STUDIES TOWARDS THE ELIMINATION OF ARYLAMINES IN DYESTUFFS BASED ON COLOUR INDITEX REACTIVE BLACK 5

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1 PURPOSE OF THE STUDY

The purpose of this study is to devise substitutes for black dyes for natural and regenerated fibers (mainly cellulosics and wool) based on C.I. Reactive Black 5. Substitutes should be based on dyes which are free of banned arylamines.

2 STRATEGY

The strategy employed in this study aimed at the elimination of the use of C.I. Reactive Black 5 based products has been:

- To study the presence of 4-chloroaniline impurities in CI Reactive Black 5.
- To use *The List by Inditex* as a source of commercially available, alternative candidates not based on CI Reactive Black 5.
- Proposal of substitution.

3 TEAMS INVOLVED IN THE STUDY

This study has been carried out by a scientific team of the University of Santiago de Compostela, Spain (USC), led by Prof. F. Javier Sardina.

4 INTRODUCTION

Reactive dyes are synthetic organic dyes widely employed to dye cellulosic and protein fibres. These molecules possess a chemical group that can react with the substrate, creating a covalent bond between the dye molecule and hydroxyl groups on the cellulosic fibres or amino groups in the wool fibers.

A reactive dye molecule mainly consists of four parts: a chromogen; a reactive system, which is the part that bonds to the fibre; a binding unit, which joins the two preceding parts; and a solubilising group.

C.I. Reactive Black 5 is a reactive dye of the vinyl sulfone type employed for producing black and blue colours on cotton, viscose and wool.

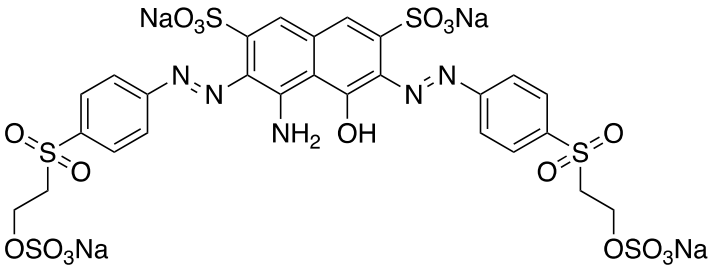


Figure 1. Structure of CI reactive Black 5

4.1 Arylamines from azodyes

Azo dyes are a group of synthetic colorants characterized by having one or more "azo" group (-N=N-) in their structure. These compounds are widely used to dye textile articles made of natural (cotton and wool) and regenerated cellulosic fibers. However the use of azodyes which may release carcinogenic aromatic amines by reductive cleavage of azo groups, is banned in textile and leather articles.[1]

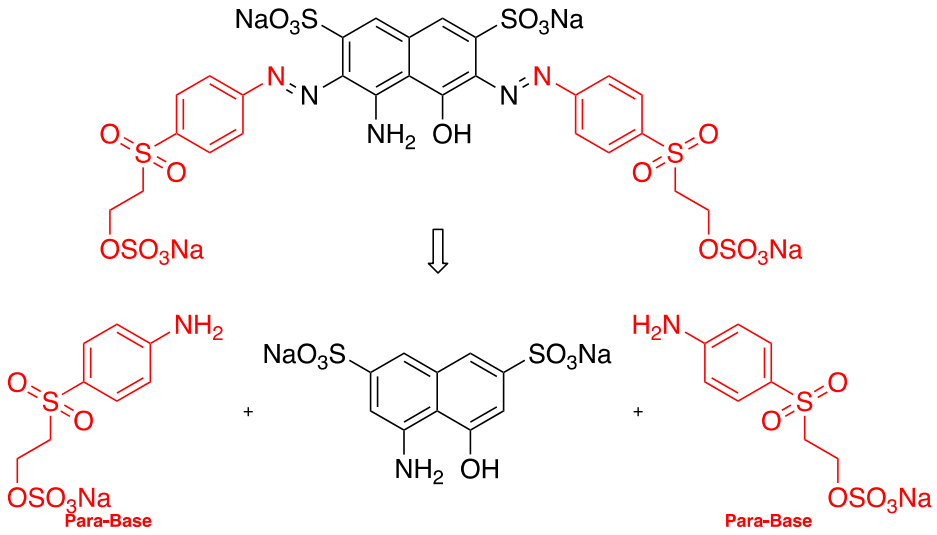
The purposeful use of banned azodyes is extremely rare nowadays, however sometimes the presence of banned arylamines in the final article can be traced to the existence of impurities in the dyestuff employed. These impurities may contain banned arylmines which are carried over to the dyed fabrics or garments. The sources of these impurities in the commercial dyestuffs can be:

- Unreacted starting materials remaining from a step of the chemical synthesis of dyestuffs.
- Impurities present in any of the starting materials employed for the synthesis of the dyestuffs.
- Unwanted byproducts formed in any of the reactions carried out to synthesize the dyestuffs.

