A STUDY OF SOME TOXICOLOGICAL CHARACTERISTICS OF AZO DYES

A. Bertea[1], R. Butnaru[1], L. Dobreanu[2], O. Voroniuc[3]
[1]Technical University, Iassy, [2]LACECA, Bucuresti
[3]University of General Medicine and Pharmacy, Iassy

INTRODUCTION

In the last years azo colorants have been regulated, especially for use in drugs, cosmetics, food and in connection with packaging of food. In France, the Netherlands, Austria and Germany restrictions on the use of azo colorants in textiles have been or are being implemented. In Netherlands the restrictions refer to the individual azo colorants. In Germany, however, the restrictions are related to the possible presence of intermediates/metabolites, i.e. the 22 potentially carcinogenic aromatic amines in the working environment (MAK Werte Liste).

Aromatic amines from this list may be grouped into five groups, the first three of them being components of the majority of the industrially important azo dyes /1-3/.

- Anilines, e.g. o-toluidine.
- Extended anilines, e.g. benzidine.
- Fused ring amines, e.g. 2-naphthylamine
- Aminoazo and other azo compounds, e.g. 4-(phenylazo)aniline.
- Heterocyclic amines.

Recently, the directive 2002/61/ec of the European Parliament and of the Council of Europe from 19 July 2002 brought some supplementary specifications. On article 4 there is stated „The Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), after being consulted by the Commission, has confirmed that cancer risks posed by textile and leather goods coloured by certain azodyes, give cause for concern"/4/. The directive also amends the former directive as follows: „Azodyes which, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in the Appendix, in detectable concentrations, i.e. above 30 ppm in the finished articles or in the dyed parts thereof, (…), may not be used in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity, such as: clothing, bedding, towels, etc.

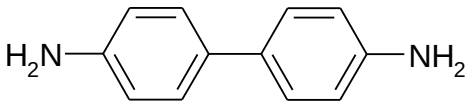
Because the reductive cleavage of the potentially carcinogens amines may take place if the dye is bound to the textile material, it is of interest to find in what measure the binding between the dye and the fibre affects the cleavage process.

1. EXPERIMENTS

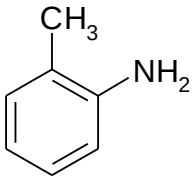
In the paper has been studied the possibility to identify the forbidden amines that can be released by reductive cleavage of the azo groups of the dyes. The experiments have been conducted using the thin layer technique. In all the experiments it has been presumed that the nature of the dye and of the textile material that has been dyed are known, but not the chemical structure of the dye.

1.1. Materials

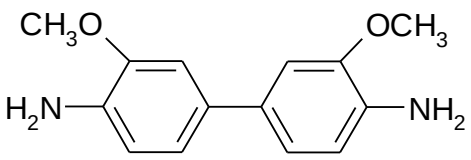
The analyse of the samples was conducted in the same manner for the dyestuffs and the dye on the dyed textile material (same duration, temperature, concentration of the reagents that have been used). We used the following standards:



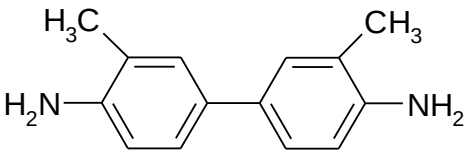
benzidine



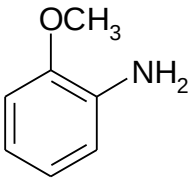
o-toluidine



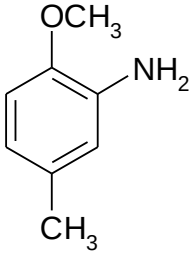
o-dianisidine
(3,3'-dimethoxybenzidine)



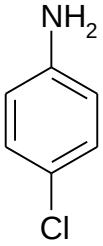
o-Tolidine
(3,3'-Dimethylbenzidine)



o-anisidine
(2-methoxy-1-aminobenzene)



p-cresidine



p-cloroaniline

1.2. The procedure of dye extraction from the dyed textile material

Several extraction methods have been used, and after that the dyes have been treated in a reductive medium. The test revealed the fact that in acid medium the reductive cleavage leads to unsatisfactory results. To extract the dyes we have used pure solvents as well as mixtures. The solvents that have been used were:

- dimethylformamide;
- alcools with C_1 to C_4;
- pyridine;
- ketones;
- chlorinated solvents.

For the samples dyed with direct and reactive dyes the extraction was not satisfactory, so the hydrolyse and alkaline reduction was performed on the textile material, in strictly controlled temperature and duration conditions. After the textile material was removed, the amines have been extracted with an appropriate solvent.

For the other classes of dye, after extracting with an suitable solvent, the extracts are concentrated (vacuum evaporation, absorption followed by desorption) and are identified chromatographically.
Eluents: chloroform / methanol and acetic acid / butyl acetate.

The development has been performed with an acid solution of p-DABA for the both eluents.

The chromatography has been performed separately, according to:

- the nature of the sample;
- the class of the dye.

