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Disperse dyes' derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine: Synthesis and characterization

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Abstract

This paper presents the synthesis of new disperse dyes' derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine. These dyes have been characterized by elemental analysis, melting points, IR, UV–VIS and NMR spectroscopic methods. The separation and purification of synthesized compounds by TLC and HPLC methods are also presented. The tinctorial properties of obtained disperse dyes were tested upon some polyacrylic fibres by painting. A large scale of full-bodied brightness shadow was obtained, generally based on the nature of diazotized amine. The resulting paintings have very good fastness to wet treatments. The fastness to light is dependent on the structure of diazo thermal fastness by coupling agent. The relationships between chemical structures of disperse dyes and perspiration/light fastness are discussed.

Keywords: Disperse dye; Diazotizing-coupling reaction; 2-Aminothiazolo[5,4-*c*]pyridine; Spectral analysis; Tinctorial test; Acute toxicity

1. Introduction

Disperse dyes are used mainly not only for polyester, but also for cellulose (acetate and triacetate), polyamide and acrylic fibres. In general, disperse dyes are characterized by some tinctorial properties: fastness to light is quite good, while fastness to washing is highly dependent on the fibre. In particular, in polyamides and acrylic fibres they are used mostly for pastel shades because in dark shades they have limited build-up properties and poor wash fastness. Also, it is known [1] that the disperse dyes are characterized by the absence of solubilising groups and low molecular weight. From a chemical point of view more than 50% of disperse dyes are simple azo compounds, about 25% are anthraquinones and the rest are methine, nitro and naphthoquinone dyes.

The dye–fibre affinity is a result of different types of interactions: hydrogen bonds, dipole–dipole interactions and van der Waals forces. Disperse dyes have hydrogen atoms in their molecule, which are capable of forming hydrogen bonds with oxygen and nitrogen atoms in the fibre. Dipole–dipole interactions result from the asymmetrical structure of the dye molecules, which makes possible electrostatic interactions between dipoles on the dye molecules and polarised bond on the fibre. Van der Waals forces take effect when the molecules of the fibre and colorant are aligned close to each other. These forces are very important in polyester fibre because they can take effect between the aromatic groups of the fibre and those of the colorant [2].

In this paper are presented 9 disperse dyes, completely new and original. The structures of synthesized disperse dyes were studied by spectral analysis, elemental analysis and melting points. The purification

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methods such as TLC and HPLC were used. Finally, the toxicity tests for the disperse dyes were realized.

2. Experimental

2.1. Reagents

Experiments were performed using:

- sulfuric acid, 96% (Merck)
- $NaNO_2$ solid p.a.
- acetic acid glacial (Merck)
- 2-aminothiazolo[5,4-*c*]pyridine obtained by synthesis [3,4,10]
- coupling compounds: *N*-methylaniline, *N*,*N*-dimethylaniline, *N*-ethylaniline, *N*,*N*-diethylaniline, *N*-ethanolaniline, *N*,*N*-diethanolaniline, *N*-methyl-*N*-ethanolaniline, *N*-ethyl-*N*-ethanolaniline, *N*-ethyl-*N*-cyanoaniline (Fluka).

2.2. The general procedures for the preparation of disperse dyes

2.2.1. The diazotizing reaction

A mixture of ~16.8 mL water and 13 mL 96% sulfuric acid was introduced into Berzelius under stirring, by maintaining the temperature at 18–20 °C with ice and cool water. After that 0.024 mol heterocyclic system 2-aminothiazolo[5,4-*c*]pyridine, was added under stirring for 5 min; the mixture was stirred for 1 h at 18 °C, then the temperature was decreased to 0–3 °C (with ice and salt). A solution of 5.75 g $NaNO_2$ in 13.4 mL water was added on the obtained reaction mass within 45 min. The mixture was stirred for 1 h at 0–3 °C when the diazonium salt was obtained [3,5].

2.2.2. The coupling reaction

A mixture of ~2.2 mL water and ~1.5 mL 96% sulfuric acid was introduced into Berzelius at 0–3 °C and after that were added 0.02 mol coupling compounds and 23 mL acetic acid glacial. In 10 min at 5–0° C the diazonium salt was added. The reaction mass was maintained at this temperature, 1 h, under stirring.

