Reactive Dyes with α,β–chlorohydrinic Structure in the Molecule (II)

MARIN BULEARCĂ*, ION SEBE
Polytechnical University of Bucharest, Faculty of Applied Chemistry and Materials Science, Dyes Laboratory, 149 Victoriei Str., 010072, Bucharest, Romania

In this paper is presented the synthesis of a series of 11 new reactive dyes having α,β chlorohydrinic structure in the molecule, starting from monoazoic dyes, that were transformed into disazoic dyes. The obtained reactive red and violet dyes were applied on wool, polyamidic fibers and ethoxylated aluminium.

Keywords: reactive dyes with α,β-clorohydrinic structure, epychlorohydrine, monoazoic and disazoic dyes

The reactive dyes are anionic compounds soluble in water due to the existence of the sulfonic group in the molecule as disodium salts. Due to the presence of reactive group, they are able to be covalently fixed to textile fibers macromolecules on which they are applied, forming etheric, thioetheric, aminic or amidic bonds. After dying, the dye molecules and the textile fibers macromolecules are forming unique colored molecules with very good resistances at wet treatments. An important class of dyes is the class of reactive dyes with epoxidic cycle or with only one α-chlorohydrinic group in the molecule. They are obtained from an amino dye and epychlorohydrine, in acidic medium resulting chlorohydrinic compounds and in alkaline medium forming epoxy compounds.

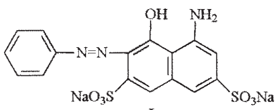
Particularly, some reactive dyes have been synthesized having in their structure naphthalinsulfonic acids (H, J, γ etc.), residues that are dyeing with good fastnesses. Even it is known since the first reactive dyes were introduced for the cellulose fibers in 1956, that the covalent bond is formed between the dye and the fiber during the painting process, it was not easy to find the definition and the true experimental proves for these bonds [1].

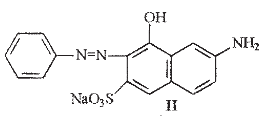
It was motivated that the reactive groups hydrolysis is easier with the OH groups from water, than the reaction with the OH groups from cellulose.

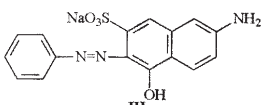
This problem was studied by Zollinger and co-workers [2] in 1960. Taking into account the high rate of the reactive dyes improvement for cellulose fibers [3-20], new researches regarding the synthesis of some new reactive dyes with epychlorohydrine are imposed.

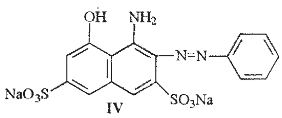
In this paper, is presented the synthesis of new disazoic (IX – XI) and ethylenechlorohydrinic (XII – XXII) dyes starting from the known I – VIII dyes [18].

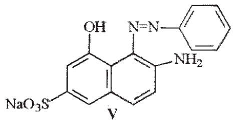
The structure of the monoazoic known dyes:

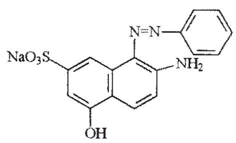

I


II

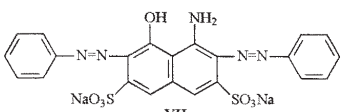

III

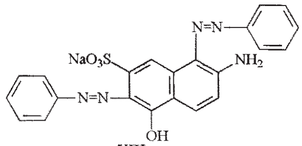

IV

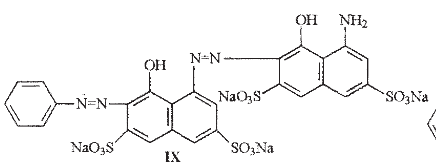

V

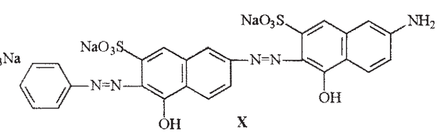

VI

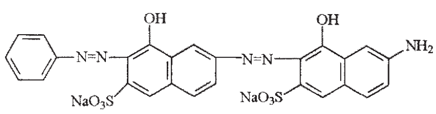
The structure of the disazoic dyes (VII-VIII known and IX-XI new dyes):


