U.P.B. Sci. Bull., Series B, Vol. 68, No. 3, 2006

SYNTHESIS OF REACTIVE DYES BASED ON EPYCHLOROHYDRINE

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În lucrare se prezintă sinteza unor coloranţi reactivi cu grupe α, β clorhidrinice în moleculă, pornind de la coloranţi monoazoici transformaţi în coloranti disazoici. Coloranţii reactivi rosu si violet obtinuţi au fost aplicaţi pe lână, fibre poliamidice şi aluminiu etoxilat.

In this paper is presented the synthesis of some reactive dyes having α, β chlorohydrinic groups 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-clorohydrine structure, epychlorohydrine, monoazoic and disazoic dyes.

Introduction

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-chlorhydrinic 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.

In particular, some reactive dyes have been synthesized having in their structure naphthalinsulfonic acids (H, J, γ etc.) which are painting with good resistances. 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].

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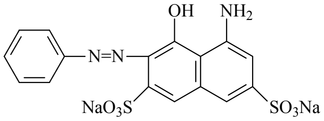
It was motivated that the reactive groups hydrolysis with the OH groups from water is easier than the reaction with the OH groups from cellulose.

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 [3-22], new researches regarding the synthesis of some 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.

1. The synthesis of the following monoazoic known dyes:



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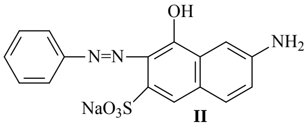

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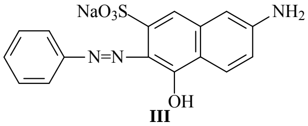

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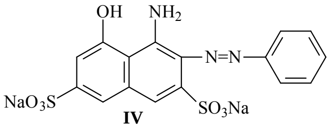

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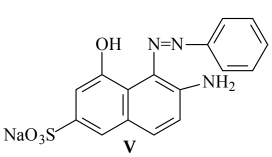

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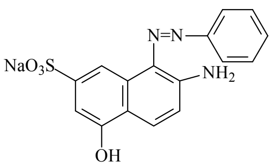
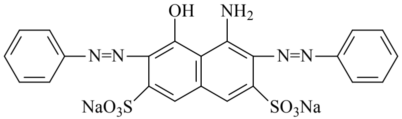


VI

2. The synthesis of the following disazoic dyes (VII – VIII known and IX – XI new dyes):



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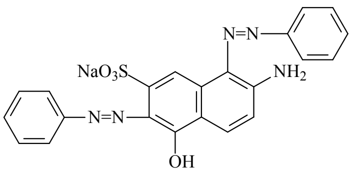
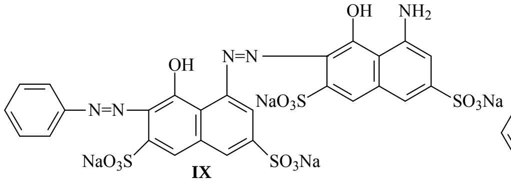
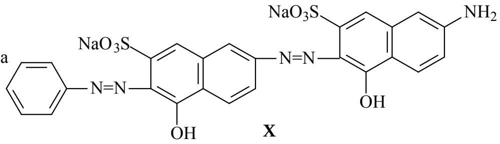


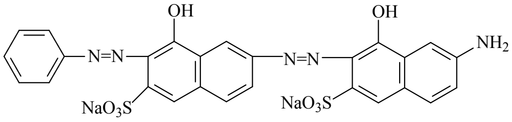
VIII



IX

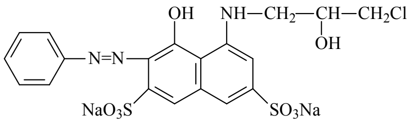


X



XI

3. The synthesis of the following ethylenechlorohydrinic new dyes:



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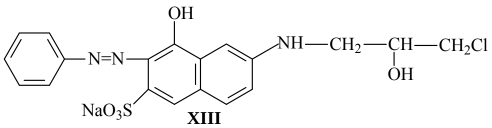