Finally, the obtained dyes are added over a mixture of ~30 g ice and 70 mL water. The pigments were precipitated in 24 h; after that they were filtered, and washed on filter paper with hot solution of Na_2CO_3, at pH > 6 and the final compounds were dried at ordinary temperature. The disperse dyes (Fig. 1 and Table 1) were purified by recrystallization from ethyl alcohol. All dyes obtained by synthesis were purified and separated by TLC and HPLC methods [3,5].

The high performance liquid chromatography results were obtained by using an apparatus *Jasco 800* with Nucleosil® $7C_{18}$ gel permeation columns. They were considered to be the most appropriate because they allow retention times long enough for an efficient separation and do not present the colmation phenomenon for the dyes [3,7].

The thin-layer chromatography method uses: the absorbent layer silica gel, the plate material aluminum and the eluents which were chosen different for each dye (if is the case) [6].

The results obtained from purification methods by TLC and HPLC of synthesized dyes **3–11** are presented in Table 2 and the results from the melting points and the yields are presented in Table 3. The melting points were calculated with a Boetius apparatus, with microscope and heating plate, without correction.

The elemental analysis for the organic products were realized by using a Carlo-Erba M 1106 analyzer for the determination of the content of carbon, hydrogen, nitrogen and a Multi EA® 3000 apparatus for the determination of the content of oxygen and sulfur.

2.2.3. The spectral analysis

All the dyes obtained by synthesis were studied employing chemical, *UV–VIS*, *NMR* and *IR* spectroscopies confirming the structures proposed.

The *VIS* electronic spectra were performed with *Secoman S 750* apparatus in quartz cells ($l = 1$ cm) for ethyl alcohol of $c \sim 2 \times 10^{-5}$ M dyes solution. The characteristic absorbance was presented depending on the maximum wavelength (Tables 1 and 3).

The molar coefficient of extinction was calculated for these dyes, $\varepsilon_{max} = 27\,000$–$34\,000$.

The *IR* spectra were made including the compounds synthesized in KBr disks; the absorption has been measured with *FT-IR Jasco 620* Spectrophotometer.

The disperse dyes **3–11** were analyzed by *NMR* spectroscopy using *Varian Gemini 300 BB* apparatus,

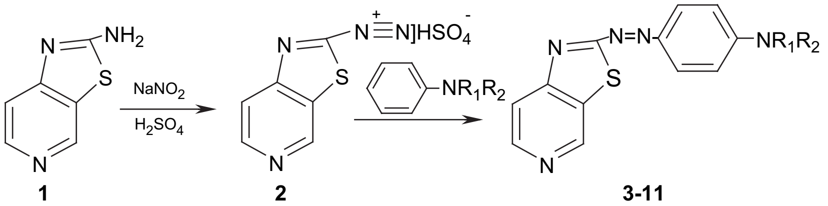


Fig. 1. The synthesis reactions of disperse dyes with R_1 = H, CH_3, C_2H_5, C_2H_4OH and R_2 = CH_3, C_2H_5, C_2H_4OH and CN in accordance with Table 1.

