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HARMFUL AZO DYES AND ITS IMPACT ON BANGLADESHI TEXTILE SECTORS

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ABSTRACT

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Azo dyes are synthetic dyes having an azo group (-N=N-) in the structure. Azo dyes are commonly used for dyeing textiles and leather. Some azo dyes may produce carcinogenic aromatic amines under certain conditions. In Europe, REACH (Registration, Evaluation, Authorisation and restriction of Chemicals) regulation (EC) No 1907/2006, Annex XVII restricts 22 carcinogenic aromatic amines in textiles and leather. Some other dyes used in the textile industry are classified as having adverse effects on humans. These dyes may be absorbed through the skin with prolonged skin contact. Bangladesh is the largest producer of textile and readymade clothing in the world. As all the buyers all over the world is very alert regarding forbidden azo dyes, all most the garment industry in Bangladesh are also doing the azo test of the garment before delivery to the buyers.

***Key words**: azo dyes, Bangladeshi textiles, garment*

INTRODUCTION

Azo dyes allow colours with outstanding fastness and wide huge spectrum. About 60% - 70% of the dyes used nowadays are Azo dyes. In the body, Azo compounds can be broken down by certain enzyme systems. Non-fixed, water-soluble Azo dyes can also come into contact with skin through perspiration fluid. However, these dyes may undergo in vivo reductive cleavage to aromatic amines and some of them are proven or suspected carcinogenic. The first amine that identified to be human carcinogenic is benzidine.

Azo dye & their amines

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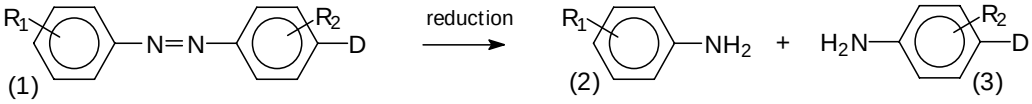
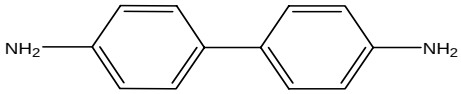
- However, these dyes may undergo in vivo reductive cleavage to aromatic amines and some of them are proven or suspected carcinogenic.

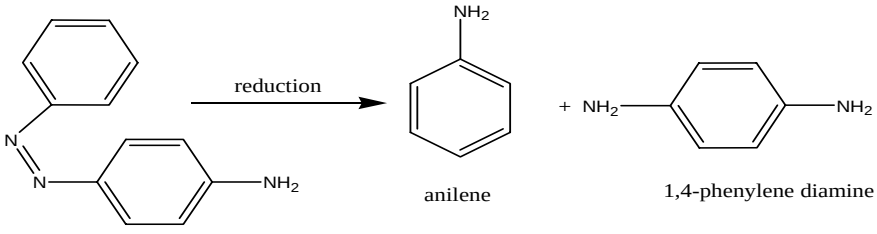


- The first amine that identified to be human –carcinogenic is benzidine.



Benzidine CAS 92-87-5

A new test method has been developed to detect the presence of 4-aminoazobenzene



In the body, Azo compounds can be broken down by certain enzyme systems. Non-fixed, water-soluble Azo dyes can also come into contact with skin through perspiration fluid.

The main routes of human exposure to Azo dyes are

Oral ingestion,
Mainly referring to the sucking of textiles by babies and young children,

Dermal absorption,
The route of primary concern for consumers wearing Azo compound-dyed products, as well as for workers in dye production and use plants,

Inhalation,
A route of concern for workers in the dye production and use industries.

The use of Azo dyes that may cleave to one of the 22 potentially carcinogenic aromatic amines listed above is banned according to the 19th amendment of Directive 76/769/EEC on dangerous substances and preparation.

Toxic Hazard to Consumer:
Textiles dyed with certain Azo Dyes are supposed to be a health risk to the consumer because, after direct skin contact and migration into the body, carcinogenic amines could be cleaved from the Azo Dyes. The list of 22 /24 carcinogenic amines according to the EU directive is also part of the Oeko-Tex Standards.

Limit Values:
The listed aromatic amines must not exceed the limit of 20 ppm per single component. The limit according to the EU directive is 30 ppm.

