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COLOR CHANGE STUDY BY RETREATMENT WITH DIRECT DYES. STUDY CASE

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Abstract: *In this paper we presented a study on the color change by retreatment with different agents, of materials dyed with direct dyes.Direct dyes are organic or inorganic substances that contain double-bonded chromophore groups, which have a major role in the affinity of dyes for cellulosic fibers. Direct dye fixation is done by: hydrogen bonds, van der Waals bonds, dipole forces between dye and fiber.The dyeing process is influenced by the following parameters: dye concentration, electrolyte concentration, temperature and bath hydromodule.Most direct dyes do not have adequate color fastness to wet or light treatments. Therefore, these color fastness need to be improved by various retreatment processes.In order to improve the color fastness to wet and light treatments, it is possible to change the structure of the dye by complexing (metal salt treatment), redoing by diazotization and coupling, insolubilization with cationic agents (cationic salts or synthetic resins). The optimal method of treatment is dictated by the structure of the dye and the advantages and disadvantages of each method.In this study, metal salts of* $CuSO_4$, $K_2Cr_2O_7$ *and cationic salts (Aniofix D) were used for the retreatment. Following these retreatments, varieties of tint and color variations of the dyeing colors appeared. Tint and color changes must be considered when making dyeing recipes.*

Key words: *retreatment, color fastness, direct dyes, metal salts, cationic salts*

1. INTRODUCTION

Direct dyes are applied relatively easily with good migration properties and low costs. These dyes have in their structure sulphonic groups that give them solubility in water, but reduce the affinity of dyeing on the cellulosic substrate [1].

Both cellulose fibers and direct dyes have negative loading in the watery environment. The presence of sulphonic groups decreases the interaction between water-dye and consequently decreases the attraction of dye-fiber [2].

Cellulosic materials dyed with direct dyes have poor resistance to washing. Various fasteners are used to improve the resistance to washing: formaldehyde, cationic and metallic salts [3].

Some studies have shown that fixation agents without formaldehyde show better fixation results than formaldehyde fixing agents [4].

During solubilization of the dye in the solution, association of dye anions may also appear, forming dimers, trimers, tetramers or oligomers. These associates have a larger volume and hardly

get into the material. Temperature has an important role in dissolving these associate dyes from the solution and favors the diffusion of the dye into the fiber.[2]

The diffusion coefficient increases with the increase in dye concentration. The electrolyte increases the amount of dye adsorbed in the solution.[1,2]

For the same dye concentration expressed as % of the fiber mass and for the same dyeing parameters, the increase of the fiber to liquor ratio reduces the amount of dye adsorbed to equilibrium.[2]

2. EXPERIMENTAL PART

2.1Materials and methodes

In this study we used 100% cotton fabrics for dyeing samples. The dyeing was performed with Diazol RED 3B (C.I. 12356 – with molecular formula $C_{45}H_{32}N_{10}O_{21}S_6$6Na) direct dye by the batch process and by the semi-continuous process (pad - steam), according to STAS 5777-88 standard .

For dyeing is used softened water without Ca and Mg ions, which can precipitate dyes from the dyeing bath.[2],

The dyeing experiments are shown in Table 1.

Table 1.: *Dyeing procedures[2]*

1. Discontinuous process		
Treatment conditions		
Diazol RED direct concentration 3B	3%	
Concentration of NaCl electrolyte	10%	
Concentration of alkali substance Na_2CO_3	2%	
Temperature	95^0C	
HydroModulum	1:50	
Final treatments	Washing with warm water, soap, rinsing Washing with warm water, retreatment, rinsing	
2. Semi-continuous process (pad –steam)		
Name of the phase	Treatment conditions	
Impregnation	Diazol RED 3B direct dye concentration	10 g/l
	Concentration of NaCl electrolyte	10g/l
	Concentration of alkali substance Na_2CO_3	2g/l
	wetting agent	1g/l
	Requestring agent (Trilon B)	5g/l
	urea	30 g/l
	temperature	20-25^{0}C
Squeeze		
Fixation	Steaming for 8-10 min	
Final treatment	Washing with warm water, soap, rinsing Washing with warm water, retreatment, rinsing	

Dyeing by the batch process was carried out according to the dyeing diagram [2] shown in Fig.1