VII


VIII


IX


X


XI

*marinbulearca@yahoo.com, Tel. 021.402.27.20

The structure of the ethylenechlorohydrinic new dyes:

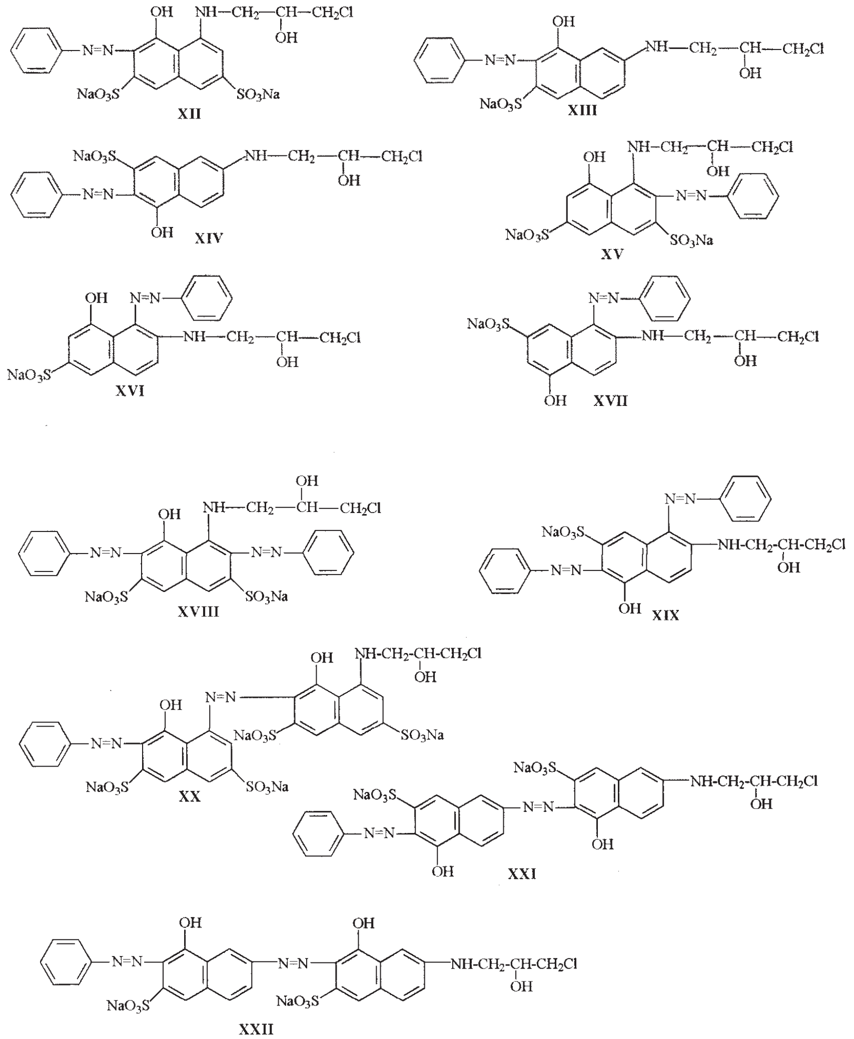


Table 1
SYNTHESIS CONDITIONS FOR THE MONOAZOIC DYES I - VI

Dye	Amine	Coupling agent	Diazotation agent [g]	Coupling agent [g]	Temp [^{0}C]	Time [h]	pH	Yield [%]
I	Aniline	H acid	9.3	34.1	15 - 20	2	8 - 9	77.5
II	Aniline	γ acid	9.3	23.9	5	8	8 - 9	95.8
III	Aniline	J acid	9.3	23.9	5 - 10	8	8 - 9	93
IV	Aniline	H acid	9.3	34.1	10	2	6.5	90
V	Aniline	γ acid	9.3	23.9	5	3	6	90
VI	Aniline	J acid	9.3	23.9	15	1	6 - 7	94.5

Experimental part

The known dyes have been synthesized by the classical diazotation - coupling procedure [21], and the working conditions are given in table 1.

The I - VI dyes were purified using the recrystallization method.