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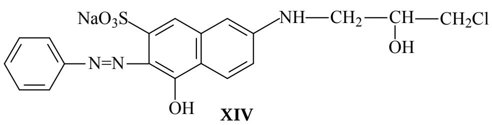
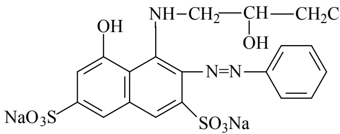


XIV



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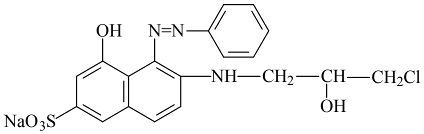

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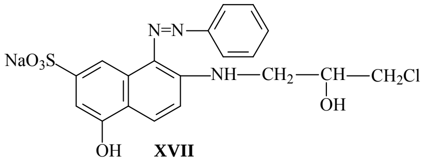
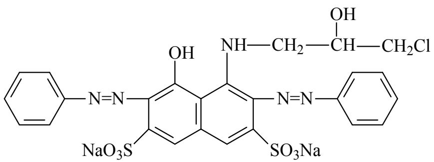


XVII



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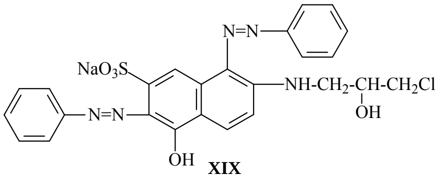
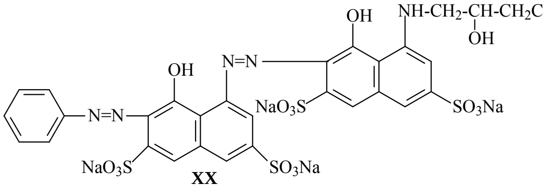
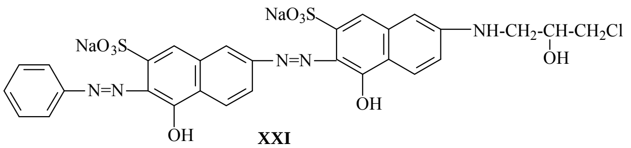


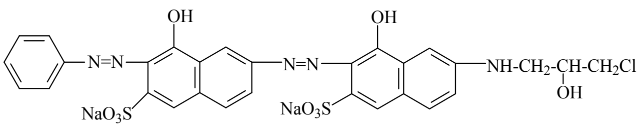
XIX



XX



XXI



XXII

Experimental

The dyes have been synthesized by the classical diazotation – coupling procedure [23].

1. *Synthesis of monoazoic dyes*
   Synthesis of monoazoic dye I

1.1.Aniline diazotation. 9.3 g (9.1 mL; 0.1 moles) aniline are dissolved in a solution prepared by mixing 33.5 g (28.2 mL; 0.27 moles) hydrochloric acid 30% with 100 mL water, adding ice in order to reach the temperature of 0^0C and to compensate the diazotation reaction heat (totally, around 85 g ice). Then 23 g (19 mL; 0.1 moles) $NaNO_2$ 30% solution is added drop by drop, slowly under stirring, carefully that the temperature reaction mixture not to exceed 5^0C. The total volume of the solution is around 240 mL. Always verify that the reaction mass is acidic (positive reaction – blue- on the Congo red paper) and it should contain nitrous acid (positive reaction – blue - on iodamidonated paper).

After the nitrite solution was added, the reaction mass is stirred for 4-5 hours for the reaction perfection; in this mixture only a small excess of nitrous acid should be present. Then the excess of nitrous acid is destroyed by adding in the reaction mass, under stirring, urea until the reaction with the iodamidonated paper is no more positive.

*1.2.Coupling of the aniline diazonium salt with the H acid at an alkaline pH***.** 34.1 g (0.1 moles) monoazoic salt of the H acid are dissolved in 280 mL water obtaining a solution with a pH = 6-7, verified with a turnesol paper. 14.3 g Na_2CO_3 are added and then around 100 g ice in order to reach the temperature of 0^0C. Under stirring, the diazonium salt solution is added drop by drop during 20 minutes. The reaction mass should always present a slightly alkaline reaction (pH = 8–9) controlled with yellow-brilliant paper (red color). After 2 hours of mixing at 15 – 20^0C is checked the absence of the diazoderivative from the mixture (tested with the halo of a sample salted by touching on the filter paper with an alkaline solution of R salt).