Table 1
Disperse dyes obtained by synthesis

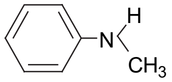
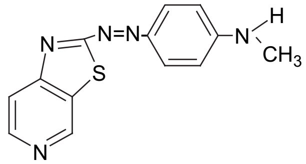
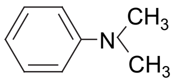
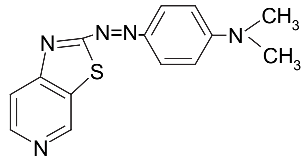
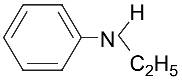
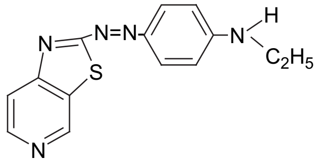
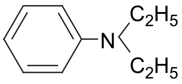
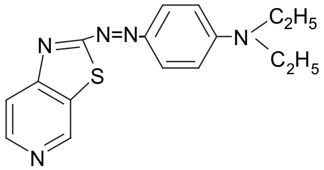
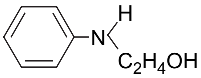
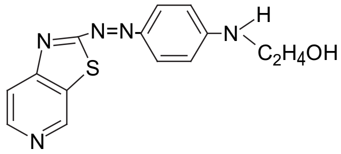
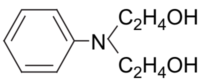
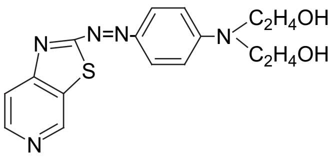
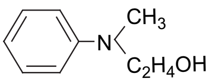
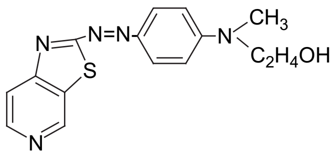
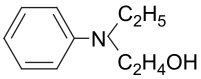
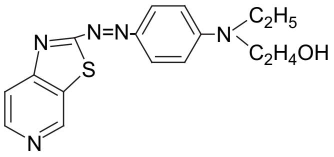
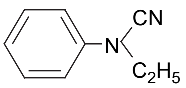
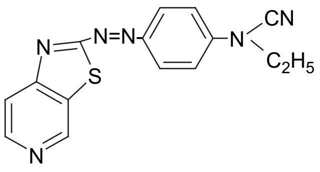
No	R_1	R_2	Colour coupler	Disperse dye	Color λ_{max}, nm
3	H	CH_3			Green-dark 614 nm
4	CH_3	CH_3			Green-dark 621 nm
5	H	C_2H_5			Green-dark 628 nm
6	C_2H_5	C_2H_5			Green-dark 643 nm
7	H	C_2H_4OH			Green-blue 646 nm
8	C_2H_4OH	C_2H_4OH			Green-blue 659 nm
9	CN	C_2H_5			Green-blue 661 nm
10	CH_3	C_2H_4OH			Green-blue 648 nm
11	C_2H_5	C_2H_4OH			Green-blue 653 nm

Table 2
The purification and separation by TLC and HPLC methods for disperse dyes

Dye	Thin-layer chromatography	HPLC chromatography
3–11	*Substratum*: silica gel F_{254} (Merck) on aluminum layer *Eluent*: acetic acid: ethanol = 90:10 (vol/vol) *Solvent*: mixture xylene (*o*, *m*, *p*); 0.01%	*Column*: Nucleosil® $7C_{18}$ *Eluent*: 1.0 mM sodium hexansulfonate + 4.0 mL concentrated acetic acid with pH adjusted to 4.0 with NaOH, after that is added methyl alcohol until at 4% concentration *Flow*: 0.8 mL/min *Detection*: 614–661 nm

Table 3
The *VIS* spectra, the melting points and yields for disperse dyes **3–11**

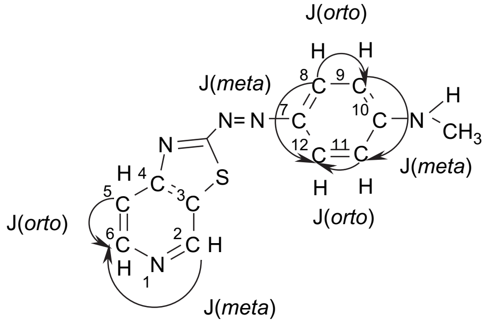
Disperse dye	Melting point (°C)	Wavelength λ_{max} (nm) (absorbance)	Yield (%)	R_f
3	250–251	614.2(1.805)	79	0.85
4	248–250	621.0(1.940)	78.5	0.73
5	247–250	628.1(1.804)	81.5	0.68
6	249–250	643.0(1.839)	80	0.62
7	250–252	646.0(1.750)	83	0.58
8	251–254	659.3(1.670)	82.4	0.40
9	249–251	661.6(1.767)	87	0.73
10	253–255	648.7(1.820)	83.7	0.60
11	251–255	653.0(1.889)	88	0.51

with frequency of registration for proton spectrum, *^1H NMR*, being 300 MHz and for carbon spectrum, *^{13}C NMR*, being 75 Hz. The purified dye was dissolved in deuterio-dimethylsulfoxide, DMSO-d_6, and the signals were reported at TMS.

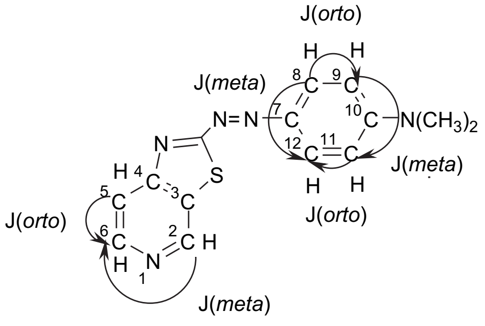
3. Results and discussions

From literature [1] it is known that the heterocyclic diazo compounds (aromatic character) can participate, without any difficulty, in the coupling reaction if the $pH < 2$ and the temperature is 0–5 °C. The second order kinetics of azo-coupling reaction and the constant of action, k, are very strongly influenced by the pH of reaction medium.