In order to determine the purity of the dyes, the thin layer chromatography was used working with Silicagel 60-G-Merck as stationary phase deposited on aluminium foil and, as mobile phase, a mixture of butylic alcohol : propylic alcohol : ethyl acetate : water (2 : 4 : 1 : 3 vol). The dyes solubilization was realized in the presence of dimethyl-formamide, having a concentration of 1%, and the samples were spotulated at a level of 10 µL. The identification is realized by direct vizualization of the colored spots. The Rfs values of I - VI dyes are: 0.17, 0.63, 0.69, 0.18, 0.62 and 0.67, respectively.

The I-VI dyes were analyzed from the spectral point of view by IR spectroscopy, under the form of KBr tablet with the SPECORD M80 apparatus, [22]. The results are given in table 2.

Synthesis of disazoic dyes

Synthesis of VII disazoic dye

Aniline diazotation was made according to the classical procedure [21].

Coupling of the aniline diazonium salt with IV dye in alkaline medium was performed as follows:

- 42.0 g (0.09 moles) of IV dye are dissolved in 380 mL water and 100 g ice, then, under stirring, the aniline diazonium salt solution which was buffered by acidity with sodium acetate (56.58 g) was added. 90.1 g Na_2CO_3 20% solution are added, for the acidity buffering and for maintaining the *p*H alkaline (8 - 9). The reaction mass is stirred for 6 h at 10^{0}C for the reaction perfection.;

Table 2
IR SPECTRUM OF THE I - VI MONOAZOIC DYES

Dye	ν_{OH} [cm^{-1}]	ν_{NH2} [cm^{-1}]	ν_{SO3H} [cm^{-1}]	ν_{CH2} [cm^{-1}]	$\nu_{N=N}$ [cm^{-1}]	ν_{C-N} [cm^{-1}]
I	1140	3405	1250fi	3050as	1569	1585
II	1140	3500	1260	3050	1570	1650
III	1145	3500	1260	3400	1559	1580
IV	1140	3400	1250	3500	1550	1600
V	1140	3400	1250	3500	1569	1580
VI	1140	3400	1260	3050	1570	1580

Table 3
SYNTHESIS CONDITIONS OF VIII - XI DISAZOIC DYES

Dye	Diazotation agent	Coupling agent	Diazotation agent [moles]	Coupling agent [moles]	Temp [^{0}C]	Time [h]	pH	Yield [%]
VII	Aniline	IV dye	0.1	0.09	10	6	8	82
VIII	Aniline	III dye	0.1	0.09	15	4	8 - 9	86
IX	I dye	H acid	0.075	0.075	3 - 5	3	8 - 9	85.7
X	III dye	J acid	0.093	0.093	20	12	8	98
XI	II dye	Γ acid	0.095	0.095	0 - 5	3	8	92

- the mixture is heated at 10^{0}C, it is salted with NaCl (9.5% from the volume), at a *p*H equal with 7, realized by adding hydrochloric acid 30% and the resulted suspension is filtered and the precipitate is pressed and dried at 80^{0}C.
- 41.6 g dried product are obtained. The yield is 82%.

Synthesis of VIII - XI disazoic dyes

It was done in the same manner as in the case of the VII disazoic dye. The synthesis conditions of VIII - XI disazoic dyes are given in table 3.

The VII - XI dyes were purified by recrystallization method, the purity control being identical with the one for I - VI dyes. The Rfs values of VII - XI dyes are: 0.19, 0.64, 0.23, 0.74 and 0.66, respectively. The VII - XI dyes were analyzed from the spectral point of view by IR spectroscopy, under the form of KBr tablet with the SPECORD M80 apparatus, [22]. The results are given in table 4.

Monoazoic and disazoic dyes condensation with epychlorohydrine

Condensation of the I dye with epychlorohydrine

46.7 g (0.1 moles) sodium salt of the I dye are dissolved in 500 mL water, then 15.6 mL (18.5 g; 0.2 moles) epychlorohydrine are added and then stir well. The *p*H should be 6.5 - 7. If the *p*H is different, the mixture is treated with HCl or NaOH solution. The mixing is carried out at 25 ^{0}C for 30 h, always verifying the pH that must be equal with 6.5 -7. After the reaction has finished (chromatographic control) the mass with the dark color is salted with NaCl (50 g) under stirring for 2 h. The precipitated dye is filtered, washed on the filter paper with a saturated solution of NaCl (20 mL) in two steps, then pressed and dried at 60 - 80 ^{0}C.