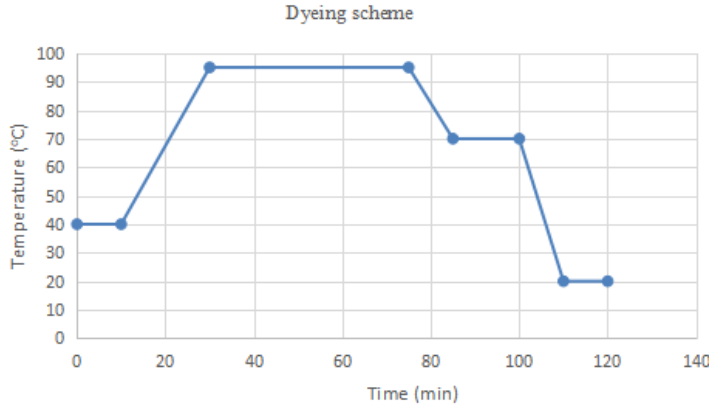
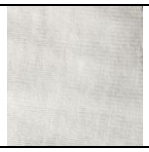


Fig. 1. *Dyeing scheme*

2.2 RESULTS

The color of samples dyed by these processes is presented in table no.2

Table 2: *Color of Dyeing*

Sample is not dyed	Sample 1 dyed by the batch process	Sample 2 dyed by the semi-continuous process
		

After dyeing, the *color fastness* of the dyes to wet and light treatments was tested. For determination of wash color fastness, the sandwich treatment method was used at 40 ° C for 30 minutes with 2g / l of washing agent and 2g / l of Na_2CO_3. The color fastness to washing with the gray scale was then determined according to ISO 105 -C06 standard.[4,5]

For the determination of light color fastness, the samples were exposed to light for 36 hours The light color fastness was determined by the blue scale according to ISO 105 B02 standard. [4, 5].The color fastness of the dyes are shown in Table 3.

Table 3*:. The color fastness of the dyes*

color fastness of the dyes	**Sample 1**	**Sample 2**
the color fastness of the dyes to washing 40^0C	CO/CO/WO 2-3/2/4	CO/CO/WO 2/2-3/4
the color fastness of the dyes to light	6-7	7

For the retreatment were used methods of complexation with Cu SO_4, $K_2Cr_2O_7$ and $CuSO_4$ and $K_2Cr_2O_7$ mixture and the method of coupling by insolubilization with cationic agents (Aniofix D).[2] The conditions for carrying out the retreatment operation are presented in Table 4.

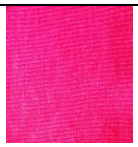
From the analysis of the dyeing color fastness, it appears that this dye presents reduced color fastness to light and wash. That is why the dyeing have been restored with Cu and Cr metal salts which change the structure of the dye by complexation and cationic salts (Aniofix D), resulting in good color fastness to wet treatments and light.

Table.4: *The dyeing retreatment*

Retreatment method	Treatment conditions
Complexation with Cu SO_4	3% $CuSO_4$ + 2% CH_3COOH 60%, T=70-80^{0}C, t=20-30 min, wash
Complexation with $K_2Cr_2O_7$	3% $K_2Cr_2O_7$ + 2% CH_3COOH 60%, T=80-90^{0}C, t=20-30 min, wash
Complexation with $K_2Cr_2O_7$+ Cu SO_4	2% $CuSO_4$ + 2% $K_2Cr_2O_7$ +2% CH_3COOH 60%, T=70-80^{0}C, t=20-30 min, wash
Coupling with Aniofix D	3% Aniofix D, T=25-30^{0}C, t=20-30 min, wash

During the retreatment, the hue and the color changes of the dyeing samples occurs. The modification of the color is shown in Table 5.

Table 5*: The color of the retreated samples*

Sample	Samples without retreatment	Cu SO_4	$K_2Cr_2O_7$	$K_2Cr_2O_7$ + Cu SO_4	Aniofix D
Sample 1					
Sample 2					

After retreatment the color fastness of the dyes were again determined on wet treatments and light and an improvement of these color fastness was observed according the results shown in Table 6.

Table 6: *Color fastness e of the dyeings after retreatment*

color fastness	Sample 1	Sample 2
the color fastness of the dyes to washing 40^{0}C	5/5/5	5/5/5
the color fastness of the dyes to light	8	8

3. CONCLUSIONS

Dye color fastness with Diazol Red 3B direct dye to wet treatments and light are poor and require retreatment. After dyeing, color changes occurred. By comparing color changes after retreatment, it results that Aniofix D and $K_2Cr_2O_7$ have a lower color influence, whereas $CuSO_4$ and $CuSO_4$+$K_2Cr_2O_7$ produce a noticeable change in color. Hue and color changes must be considered when making dyeing recipes.

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