The identification of the forbidden aromatical amines separated from the analysed samples was made conform to the elution rate and the spot colours, after comparisons with elution rate and the spot colours of the standard amines.

2. RESULTS AND DISCUSSIONS

In table 1 are presented schematically the results of the thin layer chromatography.

Table 1.

Nr.	Sample	Identified amine
Dye		
1	Direct Blue A	benzidine
2	Direct Brown LBBN	benzidine
3	Direct Bordeaux AL	-
4	Direct Blue FAL	-
5	Reactive Red M3A	.
6	Procion blue reactiv H- EGN	.
7	Colacid Red	o-toluidine
8	Colacid Red extra 6A	-
9	Colacid Red rezistent GN	benzidine
10	Acid Blue rezistent BS	-
11	Bordeaux Magra GRL (metal-complex)	-
12	Gri Magra BL (metal-complex)	-
13	Melacril Red BL (bazic)	-
14	Melacril Blue FM	-
15	Disperse Blue 2R	-
16	Disperse Blue RE	
17	Disperse Black 4BL	
A. 100% cotton fanric dyed with direct dyes		
18	Direct Blue A	benzidine
19	Direct Brown LBBN	benzidine
20	Bordeaux Direct AL	-
21	Direct Blue FAL	-
B 100% wool fabric dyed with acid and metal-complex dyes		
22	Colacid Red	o-toluidine
23	Colacid Red extra 6A	-
24	Colacid Blue rezistent BS	-
25	Colacid Violet 2R	-

26	Bordeaux Magra GRL	-
27	Gri Magra BL (metal-complex)	-
C. 100% PAN fabric dyed with basic dyes		
28	Melacril Red BL	-
29	Melacril Blue FM	-
D. 100% poliesther fabric dyed with disperse dyes		
30	Disperse Blue RE	-
31	Disperse Blue 2R	-
32	Disperse Black 4BL	-

The samples that at the thin layer chromatography showed no forbidden amines content had on the spotting passage no coloured spot, or the coloured spot that appeared had elution rates and development colours different to the standard amines.

For some of the studied dyes we have tried to identify their chemical structure. There have been tested the following direct dyes:

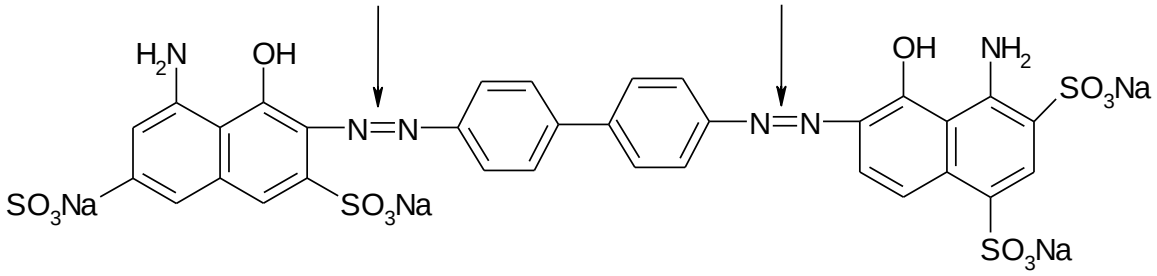
1. Direct Blue A (Blue Direct 6)
2. Brown LBBN
3. Bordeaux AL

Besides the solvent mixtures chlorophorm / methanol and glacial acetic acid / butyl acetate it has been used a mixture of n–buthanol/acetone/water/amoniac for all the three dyes. The first two dyes are metabolised to benzidine, as all the eluents have revealed.

For Direct Blue A the chromatographically analyse permitted to identify 3 components with different elution rates:

- *a benzidine* component with a medium elution rate, developed in orange;
- two much heavy components, with elution rates much smaller then benzidine. The heaviest is developing in yellow, and the other one pink. As the chemical structure of this dye is known, it can be presumed that these components are Acid H and Acid Chicago SS, that have similar molecular masses and are separated through sterical stability.

According to Colour Index, the chemical structure of this dye is:



Acid H Benzidine Acid Chicago SS

The dye **Direct Brown LBBN** has four components with different elution rates:

- a component with high elution rate, developed in yellow;
- benzidine, developed in orange;
- the heavier components identical with the one of the previous dye, respectively Acid H and Acid Chicago SS.

Bordeaux Direct AL has three components with different elution rates:

- a component with elution rate higher then benzidine or anisidine that develops in yellow, different to the one found in Brown LBBN.
- a component with the same elution rate and colour of development as the heavy component of the previous two dyes, that can be either Acid H or Acid Chicago SS.
- a component near the start line, developed in red, similar but not identical to o-tolidine.

It has to be mentioned that for this dye the reductive cleavage had a low efficiency.

3. CONCLUSIONS

It can be concluded that from all the 32 individual dyes that we have tested, only 2 dyes produce benzidine after the reductive cleavage, and hence these dyes must be interdicted according to the European legislation.

Bibliography

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4. xxx, Official Journal of the European Communities, 11.9.2002