AZO DYES COMPLEXES. SYNTHESIS AND TINCTORIAL PROPERTIES

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Se prezintă rezultatele experimentale privitoare la sinteza unor combinaţii complexe de cupru, cobalt şi crom cu coloranţi azoici obţinuţi pornind de la acidul 1-diazo-2–naftol-4-sulfonic şi acidul 6-nitro-1-diazo-2–naftol-4-sulfonic prin cuplarea acestora cu β–naftol şi N,N–dietil–m-amino-naftol. Combinaţiile complexe sintetizate au fost caracterizate prin analiza chimică elementală, spectre electronice şi IR. S-au determinat rezistenţele lor la vopsire pe fibre de lână şi poliamidice.

Experimental results concerning synthesis of copper, cobalt and chromium complex combinations with azo dyes starting from 1-diazo-2-naphthol-4-sulphonic, and 6-nitro-1-diazo-2-naphthol-4-sulphonic acids by coupling with β-naphthol, or N, N-diethyl-m-amino-naphthol are presented. These complex combinations were analyzed by elemental chemical analysis, electronic and IR spectra. Their dyeing resistances on wool and polyamide were determined.

Keywords: 1-diazo-2-naphthol-4-sulphonic acid, 6-nitro-1-diazo-2-naphthol-4-sulphonic acid, azo dyes, cobalt, cupper, and chromium complex combinations

1. Introduction

The development of natural and synthetic fibre production requires the study and implementation of new types of dyes with improved properties and superior results in terms of yield, resistance to light, and resistance to dyeing of wool and polyamide fibres.

For many years, the azo compounds have been the main class of dyes used in various applications such as textile fibres dyeing, colouring of different materials and advanced organic synthesis. The synthesis and dyeing properties of azo compounds are described in many papers [1-6]. Azo derivatives complex combinations have been widely used as dyes for synthetic polyamide supports and as pigments.

Complex combinations of particular importance of Cr^{3+}, Co^{3+}, Cu^{2+} can be incorporated into different classes of dyes, depending on the nature of the azo

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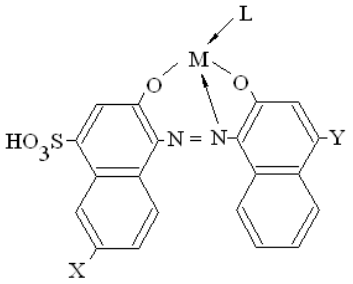
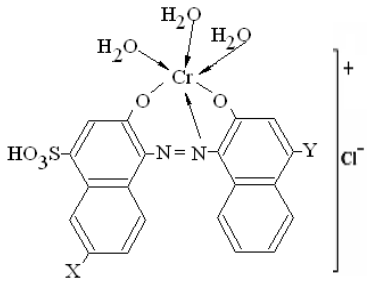
compound used as ligand. Acid dyes containing $–SO_3H$, –COOH groups are applied on wool, silk, polyamide fibres [8-9]. This paper covers the azo dyes area presenting the results for the synthesis of 4 new azo dyes and 12 complex combinations of Cr^{3+}, $Co^{3+}$and Cu^{2+} starting from 1-diazo-2-naphthol-4-sulfonic and 6-nitro-1-diazo-2-naphthol-4-sulfonic acids and two couplers: β-naphthol, and N, N-diethyl-m-amino-naphthol (formulas I - II).