The diazotizing reaction of 2-aminothiazolo[5,4-*c*] pyridine was effected in acidic medium, the $pH \sim 0.5$; this leads to the formation of diazonium salt. At $pH > 1.2$ the instability of heterocyclic system aminothiazolopyridines diazonium salt is accentuated and the resulted secondary yellow-brown compounds can be seen very well by TLC (the chromatogram presented some impurity of diazonium salt) [3,6].



Disperse dye *3*



Disperse dye *4*

The most important aspect was the avoidance of the sodium nitrite excess in reaction mass because it can lead to nitrosation of coupler compounds. The excess of HNO_2 can be destroyed with sulfamic acid (H_2N-SO_3H) added to the reaction medium (sometimes the diazo compound can be reduced and for this reason it can be utilized with success urea).

Also, the aminothiazolopyridines diazonium salt is very unstable if the sulfuric acid concentration in reaction medium is reduced and then it can appear very easily for the substitution reaction of diazo group. The temperature of diazotizing-coupling reaction was maintained at −5–0 °C because a high temperature can lead to secondary compounds [3,8,9].

The ^1H NMR (DMSO-d_6) and ^{13}C NMR (DMSO-d_6) results for disperse dyes **3** and **4** (illustrative) are presented.

Disperse dye **3**: 7.20 ppm (1H, C_6H_3N, s, $J(2,6) = 1.90$ Hz); 7.28 ppm (1H, C_6H_3N, d, $J(5,6) = 8.10$ Hz); 7.40 ppm (1H, C_6H_3N, t, $J(6,5) = 8.10$ Hz and $J(6,2) = 1.90$ Hz); 6.83 ppm (2H, C_6H_4, d, $J(8,9) = 8.60$ Hz and $J(8,12) = 1.75$ Hz); 7.78 ppm (2H, C_6H_4, d, $J(9,8) = 8.60$ Hz and $J(9,11) = 1.75$ Hz); 2.28 ppm (3H, CH_3, s); 2.79 ppm (DMSO-d_6, s).

δ_C: 140.4; 138.9; 129.8; 126.0; 114.6 ppm for C^6, C^2, C^5, $C^8(C^{12})$, $C^9(C^{11})$; 150.1; 137.8; 136.1 ppm for carbon atoms C^3, C^4 and $C^7(C^{10})$; 20.4 ppm was attributed to the carbon atom from methyl group, CH_3.

Disperse dye **4**: δ_H: 7.22 ppm (1H, C_6H_3N, s, $J(2,6) = 2.20$ Hz); 7.30 ppm (1H, C_6H_3N, d, $J(5,6) = 7.47$ Hz); 7.47 ppm (1H, C_6H_3N, t, $J(6,5) = 7.72$ Hz and

$J(6,2) = 2.20$ Hz); 6.83 ppm (2H, C_6H_4, d, $J(8,9) = 8.61$ Hz and $J(8,12) = 1.85$ Hz); 7.78 ppm (2H, C_6H_4, d, $J(9,8) = 8.70$ Hz and $J(9,11) = 1.85$ Hz); 2.35 ppm (3H, CH_3, s); 2.28 ppm (3H, CH_3, s); 2.79 ppm (DMSO-d_6, s).

δ_C: 139.0; 137.9; 124.5; 123.4; 112.6 ppm for C^6, C^2, C^5, $C^8(C^{12})$, $C^9(C^{11})$; 145.1; 121.5; 130.0 ppm for carbon atoms C^3, C^4 and $C^7(C^{10})$; 23.9 ppm and 20.6 ppm were attributed to the carbon atoms from two methyl group.

The calculated theoretical values for the chemical shifts of the investigated protons, presented illustratively for dye **4**, are: $\delta(H^2)$: 7.16 ppm; $\delta(H^6)$: 7.37 ppm; $\delta(H^5)$: 7.82 ppm; $\delta(H^8, H^{12})$: 6.72 ppm; $\delta(H^9, H^{11})$: 7.69 ppm.

So, the chemical shifts and coupling constant, J, in ^1H NMR spectra confirm the structure of dyes proposed, in concordance with the results obtained in IR spectra.