List of the restricted aromatic amine for Azo dye:

Aromatic amines from Azo dyes

Table: List of 22 aromatic amines

Aromatic amine	**CAS- No.**
4-Aminoazobenzene	60-09-3
o-Anisidine	90-04-0
2-Naphthylamine	91-59-8
3,3'-Dichlorobenzidine	91 -94-1
4-Aminodiphenyl	92-67-1
Benzidine	92-87-5
o-Toluidine	95-53-4
4-Chloro-o-toluidine	95-69-2
4-Methyl-1,3-phenylenediamine	95-80-7
o-Am inoazotoluene	97-56-3
5-Nitro-o-toluidine	99-55-8
4,4'-Methylene-bis-(2-chloraniline)	1 01 -1 4-4
4,4'-Methylenedianiline	101-77-9
4,4'-Oxydianiline	1 01 -80-4
p-Chloraniline	1 06-47-8
3,3'-Dimethoxybenzidine	119-90-4
3,3'-Dimethylbenzidine	1 1 9-93-7
p-Cresidine	120-71-8
2,4,5-Trimethylaniline	1 37-1 7-7
4,4'-Thiodianiline	1 39-65-1
4-methoxy-m-phenylenediamine	61 5-05-4
4,4'-Methylenedi-o-toluidine	838-88-0

MATERIALS AND METHODS

Instrument used for forbidden azo dyes testing

1. Gas chromatography-mass spectrometry (GC-MS)

In Textile testing, Gas chromatography-mass spectrometry machine is used for qualitative analysis of banned Azo dyes, whether Azo dyes contain restricted harmful aromatic amines.

2. High performance liquid chromatography (HPLC)

High performance liquid chromatography (HPLC) is the dominant technology for both the analysis and isolation of substaces. In textile testing, if any harmful aromatic amine is detected by GC-MS machine, then conformation and quantitation should be made by using HPLC-DAD.

Figure: Example of a GC-MS instrument

Azo dyes and Bangladeshi Textiles

Bangladesh produces garments for almost all over the countries of the world. Almost all buyers now ask for azo test of their garments. So before going to shipment all garments the manufacturers must test their garment sample whether it contains any forbidden azo dyes or not. In the past it was not possible in Banglagadesh to test the azo dyes, but now the international testing company such as SGS,ITS (Intertek Testing Services), Bureau Veritas Consumer Products Services (Bangladesh) Limited, Dhaka, Bangladesh are proving Azo test facility of dyed fabrics and garments.

Figure: HPLC instrument

Experimental parts

Azo dye test procedure

Testing facilities on banned azo dyes are already available in Bangladesh. The costs of testing depend on the number of samples needed.

Test method

EN (European Standard) and LFGB (German Food Quality and Safety Standard)

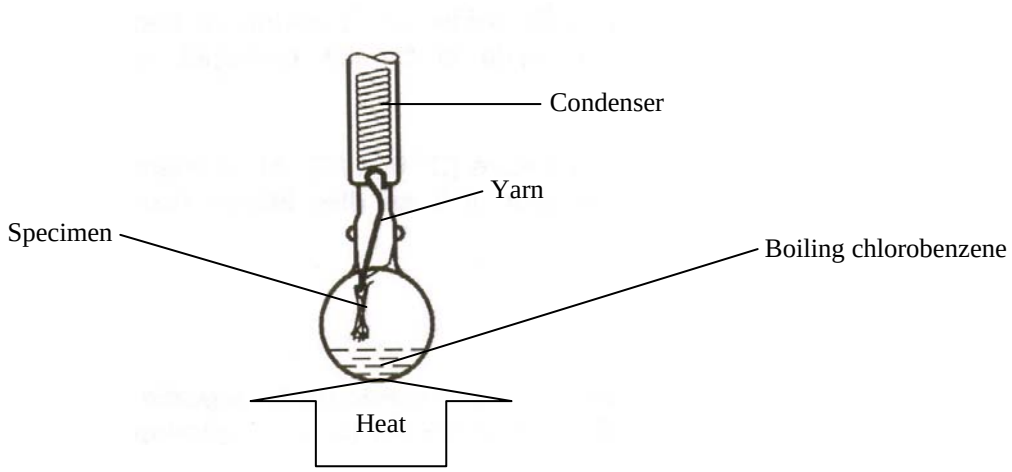
EN 14184-1 for general textiles
EN 14184-2 polyester

LFGB § 64 BVL B 82.02-2 for general textile
LFGB § 64 BVL B 82.02-4 for polyester

For textile fibres,

Subject to sample preparation procedure directly
For synthetic fibres

1. Cut the sample into small stripes of size (5±2) mm x (40±2) mm
2. Weigh 1g ± 0.01g
3. Tighten the cut stripes with a colourless yarn
4. The specimen is kept in the extractor with boiling chlorobenzene according to the setup below for 30mins:



5. Concentrate the extract to about 1mL with rotary vacuum evaporator (Keep the temperature between 45°C to 60°C)
6. Dry the extract with weak flow of nitrogen gas
7. Add 1mL of methanol into the residue
8. Put the reaction flask into an ultrasonic bath to disperse the extract

9. Transfer the extract to a reaction vessel
10. Dry the extract completely with a weak flow of nitrogen gas at less than 70°C
11. Pipette 2mL of methanol to the dried content of extract
12. Add 7g NaCl to the sample/reaction mixture
13. Pipette 9mL of 2% aqueous NaOH solution and mix (not necessary for polyester extract)
14. Pipette 1.0mL of freshly prepared sodium dithionite solution and mix
15. Put the reaction mixture into water bath/oven of 40 ± 2°C for 30 ± 1 min
16. Cool the reacted mixture to room temperature
17. Add 5mL of t-butyl methyl ether to the cooled mixture
18. Shake the solution for 45 min with mechanical shaker
19. Take the organic layer for instrumental analysis
20. The extract is subjected to GC-MS for qualitative analysis
21. Scan mode is selected for screening
22. 1 targeting ion and 2 qualifying ions are selected as according to its mass spectrum
23. If 4-aminoazobenzene are detected by GC-MS, confirmation and quantitation should be made by using HPLC-DAD
24. Identify the presence of target analyte in HPLC-DAD is based on the RT and comparison of the maxima and minima in PDA spectrum of sample mass spectrum
25. Absorption at the wavelength of 305nm is selected for quantitation.

CASE STUDY: o-Toluidine

In a denim industry in Bangladesh a fabric with the specification $\frac{(16\text{Ringslub})+(16\text{ open end}\times 300\text{D,Polyester}+40\text{D,Lycra})}{71\times 50}$ was tested in Bureau Veritas and SGS. After testing the Azo element, o-Toluidine was found. The Customer requirement o-Toluidine was 20 ppm, but after testing Bereau Veritas result has come 134 ppm, which was not acceptable.

Customer opend the L/C for denim fabric 200,000 yds. Accordingly the whole yarn was procured from China. But when the content of o-Toluidine was found, the following experiments were carried out to reduce o-Toluidine content from the fabric.

Experiment 1:

The fabric was treated at 200°C by stenter machine. Then wash the fabric as per customer standard and was sent to Bereau Veritas. In that test o-Toluidine was found 17.5 ppm which was supposed to be acceptable. But the fabric quality (shrinkage, stretch ability, GSM) was greatly negatively affected with this test. That's why the second experiment was carried out.

Experiment 2:

In washing machine, the fabric was tested with the following recipe:

Hostaphol DTC (clariant)	1.5 g/l
Tempearture	90°C
Time	25 min.
Water volume	200 litre

The following experiment reduced the o-Toluidine but not the expected level, so the 3rd experiment was carried out.

Experiment 3:

Fabric was treated in the mercerizing machine (DHALL, India) with the following recipe:

Alvatex 640	1 g/l
Alvatex	1 g/l
Soda Ash	1 g/l
Desize Box Temperature	85°C
Machine speed	18 metre/min

After that the fabric was washed seven times at 65°C and dried with steamer box at 110°C.

Test result: o-Toluidine content after Bereau Veritas result was found 5.0 ppm which was below than the customer requirement. But the customer refused to accept the test result as well as the fabric complaining that o-Toludine may again be found in the garment after washing if it is produced with this fabric.

RESULTS AND DISCUSSION

If any harmful azo dye is found in the dyed garment and if it is out of tolerance limit value then there is nothing but reject the whole garments. Though several experiments may reduce the harmful azo content, the customer

may not accept the fabric. It causes huge loss of the garment producers. The best way to avoid problems with banned azo dyes is to use only dyes which cannot split off the hazardous amines. The following advice can be given:

- Ask your suppliers for azo-safe certificates. Your EU buyer might request them from you as well.
- Use dyestuff supplied by reputable producers, who provide the Color Index Numbers, the generic names and material data sheets (MSDS) indicating the hazardous properties and preventive measures to be taken. Good example of these kinds of producers is the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) members.
- If you want to test your product, choose recognized certified (accredited) laboratories and ask them to use the test methods that are specified in the EU legislation.
- Ask your importer to send you the latest information on the legislative requirements on azo dyes or check the CBI database for the latest EU legislation.

CONCLUSION

Garments free from harmful azo dyes are the basic requirements of readymade garment industry in Bangladesh. This is so important issue that none can accept a garment that contains harmful azo dyes. It is carcinogenic and also causes deadly cancer. Textile and garment manufacturers should very much conscious regarding this matter. Not only textile but also other things of our daily life that is dyed should free from harmful azo dyes.

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