Complex I	X	Y	L (ligand)	M(metal)
Cu1	NO_2	H	CH_3OH	Cu
Cu2	H	H	CH_3OH	Cu
Cu3	NO_2	NEt_2	H_2O	Cu
Cu4	H	NEt_2	H_2O	Cu
Co1	NO_2	H	CH_3OH	Co
Co2	H	H	CH_3OH	Co
Co3	NO_2	NEt_2	CH_3OH	Co
Co4	H	NEt_2	CH_3OH	Co

Fig.1. Formula of the synthesized Cu and Co complexes **I**

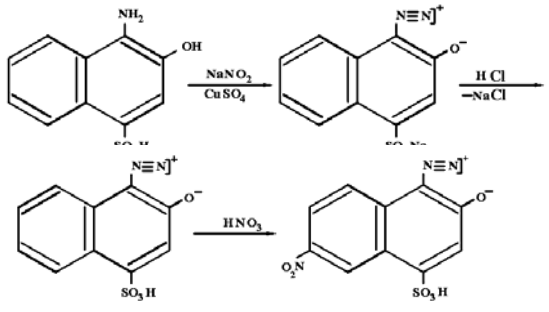


Complex II	X	Y	L (ligand)	M(metal)
Cr1	NO_2	H	$3H_2O$	Cr
Cr2	H	H	$3H_2O$	Cr
Cr3	NO_2	NEt_2	$3H_2O$	Cr
Cr4	H	NEt_2	$3H_2O$	Cr

Fig.2. Formula of the synthesized Cr complexes **II**

2. Experimental

1-diazo-2-naphthol-4-sulfonic acid (**A1)** and 6-nitro-1-diazo-2-naphthol-4-sulfonic acid (**A2**) have been obtained according to the following general procedure (Scheme 1) (9).



A1 **A2**

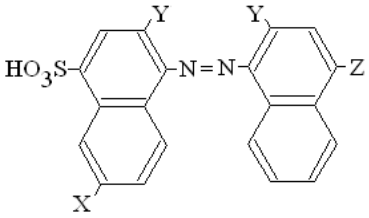
Scheme 1

By coupling **A1** and **A2** with β-naphthol, and N, N-diethyl-m-amino-naphthol, respectively, the azo dyes (Fig. 3) from Table 1 were obtained.

Table 1

Acids and couplers for obtaining the dyes of type I and II

Acid	Coupling compound	Azo dye
A1	β-naphthol	**Ib**
A1	N, N-diethyl-m-amino-naphthol	**IIb**
A2	β-naphthol	**Ia**
A2	N, N-diethyl-m-amino-naphthol	**IIa**



Azo dye	**X**	**Y**	**Z**
Ib	H	OH	H
IIb	H	OH	NEt_2
Ia	NO_2	OH	H
IIa	NO_2	OH	NEt_2

Fig.3. Formula of the synthesized azo dyes

The reaction conditions for acids **A1** and **A2** syntheses were optimised, leading to superior yields in respect to the given values in the literature [1, 8, 9, 10]. Therefore, each synthesis conditions have been described further in detail.

*a) Preparation of **A1***. To 14.4 g (0.06 moles) 1-amino-2-naphthol-4-sulfonic acid diluted with 65 mL H_2O, 0.4 g (0.0015 moles) $CuSO_4 \cdot 5H_2O$ as aqueous concentrated solution was added and the mixture was vigorously shaken. The reaction mass was cooled to 5^0 and then 23.5 g 40% $NaNO_2$ solution was added. The obtained 1-amino-2-naphthol-4-sulfonic acid was diazotized and it dissolved as sodium salt of 1,2-diazoxy-naphthalene-4-sulfonic acid. The solution was filtered. 36 g of concentrated HCl are added in the filtrate, under stirring. After the diazoxide precipitated, the mixture is kept under stirring for an hour. Then it is filtered and washed with diluted HCl. The diazoxide is dried in the oven at 60-70^0. 23.5 g **A1** were obtained (yield 94%).