In *IR* spectra the absorption bands proper to the vibration specific groups for each synthesized compound were identified.

- The *IR* spectra for heterocyclic system thiazolo-pyridine indicated the presence of pyridinic ring at frequencies 1550 cm^{-1} and 1770 cm^{-1} (usually at this frequency appeared the carbonyl groups, but in this case is not real). The frequency $\nu_{C=N(pyridine)}$ was attributed to the bands from 1475 cm^{-1} and 1490 cm^{-1}.
- The thiazolic ring was attributed to the frequencies 1110; 1620; 2190 cm^{-1}, in accordance with data obtained from *NMR* spectra. The identification of bands of coupling bonds C–S is very difficult due the vibrations of deformation CH in outside of the plan of pyridinic ring (the nitrogen atom challenged by $-I$ and $-E$ effect, a general impoverishment of electrons, accentuated in *2* and *4* position of pyridinic ring) than appeared in these regions [11,12]. The structure –N=C–S– was discussed for the emphasis of thiazolic ring; for this structure was attributed one band at 1480–1600 cm^{-1}; other authors attributed one band of 1300 cm^{-1} to the vibration C–N that involved a marked character of double coupling bond C=N and one low frequency for C–S.
- The $-N(CH_3)_2$ group was identified in disperse dye **4** (for example) because the absorption band for this group (especially when it is bound to aromatic ring) is one single and appears at 2865 cm^{-1}.
- The azo chromophores group, –N=N–, is characterized as faint absorptions, as small intensity, at 1540 and 1560 cm^{-1}.

The elemental analysis results were presented in Table 4.

3.1. Toxicity tests

White mice of Swiss race weighing 20 ± 2 g and white rats of Wistar race weighing 140 ± 20 g were used in batches of 20 animals (10 males and 10 females) and the dose was tested. The solutions of disperse dyes were injected as water-solutions, in a unique dose [13–15].

The animals were supervised for 14 days and the modifications in their behavior and the mortality have been registered. At the end of the testing period, biochemical determinations and anatomic–pathological exams of the rats in order to disclose possible damages to their principal internal organs were performed. The conclusions are:

1. For the maximum tolerated dose administered p.o. (per oral) and i.p. (intraperitoneal) no particular clinical phenomena or no mortality occurred. The biochemical tests applied did not show any modification compared to the witnesses. The anatomic–pathological exams of the rat at the end of the testing period do not show modifications in the principal internal organs for any dose of dyes used.
2. The studies of acute toxicity applied on 2 species and using 2 ways of administration, with solutions of 1.0, 0.1 and 0.01% of disperse dyes proved no toxicity for both p.o. and i.p. administration. Therefore, the DL_{50} could not be calculated but it was determined the maximum dose.

Table 4
Elemental analysis results for dyes **3–11**

Dye	Molecular weight	C (%)		H (%)		N (%)		S (%)		O (%)	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$\mathbf{C_{13}H_{11}N_5S}$	269	57.99	57.93	4.08	4.02	26.02	26.11	11.89	11.78	–	–
$\mathbf{C_{14}H_{13}N_5S}$	283	59.36	59.28	4.59	4.53	24.73	24.68	11.30	11.22	–	–
$\mathbf{C_{14}H_{13}N_5S}$	283	59.36	59.29	4.59	4.55	24.73	24.65	11.30	11.25	–	–
$\mathbf{C_{16}H_{17}N_5S}$	311	61.73	61.81	5.46	5.50	22.50	22.57	10.28	10.33	–	–
$\mathbf{C_{14}H_{13}N_5SO}$	299	56.18	56.24	4.34	4.39	23.41	23.37	10.70	10.63	5.35	5.41
$\mathbf{C_{16}H_{17}N_5SO_2}$	343	55.97	55.92	4.95	4.87	20.40	20.46	9.32	9.25	9.32	9.42
$\mathbf{C_{15}H_{15}N_5SO}$	313	57.50	57.57	4.79	4.85	22.36	22.27	10.22	10.17	5.11	5.03
$\mathbf{C_{16}H_{17}N_5SO}$	327	58.71	58.64	4.89	4.81	21.40	21.49	9.78	9.86	4.89	4.83
$\mathbf{C_{15}H_{12}N_6S}$	308	58.44	58.49	3.89	3.81	27.27	27.33	10.38	10.46	–	–