4.2 4-chloroaniline from CI Reactive Black 5

CI Reactive Black 5 can be synthetized by a double diazocoupling of para-base with the corresponding coupling agent (see the following scheme).

[1] See Annex XVII, Entry 43 of REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).



Scheme 1. CI Reactive Black 5 synthesis

The para-base is the key starting material for the preparation of C.I. Reactive Black 5, but it can be contaminated with 4-cloroaniline (formed by a hydrolysis of 4-chloroacetanilide, which can be formed as byproduct during the para-base preparation). This impurity can be converted into a banned azo dyestuff which accompanies the CI Reactive Black 5 as a contaminant.

5 TOXICOLOGICAL CLASSIFICATION OF 4-CHLOROANILINE

The following table summarizes the health and environmental hazards associated to 4-chloroaniline. Hazards were assigned by considering Table 3.1 of Annex VI of the CLP Regulation ((EC) No. 1272/2008).[2]

Table 1. Health and environmental hazards associated to 4-chloroaniline

Entry	Substances	CAS No.	Hazards
1	4-chloroaniline	106-47-8	Carc. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1 Acute Tox. 3

[2] European Regulation on Classification, Labelling and Packaging of Substances and Mixtures

6 THE LIST BY INDITEX

"*The List by Inditex"* is a pioneering program developed by the Inditex Group in order to eliminate textile and leather dyeing, printing, tanning and finishing protocols which may employ harmful substances, even when these are present as unintended impurities. "*The List by Inditex"* (current edition: 3rd edition)includes instructions and advice to select appropriate dyestuffs, auxiliaries and water and oil repellents. The result of this program is a listing of close to 20,000 commercially available chemical products used in textile and leather manufacturing processes. Chemical products listed in "Dyestuffs and Auxiliaries for Textile and Leather" chapter are classified as "A", "B" or "C", according to their degree of compliance with the different Clear to Wear (Inditex Group's product health manual) categories for several substances and parameters, including banned arylamines.

7 PROPOSAL FOR THE SUBSTITUTION OF REACTIVE BLACK 5 BASED DYES

Considering that:

I. Reactive Black 5 base dyes often contain 4-chloroaniline-containing dyestuffs as impurities or other 4-chloroaniline releasing impurities.

II. The toxicological classification of 4-chloroaniline, a banned arylamine in textile and leather articles.

Inditex Group considers that reactive black dyes based on CI Reactive Black 5 must be substituted by:

a. reactive dyes which do not require the use of para-base as starting material.

b. reactive dyes with undetectable levels of banned arylamines.

During the work developed towards the compilation of *The List by Inditex, Edition III,* several alternative reactive black dyestuffs not based on CI Reactive Black 5 were identified. From these alternatives, candidates that do not content any other banned arylamines have been selected. The following table includes the reactive black dyestuffs that are proposed to be used as alternatives to that ones based on CI Reactive Black 5.

Table 2. Reactive black dyestuffs proposed as alternatives

Product Name	Manufacturer	Type	Banned arylamines level (ppm)
Levafix ECO Black	DyStar	Reactive	N.D.
Avitera Black SE	Huntsman	Reactive	N.D.

On the other hand, below table shows the arylamine detections found in two commercially available dyestuffs randomly selected and based on C.I. Reactive Black 5:

Table 3. Example of arylamine vales in commercially available reactive black 5 dyestuffs

Product Description	Arylamine type	Arylamine level (ppm)
Reactive Black 5- I	4-Chloroaniline	174.8
Reactive Black 5- II	4-Chloroaniline	101.3

Arylamine content in finished good

Cellulosic dyeing were performed using the chemicals analysed in the previous section (standard black reactive 5 –I and II- and alternative one). Applications were carried out in a jet machine, using in all cases an 8 % of dyestuff. Arylamine content was checked in the fabric after dyeing and after performing the soaping process posterior to the dyeing bath.

Table 4. Arylamines detections in black dyeing

Product Description	Arylamine type	Arylamines concentration after dyeing	Arylamine concentration after dyeing and soaping
Reactive Black 5- I	4-Chloroaniline	7.3 ppm	6.4 ppm
Reactive Black 5- II	4-Chloroaniline	4.6 ppm	3.6 ppm
Reactive Black 5 Alternative	-	No Detection	No Detection

Furthermore, the fabric dyed by the reactive black presented as an alternative to standard reactive black 5 provided slighthy greater values of colour fastness.

Product Name	ColourFastness				
	To Water	To Perspiration	To Saliva	To Dry Rubbing	To Wet Rubbing
Reactive Black 5- I	4-5	4	3-4	4	2
Reactive Black 5- II	4-5	4-5	4	4	2
Reactive Black 5 Alternative	4-5	4-5	4-5	4	4

Costs associated to black reactives alternatives

If the standard price of black 5 dyestuff is set to 100, using the reactive black 5 alternatives would mean an increase of the 300 % of the cost. However, such increase in the chemical products represents only an increase of 0.12€ per garment.