*b) Preparation of **A2***. 3.5 mL H_2SO_4 96% was placed in a 250 mL three-necked flask equipped with stirrer and thermometer. The content of the flask was brought to 0^0 with external cooling. Then 5 g (0.02 moles) dried diazoxide **A1** was introduced and they were stirred until complete dissolution. A mixture composed of 1.6 mL H_2SO_4 and 1.1 mL 92% HNO_3 was added drop wise during 8 hours, while the temperature was kept between 0^0 and 2^0. The stirring was continued for other four hours when the temperature reached 15°, and then the content was poured into a bowl which has a water volume equal to the nitration volume (33

mL H_2O), meanwhile keeping the temperature at 15^0. The nitrated derivative precipitated, and then it was filtered and dried at $50\text{-}60^0$. It resulted 5.5 g **A2 (**yield 93.2%).

c) Preparation of the azo dye ***Ia***. 5g (0.03 moles) β-naphthol were dissolved in 66 mL H_2O in a Berzelius glass and 4.5 g (0.11 mole) NaOH were added. After the dissolution of β-naphthol, 16.5 g (0.15 moles) of Na_2CO_3 in 50 mL H_2O were added. In the obtained solution 9 g (0.03 moles) of **A2** are introduced in the next 8 hours at a maximum temperature of 25 - 28^0. The coupling mass was than acidified with concentrated H_2SO_4, when the dye precipitated. After filtration the precipitate was washed with water and dried at 50^0. It resulted 12.1g azo dye **Ia** (yield 90.9%).

The dyes **Ib, IIa** and **IIb** are obtained in a similar way as the dye **Ia**, in conditions given in Table 2.

Table 2

Reagents and reaction conditions for obtaining dyes Ib, IIa and IIb

Reagents &Reaction conditions	**Dye I_b**	**Dye II_a**	**Dye II_b**
β–naphthol (g)/ H_2O (mL)	3.2/ 43	0	0
NaOH in g (moles)	2.95 (0,07)	0	0
N,N–diethyl–m-amino-β-naphthol in g (moles)/mL	0	3.45 (0,01)/ 40	3.45 (0,01) / 40
KOH in g (moles)	0	4,2 (0,07)	4,2 (0,07)
Na_2CO_3 in g (moles) / H_2O (mL)	10.6 (0.1) / 32	10.6 (0.1) / 32	10.6 (0.1) / 32
Time (h)	8	8	8
Amount of **A2** in g (moles)	0	5.9 (0.02)	0
Amount of **A1** in g (moles)	5 (0.02)	0	5 (0.02)
Maximum temperature (^{0})	25 - 28	25 - 28	25 - 28
Drying temperature (^{0})	50	50	50
Reaction Yield (%)	90.5	87.82	91.02

The complex dyes **Cu1÷Cu4**, **Co1÷Co4**, **Cr1÷Cr4** were obtained from the metal inorganic salts and the specific ligand.

The dyes **I_a, I_b, II_a, II_b,** and their complex combinations **Cu1÷Cu4**, **Co1÷Co4**, **Cr1÷Cr4** were characterised by elemental analysis (central metal, anion Cl^-) - Spacu gravimetric method (Co, Cu, Cr) and gravimetric dosing with $AgNO_3$ (anion Cl^-), electronic spectra in 250-900 nm in dioxane solution and on MgO, IR vibrating spectra in the 650-4000cm^{-1} in KBr, and electrical conductivity. The electronic spectra were recorded with a VSV-2 CARL ZEISS (Jena) device. The IR spectra were recorded on a PERKIN – ELMER device in KBr from Merck.

The next experimental step was dyeing wool and polyamide fibres with these new complex combinations using the procedures described in Tables 3 and

4, followed by determination of the resistance (to cold water, to washing at 40^0, alkaline sweat and friction) [7].