Table 5
The fastness[a] test of disperse dyes on polyacrylic fibres

Disperse dye	Fastness to cool water	Fastness to light	Fastness to washing at 40 °C	Fastness to acid perspiration (pH = 5.5)	Fastness to alkali perspiration (pH = 8)	Fastness to ironing	Fastness to friction
3	4–5	4–5	4	4–5	4	4–5	4
4	4–5	4–5	4	4–5	4	4–5	4
5	4–5	4–5	4	4–5	4	4–5	4
6	4–5	4–5	4	4–5	4	4–5	4
7	4	4–5	4	4	4	4–5	4–5
8	4	4–5	4	4	4	4–5	4–5
9	4	4–5	4	4	4	4	4–5
10	4	4–5	4	4	4	4	4–5
11	4	4–5	4	4	4	4	4

[a] These fastness measures were made in accordance with strength standards.

3.2. Tinctorial tests

The polyacrylic fibres are hydrophobic and contain anionic groups in their molecule. As a result, they can be dyed with disperse and cationic dyes. In this case we used disperse dyes obtained by synthesis. Dyeing with disperse dyes can be performed at temperatures below 100 °C without carriers. Furthermore, due to the good migration properties of disperse dyes, leveling agents are not required. Batch dyeing is commonly applied for cable; the pH = 4–5 by acetic acid.

Dyeing polyester fibres under atmospheric conditions (below 100 °C) was also frequently done in the past with the aid of carriers. Because of environmental problems associated with the use of these substances, polyester is preferably dyed under pressure at temperature > 100 °C without carriers. So, the dyeing technique for polyester fibres with disperse dyes obtained by synthesis, used batch dyeing at 125–135 °C, under pressure and pH = 4–5 by acetic acid. The fibres need only to be soaped after dyeing. Usually, the disperse dyes are used to produce light to medium-deep shades [3,8].

The polyacrylic and polyester fibres were analyzed on qualitative tests by estimation fastness shades with grey scale; the results were expressed by note from 1 at 5.

The perspiration/light fastness at disperse dyes increases if 2–3% colorant solution is used. This aspect determines the improvement in the dyeing fastness with ½–1 tone.

The disperse dyes' obtained from 2-aminothiazolo[5,4-*c*]pyridine colour polyacrylic and polyester fibres in green-dark and green-blue shades, with good perspiration/light fastness, good ironing fastness and friction fastness, but less good washing fastness at 40 °C (Tables 5 and 6).

The relationship between color and perspiration/light fastness test was influenced by coupler colorant (Table 1). Also the number of electrons donating group in disperse dye molecule lead to displacement of absorption maximum at greatest wavelengths and implicit at light fastness diminution. The affinity of synthesized disperse dyes depends not only on the presence of functional groups in dye molecule, but also on the dispersion degree of the dye and the fibres nature dyeing submitted.

4. Conclusions

In this work 9 new green-dark and green-blue disperse dyes, unknown in speciality literature, by classic method

Table 6
The fastness[a] test of disperse dyes on polyester fibres

Disperse dye	Fastness to cool water	Fastness to light	Fastness to washing at 40 °C	Fastness to acid perspiration (pH = 5.5)	Fastness to alkali perspiration (pH = 8)	Fastness to ironing	Fastness to friction
3	4–5	5	4	4–5	4–5	5	4
4	4–5	5	4–5	4–5	4–5	5	5
5	4–5	5	4	4–5	4–5	5	5
6	4–5	5	4–5	4–5	4–5	5	4–5
7	4	5	4	4–5	4–5	5	4–5
8	4–5	5	4	4–5	4–5	4–5	4–5
9	4–5	5	4	4–5	4–5	5	4–5
10	4–5	5	4	4–5	4–5	5	4
11	4	5	4	4	4–5	4–5	4

[a] These fastness measures were made in accordance with strength standards.

of diazotizing-coupling were synthesized. For synthesized disperse dyes were established the processed optimal parameters and also, they were purified and separated by TLC and HPLC methods. The dyes were characterized by elemental analysis, *IR*, *VIS* and *NMR* spectroscopies. The disperse dyes' derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine can be used with success in dyeing process of polyacrylic and polyester fibres because their toxicity is insignificant.

Also, these dyes were obtained in scope of their utilization in new cationic dyes synthesis with very good tinctorial properties for polyacrylic fibres and for obtaining heteropolysalts of organic bases.

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