55 g dye are obtained. The yield is 98.5 %.

The II - XI dyes condensation is done in the same manner and the reaction conditions are given in table 5.

Table 4
IR SPECTRUM OF THE VII - XI DISAZOIC DYES

Dye	ν_{OH} [cm^{-1}]	ν_{NH2} [cm^{-1}]	ν_{SO3H} [cm^{-1}]	ν_{CH2} [cm^{-1}]	$\nu_{N=N}$ [cm^{-1}]	ν_{C-N} [cm^{-1}]
VII	1140	3405	1250	3050as	1565	1585
VIII	1140	3500	1260 fi	3050as	1570	1650
IX	1145	3500	1260fi	3400	1560	1580
X	1140	3400	1250	3500	1570	1600
XI	1140	3400	1250	3500	1560	1580

Table 5
REACTION CONDITIONS FOR II - XI DYES CONDENSATION WITH EPYCHLOROHYDRINE

Dye	Dye [g]	Epichlorohydrine [g]	Temp [^{0}C]	Time [h]	pH	Yield [%]
II	46.7	18.5	25	30	6.5 - 7	98.5
III	36.4	18.5	25	30	6.5 - 7	87
IV	36.5	18.5	25	35	6.5 - 7	91.7
V	46.7	18.5	25	40	6.5 - 7	92
VI	36.5	18.5	25	48	6.5 - 7	85
VII	36.5	18.5	25	48	6.5 - 7	86
VIII	28.5	9.25	25	25	6.5 - 7	80
IX	23.45	9.25	25	48	6.5 - 7	80
X	42.5	9.25	25	48	6.5 - 7	86
XI	36.4	9.25	25	48	6.5 - 7	99.3

Table 6
IR SPECTRUM OF THE XII - XXII DYES

Dye	ν_{OH} [cm^{-1}]	ν_{NH2} [cm^{-1}]	ν_{NH} [cm^{-1}]	ν_{SO3H} [cm^{-1}]	ν_{CH2} [cm^{-1}]	$\nu_{N=N}$ [cm^{-1}]	ν_{C-N} [cm^{-1}]	ν_{Cl} [cm^{-1}]
XII	1142	3405	3450	1250	3050	1565	1585	750i
XIII	1141	3500	3455	1260	3045	1570	1650	740
XIV	1143	3500	3450	1260	3050	1565	1580	740
XV	1142	3410	3455	1250	3050	1550	1600	750i
XVI	1140	3410	3450	1250	3050	1565	1580	730
XVII	1143	3400	3450	1250	3050	1570	1580	750i
XVIII	1141	3400	3456	1260	3050	1570	1600	740
XIX	1142	3410	3450	1260	3050	1550	1620	750i
XX	1140	3400	3455	1250	3050	1570	1585	740
XXI	1140	3405	3456	1260	3050	1570	1580	730
XXII	1141	3500	3450	1250	3050	1565	1600	740

The XII - XXII monoazoic and disazoic epichlorohydrinic reactive dyes were purified by recrystallization method and the purity control is described above. The Rfs values of XII - XXII dyes are: 0.21, 0.65, 0.72, 0.23, 0.67, 0.70, 0.22, 0.68, 0.25, 0.77 and 0.69, respectively.

The dyes were analyzed from the spectral point of view by IR spectroscopy, under the form of KBr tablet with the SPECORD M80 apparatus, [22]. The results are given in table 6.

Results and discussions

The IX, X and XI new dyes are intermediates in the XX, XXI and XXII epichlorohydrinic reactive dyes synthesis and they can be named as acidic azoic dyes.

Because among acidic dyes are very few having red and violet colors, characterized by equalization and good resistances, the qualities of the IX, X and XI dyes have been tested.

Dyes uniformity has been tested and the resulted images are given below:

Red colors
IX

Unitary
X

Unitary
XI

According to this test of the dyes uniformity the following conclusions can be drawn:

- the IX dye: in this dye can be observed the presence of a red dye parasite and it has a good solubility and smoothness,
- the X dye: has a medium solubility and acceptable smoothness and it is unitary;
- the XI dye: has a good solubility and smoothness.