Table 3

Dyeing wool fibres with complex combinations

Dyeing procedure	Parameters	Recipe
- Dissolving the dye and the auxiliaries - Dipping the material into the dyeing bath at 40°, - Raising the dyeing bath temperature with 1° in 2 min until 98°, - Keeping dyeing bath temperature at 98° for an hour - Cooling the dyeing bath with 1°/min – Washing and avivage	- pH = 5 ÷ 5.5, - Dye concentration : 0.1÷5%, - Auxiliary concentration: 10÷20%, - Bath ratio: 1:25÷1:50, - Dyeing temperature: 98^0, - Time: 1 hour	- 1-3% dye (1% for light colours, 3% for dark colours) - 0.25 g/L $(NH_4)_2SO_4$, - 10% NaCl, - 0.5% Avivan OCl

Table 4

Dyeing polyamidic fibres with complex combinations

Dyeing procedure	Parameters	Recipe
- Dissolving the dye and the auxiliaries, - Dipping the material into the dyeing bath at 50^0, - Heating dyeing bath temperature at 70^0, temperature which is kept for 15 minutes, - Heating dyeing bath temperature at 98^0, 1^0/min, this level being kept for an hour, - Cooling the dyeing bath with 1^0/min, - Washing and introducing the re-treatment agent, - Raising the temperature to 70^0 – keeping it for 15 minutes, - Cooling	- pH = 5 ÷ 5.5, - Dye concentration: 0.1÷3%, - Concentration of the acidifying agent: 0.25 g/L, - Concentration of the equalizing agent: 1%, - Dyeing temperature: 98^0, - Concentration of the re-treatment agent: 6%	*for treatment: - 1-3% dye, - 0.25 g/L CH_3COOH, - 1% equalizing on polyamide fibre (PA), *for re-treatment: - 0.25 g/L CH_3COOH, - 6% Romatan FST

3. Results and Discussion

Preparation of the complex combinations

The complex dye **Cu1** was prepared from 1.42 g (0.005 moles) $CuSO_4 \cdot 5H_2O$ that were dissolved in 20mL H_2O in a flask fitted with reflux cooler. Then the solution was heated to boiling point and 2.5 g (0.005 moles) dye **Ia** dissolved in methanol were added stepwise. The reaction mass was heated to reflux for 16

hours, then it was cooled. The precipitated complex dye was filtered and dried at 50-60^0. It resulted 1.94g (yield = 68.14%).

The complex dyes **Cu2÷Cu4**, **Co1÷Co4**, **Cr1÷Cr4** were obtained similarly. Table 5 shows the specific reagents and reaction conditions corresponding to the mentioned metal complex dyes.

Table 5

Reagents and reaction conditions suitable to obtain dyes Cu2÷Cr4

Com-plex dye	**Disazo dye)/ solvent**	**Complexing agent**	**Amount of the disazo dye in g (moles))/ solvent (mL)**	**Amount of the complexing agent in g (moles)/ solvent (mL)/ H_2O (mL)**	**Time (h)**	**Drying temperature (^{0})**	**Yield (%)**
Cu2	**I_b**/ CH_3OH	$CuSO_4 \cdot 5H_2O/H_2O$	2 (0.005)	1.2 (0.004) / 20	16	50-60	78
Cu3*	**II_a**/ H_2O	$CuSO_4 \cdot 5H_2O/H_2O$	1.7 (0,003)/ 40	1.24 (0.004)/ 20	20	60	60
Cu4*	**II_b**/ H_2O	$CuSO_4 \cdot 5H_2O/H_2O$	2.5(0,005)/ 40	1.24 (0,004)/ 20	20	60	72
Co1	**I_a**/ CH_3OH	$CoSO_4 \cdot 7H_2O/H_2O$	2 (0.004)	1.28 (0.004)/ 20	16	50-60	68
Co2	**I_b**/ CH_3OH	$CoSO_4 \cdot 7H_2O/H_2O$	2 (0.005)	1.28 (0,004)/ 20	16	50-60	70
Co3	**II_a**/ CH_3OH	$CoSO_4 \cdot 7H_2O/H_2O$	1.7 (0,003)	1.28 (0,004)/ 20	16	50-60	69
Co4	**II_b**/ CH_3OH	$CoSO_4 \cdot 7H_2O/H_2O$	2 (0.004)	1.28 (0,004)/ 20	16	50-60	84
Cr1**	**I_a**/ H_2O	$CrCl_3$ /H_2SO_4 35% / H2O	2 (0.004)/13.2	0.72 (0.004)/ 1,1/3	27	70-80	90
Cr2**	**I_b**/ H_2O	$CrCl_3$ /H_2SO_4 35% / H2O	2 (0.005)/ 13.2	0.72 (0,004)/ 0,75/2	25	70-80	94
Cr3*	**II_a**/ H_2O	$CrCl_3$ /H_2SO_4 35% / H2O	2.2 (0,004)/ 40	0.72 (0,004)/0/ 20	20	60	56
Cr4*	**II_b**/ H_2O	$CrCl_3$ /H_2SO_4 35% / H2O	2.2 (0,004)/ 40	0.72 (0.004)/0/ 20	20	60	63

