; environmental exposure; international legislation; cancer risk; bans on marketing and use

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Nr. 451: Tributyltin
Nr. 452: Benzidinbaserede farvestoffer

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