The IX - XI dyes have been applied on wool, polyamidic fibers and ethoxylated aluminium.

Dyeing of the wool materials

This dyeing can be made with acidic dyes in neutral or in acidic medium. For these dyeings the dye concentration was 1%.

The dyeing procedures were:

a) dyeing in the presence of sulfuric acid. The dye bath contains 1% solution of dye (10g /250mL), 10% Na_2SO_4 solution (20%), 10% H_2SO_4 solution (4%).

b) dyeing in the presence of acetic and sulfuric acids. The dye bath contains 1% solution of dye (10g /250mL), 10% Na_2SO_4 solution (20%), 10% CH_3COOH solution (3%). Exhaustion with 10% H_2SO_4 solution (2%).

c) dyeing in the presence of CH_3COOH. The dye bath contains 1% solution of dye (10g /250mL), 10% Na_2SO_4 solution (20%), 10% CH_3COOH solution (3%). Exhaustion with 10% CH_3COOH solution (2%).

d) dyeing in the presence of HCOOH. The dye bath contains 1% solution of dye (10g /250mL), 10% Na_2SO_4 solution (20%), 10% CH_3COOH solution (3%). Exhaustion with 10% HCOOH solution (2%).

e) dyeing in the presence of salts with acidic character. The dye bath contains 1% solution of dye (10g/250mL), 10% Na_2SO_4 solution (20%), 10% $(NH_4)_2SO_4$ solution (3%), 10% CH_3COONH_4 solution (3%).

f) dyeing in neutral medium. The dye bath contains 1% solution of dye (10g /250mL), 10% Na_2SO_4 solution (20%).

Dyeing of polyamidic fibers

In this case the following procedures have been used:

a) dyeing in the presence of acetic acid. The dye bath contains: 1% solution of dye (10g /250 mL), 10% CH_3COOH solution (3%) in order to maintain the pH = 5 - 5.5.

b) dyeing in the presence of ammonia sulphate. The dye bath contains: 1% solution of dye (10g /250mL), 10% $(NH_4)_2SO_4$ solution (3%) in order to obtain a pH = 6.

For every dye bath before and after dyeing a spectrum of absorption in visible has been made in order to measure the amount of dye deposited on the sample.

In exhausted dye bath, an equal quantity of material has been dyed in the same conditions (time, temperature). From the absorption spectrum, according to the Lambert-Beer Law the exhausted dyeing yield was calculated. The obtained results are given in table 7.For the IX dye the maximum yield is obtained according to the procedure d (E = 95.2 %) in the presence of formic acid.

The X dye has dyed the wool and polyamidic fibers in red-Bordeaux. For this, the maximum yield was obtained

Table 7
EXHAUSTION (TINCTORIAL) YIELD [%] E FOR FIBER DYEING

Dye/ Sample material/ Procedure	Wool						PA	
	a	b	c	d	e	f	A	B
IX	94.76	95.14	92.6	95.2	47.08	51.1	73.15	65.5
X	50	81.76	80.96	77.2	37.2	41.44	79.6	66.06
XI	94.9	95.3	94.8	92.8	92.8	50.9	65.45	27.00

Table 8
EXHAUSTION (TINCTORIAL) YIELD [%] E FOR WOOL DYEING FOR VARIABLE TIME

Dye/Time	2	5	10	20	40	60
IX	5.92	93.8	94.87	95.04	95.28	95.36
X	6.66	61.6	70.96	76.3	76.83	77.10
XI	83.19	93.8	94.87	95.8	95.28	95.36

Table 9
EXHAUSTION (TINCTORIAL) YIELD [%] E FOR POLYAMIDE DYEING FOR VARIABLE TIME

Dye/Time	2	5	10	20	40	60
IX	26.87	69.46	74.63	76.7	77.3	85.75
X	83.14	93.8	94.87	95.04	95.08	95.36
XI	73.07	80.38	84.03'	87.3	89.42	96.69

according to the painting procedure b, in the presence of H_2SO_4 (E = 81.76 %); however, in industry working with H_2SO_4 is avoided. The tinctorial yield of the c procedure in the presence of acetic acid is close in value (E = 80.96 %) and taking into account the visible characteristics, it is chosen for the X dye the c dyeing procedure.