*In the synthesis of dyes **Cu3**, **Cu4**, **Cr3** and **Cr4**, CH_3COONa, has been added to the reaction mixture, in order to maintain the pH in the range 4-6.

In the preparation of dyes **Cr1 and **Cr2**, the solution obtained by dissolving the dyes in water has been acidified with H_2SO_4 until reaching pH = 7.

Disazo dyes (**I_a, I_b, II_a, II_b**) and their metal complexes (**Cu1÷Cu4**, **Co1÷Co4**, **Cr1÷Cr4)** were obtained according to the literature [10], but with improved the yields. These results confirm the method validity.

The practical importance of azo dyes (of type I and II) has been notified by dyeing resistance tests for cold water, washing at 40°, alkaline sweat friction and resistance to light.

Analysis of the complex combinations

The complex combinations were analysed using elemental analysis, and spectral methods, as well. The results of the elemental analysis (for the central metal and anion Cl^-) are presented in Table 6.

Table 6

Elemental analysis results (%) for the metal (M) and Cl^- contents

Compound	Calculated	Found
Cu2	13.11% Cu	12.57% Cu
Co2	12.22 % Co	11.73% Co
Cr2	9.75% Cr	9.38% Cr
Cr2	6.65% Cl^-	6.39% Cl^-

The examination of the electronic spectra of the synthesized dyes complexes between 250-900 nm in dioxane solution and MgO tablet showed the following:

- These dyes show a strong band at 295 nm and a low intensity band at ~ 500 nm.
- For **Co2** an intense band at 475-500 nm and a shoulder at about 600 nm overlap on the dye band.
- The shape of the **Cr2** spectrum can be interpreted in terms of a distorted octahedral structure due to non-equivalent ligands (donor atoms: O, N, Cl).
- For **Cu2** there is an intense band in the 500-600 cm^{-1} region which supports a square plan configuration. The ligand absorption band in visible spectra prevents the exact assignment of the bands for these complex combinations.

The IR spectra of these new complexes were also recorded to bring additional data on the stereochemistry of the studied combinations, especially on the way of the dye coordination. Tables 7 and 8 present the characteristic IR frequencies of the dyes and their complex combinations with their attributions. The areas that change in the colour spectrum by complexation are those attributed to – OH and –N = N– valence vibrations. The presence of ν_{O-H} frequency in the complex combinations spectra pleads for the given formulation with coordinated alcohol (water) molecules [11].