The reaction mixture is heated under stirring at 60^0C, it is salted with 100 g NaCl and mixed for 1 hour; and then it is cooled at 20^0C and filtered.

After drying at 60 – 80^0C, 36 g of dye is obtained, (the yield is 77.5 %).

2. *Synthesis of monoazoic dye II*

2.1.Aniline diazotation is identical with the method presented at 1.1.

2.2.Coupling of the aniline diazonium salt with the γ acid in alkalin medium was performed using a procedure identical with the one presented at 1.2. and the working conditions are given in the Table 1.

Table 1

Synthesis conditions for the monoazoic dyes I – VI

Dye	Amine	Coupling agent	Diazotation agent [g]	Coupling agent [g]	Temp. [^{0}C]	Time [hours]	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	8	90
VI	Aniline	J acid	9.3	23.9	15	1	6 - 7	94.5

The I – VI dyes were purified and analyzed under the form of KBr tablet with the SPECORD M80 apparatus, [24]. The results are given in Table 2.

Table 2

The 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}]	$\nu_{C\text{-}N}$ [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

3. *Synthesis of disazoic dyes*

3.1. Synthesis of VII disazoic dye

3.1.1. Aniline diazotation was made according to the procedure described at 1.1.

3.1.2. 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, add 100 g ice, then add under stirring the aniline diazonium salt solution which was buffered by acidity with sodium acetate (56.58 g). 90.1 g Na_2CO_3 20% solution are added immediately under stirring for the acidity buffering and for maintaining the pH alkaline. The reaction mass is stirred for 6 hours at 10^{0}C for the reaction perfection.

The mixture is heated at 10^0C, it is salted with NaCl (9.5% from the volume), the pH is fixed to 7 by adding hydrochloric acid 30% and the resulted suspension is filtered and the precipitate is pressed and dried at 80^0C.

41.6 g dried product are obtained. The yield is 82%.

3.2. Synthesis of VIII – XI disazoic dyes

It was done in the same way as in the case of the VII disazoic dye.

The synthesis conditions of VIII – XI disazoic dyes are given in Table 3.

Table 3

Synthesis conditions of VIII – XI disazoic dyes

Dye	Diazotation Agent	Coupling agent	Diazotation agent [moles]	Coupling agent [moles]	Temp [^{0}C]	Time [hours]	pH	Yield [%]
VII	Aniline	IV dye	0.1	0.09	10	6	7	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	7	98
XI	II dye	γ acid	0.095	0.095	0 – 5	3	7	92

The VII – XI dyes were purified and analyzed under the form of KBr tablet with the SPECORD M80 apparatus, [24]. The results are given in Table 4.

Table 4

The IR spectrum of the VII – XI 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}]
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

4. Monoazoic and disazoic dyes condensation with epychlorohydrine

4.1. 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 pH should be 6.5 – 7. If the pH is different, the mixture is treated with HCl or NaOH solution. The mixing is carried out at 25 ^{0}C for 30 hours, 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 hours. 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 – 80^0C.

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 5

Reaction conditions for the II – XI dyes condensation with epychlorohydrine

Dye	Dye [g]	Epichlorohydrine [g]	Temp [^{0}C]	Time [hours]	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

The XII – XXII monoazoic and disazoic epichlorohydrinic reactive dyes were purified and analyzed under the form of KBr tablet with the SPECORD M80 apparatus, [24]. The results are given in Table 6.

Table 6

The IR spectrum of the XII – XXII dyes

Dye	ν_{OH} [cm^{-1}]	ν_{NH2} [cm^{-1}]	ν_{NH} [cm^{-1}]	N_{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

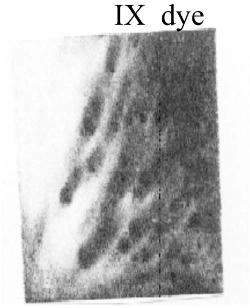
Results and discussions

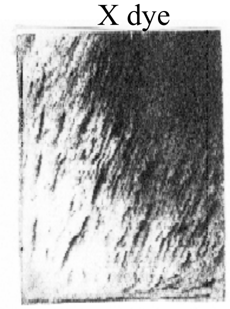
The IX, X and XI new dyes are intermediates in the XX, XXI and XXII epichlorohydrinic reactive dyes synthesis and they can be named as acidic azoic dyes.