For the XI dye, the maximum yield is obtained in the b procedure (E = 95.3 %), but from the same reasons as for the X dye, it is chosen the c dyeing procedure, through which E = 94.8 % is obtained.

A common characteristic for all three dyes is the fact that they have very good dyeing fastnesses in acidic medium but they do not dye with a good yield in neutral medium or in the presence of acidic salts.

For the polyamidic fibers, the dyeing process in the presence of acetic acid gives the maximum yield for all three dyes. As in the case of the wool dyeing, it is observed that these acidic dyes are dyeing with bad results in neutral medium, but with good results in acidic medium.

The exhaustion curves E = f(t)

The purpose is to obtain the dependence exhausting - time for every dye, on wool and polyamide. For this, six samples of wool and six samples of polyamide are dyed with each dye. The dyeing conditions are the same for all six samples (same temperature, dyeing procedure and intensity). The only variable parameter is the time. First sample is let in the dye bath for 2min, second 5 min, the others 10 , 20, 40, 60 min, respectively. Before dyeing, an absorption spectrum is made in visible domain for the initial dye bath, and after dyeing, for every dye bath, another spectrum of absorption is made in visible. According to the Lambert - Beer Law the exhaustion yield is calculated. The obtained results are given in table 8 and table 9.

The similarity between the exhaustion curves is a criterion of using a mixture of dyes in the dyeing process. After the examination of exhaustion curves for the IX - XI dyes, the following can be observed:

The IX, X and XI dyes present affinity for wool at temperatures of 60, 70 - 75 and 65 - 70 ^{0}C, respectively, and for polyamidic fibers at temperatures of 75, 85 - 95 and 85 ^{0}C, respectively. Practically, in the polyamide case, after 10 - 20 min the maximum amount of dye is retained. After this very short period of time, dyeing will continue for a good equalization of the dyes, leading to a uniform dyeing. From the analysis of the dyeing aspects and from the exhaustion curves, one may observe that all the three dyes have the same dyeing rates.

Table 10
DYEING FASTNESSES OF DYES

Dye	A	F_{ab}	T_{AC}	T_{Alc}	Sp. 40 ^{0}C
XII	5	5	4 - 5	4 - 5	3 - 4
XIII	5	5	4	4	3 - 4
XIV	5	5	4 - 5	4	3 - 4
XV	5	5	5	5	5
XVI	4 - 5	5	4 - 5	4 - 5	3 - 4
XVII	4	4 - 5	4	4	3
XVIII	4	4 - 5	3 - 4	3 - 4	3
XIX	4	4 - 5	4	4	3
XX	4	4	3 - 4	3 - 4	3
XXI	5	5	4 - 5	4 - 5	3 - 4
XXII	5	5	4 - 5	4 - 5	3 - 4

where:A = water resistance;F_{ab} = dry friction resistance;T_{AC} = acidic perspiration resistance; T_{Alc} = alkaline perspiration resistance;Sp.40 ^{0}C = washing resistance at 40 ^{0}C.

Dyeing fastness of IX - XI dyes

The dyeing fastness was tested in water (washing at 40 ^{0}C), acidic and alkaline perspiration, in wet and dry conditions.

For the polyamidic fibers fastness improvement, they were treated with ROMATAN EST (anion-active resin) which is acting like a film on the fiber surface, avoiding the dye releasing. It is remarked that these dyes have good fastness on an alkaline or acidic perspiration (value 4 -5), and on a wet or dry friction (value 4 -5). The X dye has lower fastness on washing (value 3). The polyamidic retreated dyeings have good fastness (value 4 - 5). After the application of the dyes on ethoxylated aluminium, it is observed that only the X and XI dyes are colouring the aluminium in red and in dark violet, respectively.

Applying and testing the XII - XXII reactive dyes

The XII - XXII monoazoic and disazoic epichlorohydrinic reactive dyes were applied on cotton in alkaline medium (*p*H = 8 - 9). The obtained colors are intense, with the exception of the XII, XV and XXII dyes and the dyeing fastnesses are given in table 10. It is observed a satisfactory behavior of the majority of dyes on the physical agents action.