Table 7

IR frequencies characteristic to dye I_a and Cu1, Co1, Cr1

I_a		Cu1		Co1		Cr1	
ν (cm^{-1})	Allocation	(cm^{-1})	Allocation	ν(cm^{-1})	Allocation	ν(cm^{-1})	Allocation
735	γ_{CH}	750	γ_{CH}	670	ν_{SO}	740	γ_{CH}
770	γ_{CH}	790	γ_{CH}	1050	$\nu_{SO2\ sim}$	810	γ_{CH}
810	γ_{CH}	870	γ_{CH}	1120	$\nu_{SO2\ sim}$	850	γ_{CH}
840	γ_{CH}	975	γ_{CH}	1340	$\nu_{NO2\ sim}$	900	γ_{CH}
900	γ_{CH}	1050	$\nu_{SO2\ sim}$	1530	$\nu_{NO2\ asim}$	1220	$\nu_{SO2\ asim}$
1040	$\nu_{SO2\ sim}$	1100	$\nu_{SO2\ asim}$	1590	$\nu_{-N=N-}$	1280	$\nu_{SO2\ asim}$
1175	$\nu_{SO2\ sim}$	1200	$\nu_{SO2\ asim}$	2000	γ_{CH}	1340	$\nu_{NO2\ asim}$
1220	$\nu_{SO2\ asim}$	1330	ν_{NO2}	3570	ν_{OH}	1460	$\nu_{C=C}$
1280	$\nu_{SO2\ asim}$	1460	$\nu_{C=C}$			1510	$\nu_{C=C}$
1340	$\nu_{NO\ sim}$	1530	$\nu_{C=C}$			1600	$\nu_{-N=N-}$
1530	$\nu_{-N=N-}$	1580	$\nu_{-N=N-}$			1630	$\nu_{NO2\ asim}$
1590	$\nu_{NO2\ asim}$	2000	γ_{CH}			3625	ν_{OH}
1630	$\nu_{NO2\ asim}$	3620	γ_{OH}				
2000	γ_{CH}						
3160	ν_{OH}						

Table 8

IR frequencies characteristic to dye I_b and Cu2, Co2, Cr2.

I_b		Cu2		Co2		Cr2	
ν(cm^{-1})	Allocation	ν(cm^{-1})	Allocation	ν(cm^{-1})	Allocation	ν(cm^{-1})	Allocation
710	ν_{C-S}	700	ν_{C-S}	730	γ_{CH}	710	γ_{CH}
740	γ_{CH}	760	γ_{CH}	760	γ_{CH}	750	γ_{CH}
765	γ_{CH}	840	δ_{CH}	810	γ_{CH}	850	γ_{CH}
840	γ_{CH}	1045	$\nu_{SO2\ asim}$	840	γ_{CH}	1050	$\nu_{SO2\ sim}$
960	$\nu_{SO2\ sim}$	1110	$\nu_{SO2\ asim}$	850	γ_{CH}	1180	$\nu_{SO2\ asim}$
1170	$\nu_{SO2\ asim}$	1210	$\nu_{SO2\ asim}$	1040	$\nu_{SO2\ sim}$	1210	$\nu_{SO2\ asim}$
1220	$\nu_{SO2\ asim}$	1270	ν_{C-OH}	1215	$\nu_{SO2\ asim}$	1280	ν_{C-OH}
1400	$\delta_{CH\ asim}$	1450	$\nu_{C=C}$	1310	$\nu_{SO2\ asim}$	1400	$\nu_{C=C}$
1430	$\delta_{CH\ asim}$	1560	$\nu_{-N=N-}$	1430	$\nu_{C=C}$	1435	$\nu_{C=C}$
1470	$\nu_{C=C}$	2000	γ_{CH}	1490	$\nu_{C=C}$	1510	$\nu_{C=C}$
1510	$\nu_{C=C}$	3650	ν_{OH}	1560	$\nu_{-N=N-}$	1600	$\nu_{-N=N-}$
1560	$\nu_{-N=N-}$			2000	γ_{CH}	1723	γ_{CH}
2000	γ_{CH}			3160	ν_{OH}	2000	γ_{CH}
3038	ν_{CH}					3670	ν_{OH}
3557	ν_{OH}						

Dying wool and polyamide using the complex combinations

Application of synthesized dyes on textiles was done according with specific thermal diagrams shown in Figs.4 and 5. Fig. 4 shows the characteristics of each temperature level for dyeing wool. They are, respectively: A-B - introducing the material into the dyeing bath (at 40°); B-C - raising the

temperature up to 98 °by 1 degree in 2 minutes; C-D – keeping the temperature at 98° for one hour; D-E - cooling 1/°min; E-F – refreshing the colour, washing.