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 pictures are given below:

Red colors Unitary Unitary
IX dye X dye XI dye





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 smothness.

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

Painting of the wool materials.

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

The painting procedures were:

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

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

c) Painting 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%). Depleation with 10% CH_3COOH solution (2%).

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

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

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

Painting of polyamidic fibers.

In this case the following procedures have been used:

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

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

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

In depleated dye bath, an equal quantity of material has been painted in the same conditions (time, temperature). From the absorption spectrum, according to the Lambert-Beer Law the exhausted painting yield was calculated. The obtained results are given in Table 7.

Table 7

The exhausting (tinctorial yield) [%] E for fiber painting

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

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 is painting the wool and polyamidic fibers in red- Bordeaux. For this, the maximum yield is obtained 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 painting 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 painting procedure, through which E = 94.8 % is obtained.

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

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

Chosen painting intensity standards

In order to choose the standard intensity, a scale of intensities is obtained for each sample painted with every dye using a specific procedure. In such a way, the wool and the polyamidic fibers are painted.

The IX dye: 1%, 1.25%, 1.75%, 2%

The X dye: 1.25%, 1.5%, 1.75%, 2%

The XI dye: 1%, 1.25%, 1.5%, 1.75%.

By comparison with the blank staircase of intensities, the intensity 1.25% is chosen for the IX dye, on wool and polyamide, the intensity 1.75% for the X dye, on wool and polyamide, and the intensity 1.25% for the XI dye, on wool and polyamide.

The depleation 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 painted with each dye. The painting conditions are the same for all six samples (same temperature, painting procedure and intensity). The only variable parameter is the time. First sample is let in the dye bath for 2 minutes, second 5 minutes, the others 10 minutes, 20 minutes, 40 minutes, 60 minutes, respectively. Before painting, an absorption spectrum in visible domain is made for the initial dye bath, and after painting, for every dye bath, another spectrum of absorption is made in visible. According to the Lambert – Beer Law the depleation yield is calculated. The obtained results are given in Table 8 and Table 9.

Table 8

The exhausting (tinctorial yield) [%] E for wool painting 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

The exhausting (tinctorial yield) [%] E for polyalide painting 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

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

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

Painting resistance of IX – XI dyes

The painting resistances were tested in water (washing at 40^{0}C), acidic and alkaline perspiration, in wet and dry conditions. The values for these resistances, evaluated by color changing and releasing of the companion materials, were estimated with the grey scale.

For wool and polyamidic fibers painting, the companion materials were wool and cotton. For the polyamidic fibers resistances improvement, they were treated with ROMATAN EST (anion-active resin) which is acting like a film on the fiber surface, avoiding the dye releasing. The painting resistances are given in ration books. The maximum value is 5 in all cases. It is observed that these dyes have good resistances on an alkaline or acidic perspiration (value 4 -5), and on a wet or dry friction (value 4 -5). The X dye has lower resistances on washing (value 3). The polyamidic retreated paintings have good resistances (value 4 – 5). After the application of the dyes on ethoxylated aluminium, it is observed that only the X and XI dyes are painting 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 (pH = 8 – 9). The obtained colors are intense, with the exception of the XII, XV and XXII dyes and the painting resistances are given in Table 10. It is observed a satisfactory behavior of the main of dyes on the physical agents action.

Table 10

Painting resistances 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.

Conclusions

New epichlorohydrinic reactive dyes were synthesized starting from six monoazoic dyes that were transformed into disazoic dyes with a very good yield (88 – 90%).

The obtained reactive dyes were applied on wool, polyamidic fibers and ethoxylated aluminium giving red and violet colors and having good resistances.

The obtained dyes were applied on wool, cotton and polyamidic fibers and were treated with ROMATAN EST (anion-active resin) leading to avoid the dye releasing during usage. The resistances are good to water, to acidic and alkaline perspiration and also to wet and dry friction.

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