Conclusions

A series of 11 new epichlorohydrinic reactive dyes were synthesized starting from six known monoazoic dyes, that were transformed into disazoic dyes with a very good yield (88 - 90 %).

The new obtained disazoic reactive dyes (IX - XI) were applied on wool, polyamidic fibers and ethoxylated aluminium, giving red and violet colors and having good fastnesses. Also, the polyamidic fibers used in the dyeing process were treated with ROMATAN EST (anion-active resin) leading to avoid the dye releasing during usage.

The new obtained epychlorohydrinic dyes (XII - XXII) were applied on cotton in alkaline medium. The dyeing fastnesses are good to water, acidic and alkaline perspiration and also to wet and dry friction.

References

1.RATTEC, I.D., STEPHEN, W.E., I.C.I. Britt, Patent, 772030 (1954)

2.KRAZER, B. , ZOLLINGER, H., Helv. Chim. Acta., **43**, 1960, p. 1513

3.STAMM, O.A., ZOLLINGER, H., ZUHNER H., GÄUMANN, E., Helv. Chim. Acta., **44**, 1961, p. 1123

4.MEYER, U., MÜLER, S.M., text. Chem. Col., **22** (12), 1990, p.26

5.FIEGEL, J., REDDIG, W., WOLFF, J., Melliand Textilber **76**, 2001, p. 328

6.SIEGEL, E., in Venkatamaran VI, The Chemistry of Synthetic Dyes, 1-210, academic Press, New York, 1972

7.MROTZEK, U., Deutscher Färbekalender **94**, 1990, p. 101

8.LIGI H., ZHENGHUA Z., KONGCHANG C., FAXIANG Z., Dyes and Pigments, **10**, 1989, p.195

9.HÄHNKE, M., Textilveredlung **21**, 2001, p. 285

10.BADRI, B., The influence of reactive dyes on the pyrolysis of cotton, J.Anal.Appl.Pyrolysis, **81**, 2008, p. 162

11.FREEMAN, H.S., SOKOLOWSKA, J., Rev. Prog. Coloration **25**, 1999, p. 9

12.UNGERMANN, E., Textilpraxis int. **42**, 2002, p. 411

13.WOLFF, J., HENK, H., Textilveredlung **25**, 1990, p. 213

14.BECKMANN, W., GRÜTZE, J., HOFFMANN, F., LOHNERT, W., Melliand Textilber **66**, 1985, p. 47

15.FIEBIG, O., SCHULZ, G., HERLINGER, H., Textilpraxis int. **40**, 1989

16.PREJMEREARU, I., BÂRLEA, S., BALAUR C., ANDREI, C., (Intreprinderea Medicamente şi Coloranţi Sintofarm) brevet românesc 79495 (10 februarie 1983)

17.CHUNG-HSINWU, Effects of operational parameters on the decolorization of based systems C.I.Reactive Red 198 in UV/TiO, Dyes and Pigments, **77**, 2008, p. 31

18.SEBE, I., STOICA, L., GHEORGHIU, A., Rev. Chim. (Bucureşti), **38**, nr. 11, 1987, p. 940

19.SEBE, I., BÂLĂ, G., ISCULESCU, L., Coloranţi antrachinonici pentru fibre poliamidice, Rev. Chim. (Bucureşti) **54**, no.12, 2003, p.969

20.SOLEIMANI-GORGANI, A., TAYLOR, J.A., Dyeing of nylon with reactive dyes. Part 3: Cationic reactive Dyes for nylon, Dyes and Pigments, 76, 2008, p. 610

21.H. SANIELEVICI, L.FLORU, Sinteza intermediarilor aromatici şi coloranţilor Editia II-a, Editura Didactică şi Pedagogică, Bucureşti, 1971, p. 70

22.BALABAN, A.T., BANCIU, M, POGANY, I., Aplicaţii ale metodelor fizice în chimia organică, Editura Ştiinţifică şi Enciclopedică, 1983, p. 24

Manuscript received: 15.12.2008