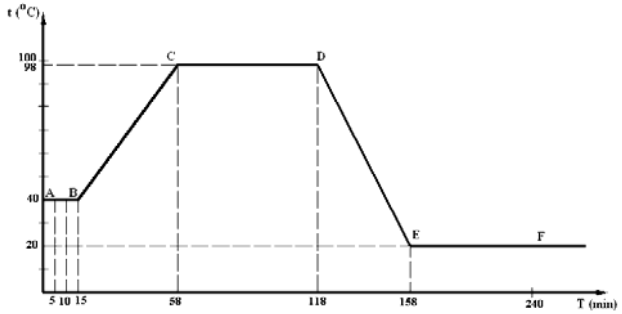


Fig. 4- Thermal diagram for the dyeing of wool

Fig. 5 shows the characteristics of each temperature level for dyeing polyamide fibres. The characteristics are: A-B - introducing the material into the dyeing bath at 50°; B-C - heating to 70°, temperature maintained 15 min; C-D - heating to 98°, all with 1°/min; D-E - keeping the temperature at 98° for one hour; E-F – cooling with 1°/min; F-G - washing and introducing the re-treatment agent; G-H - 70° t° rising; H-I - keeping the temperature at 70^0 for 15 min; I-J - cooling.

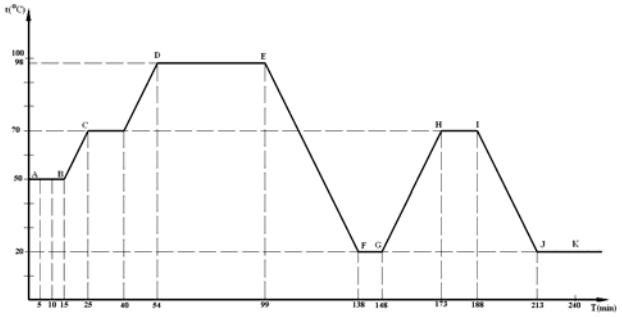


Fig. 5- Thermal diagram for dyeing polyamide fibres

To test the dyes properties the new synthesized complex combinations were used to dye the wool in dyeing experiments without using dyeing equalizers. The dyed fibres showed only small color unevenness. This illustrates that the complexes combination ions are not absorbed rapidly and at specific locations, but their access is determined by the physical structure characteristic to each variety of fibre. It shows that nonionic bonds are established within the body of the fibre, not only in privileged places. The obtained complex combination dyes have high affinity for wool and polyamide, resulting in intense, uniform dyeing.

The azo dyes (of type I and II) have practical importance as they have a good dyeing resistance for cold water, washing at 40°, alkaline sweat friction and

resistance to light. The new synthesized complex combinations have been also checked to these tests. Their dyeing resistance for cold water, washing at 40°, alkaline sweat friction has good values, between 3 and 4 on the scale "grey 5" for all these complex combinations. Except for complex combinations dyes **Co1** and **Co3**, which have values lower than 2, all the others gave good results corresponding to STAS 6624/3/76. The examinations were also in agreement with STAS 5705 - 80 / 1806 - 80 / 5707-87 / 5819-81.

For the new synthesized complex combinations the dyeing resistance for washing at 40° is greater in case of dyeing wool fibres than polyamide fibres.

4. Conclusions

The azo dyes (**I_a, I_b, II_a, II_b**) and their metal complex combinations (**Cu1÷Cu4**, **Co1÷Co4**, **Cr1÷Cr4**) were obtained using raw materials available in an easy process with yields higher than previously cited.

From the assessment of electronic spectra the presences of an intense band at 295 nm and a low intensity band at 500 nm, justify the orange and brown shades obtained in dyeing wool and polyamide fibres.

The dyeing resistance tests of the new complexed combinations on wool and polyamide fibres have good values between 3 and 4 on the "grey 5" scale.

R E F E R E N C E S

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