Analysis of the properties of active dyes

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Abstract: The range of active dyes used for dyeing materials made of natural plant fibers includes about a thousand brands belonging to more than 50 groups all over the world. Among them, bifunctional active dyes are of research and practical interest. They allow to obtain intense and durable bright color scheme due to their chemical specificity. Also they save not only the dye itself, but a number of additional textile auxiliary substances, which in turn is favorably affects the environmental performance of the dyeing process. The authors present in the article the analysis of experimental data, which make it possible to obtain or verify chemical, physicochemical and coloristic indicators of the properties of mono-, bi- and polyfunctional active dyes. Conclusions are made on the dependence of these indicators in the process of dyeing textile materials according to several technologies most often used in finishing production.

1. Introduction
Active dyes, which occupy a leading position, are used for coloring textile materials from plant fibers. The widespread use of active dyes in the finishing industry is facilitated by their ability to give colors on fabrics with increased resistance to wet treatments, which is explained by their chemical structure and the possibility of covalent fixation with fiber.

Active dyes contain chromophore, which provides color characteristics of the dye, and an active group, which is responsible for the chemical bond of the dye with the fiber. Among the active groups, the most common are: halopyrimidine, vinylsulfonic, dichloroquinoxaline and halotriazine. Also new types of active dyes include bi- and polyfunctional dyes, which contain two or more identical (homofunctional) or different (polyfunctional) active groups.

Dye manufacturing companies provide only recommendations on the dyeing technology and the corresponding dyeing solution formulation. The catalogs specify only the indicators of the solubility of dyes and the stability of colors to some physical and chemical influence. There is practically no information about the behavior of individual brands of dyes, which makes it very difficult to predict their behavior in real technological conditions when changing the parameters of their use [1-3].

In addition, it is necessary to select and use very often in industries (for economic, technological and aesthetic reasons) dyes from different companies. A very acute question arises here: the possibility of their application in one dye bath, that is, their compatibility [4-10].

In this work, the properties and behavior of about a hundred brands of active dyes from different manufacturers were studied theoretically and experimentally under various dyeing conditions. In laboratory conditions, the following was determined: affinity (-Δμ); rate constant of interaction with cellulose fiber (Kcell); chemical stability in solutions of alkalis, oxidants and reducing agents. Rational
conditions for dyeing, allowing to obtain the highest rates of intensity during dyeing by periodic, pad-steam and pad-thermo-fixing methods were set.

2. Materials and methods

2.1. Determination of affinity

The affinity of the dye for the fiber is the most important property that determines the speed and degree of removal of the dye from the dye bath. When dyeing textile materials by the method of exhaustion at high temperatures, the dyes used should have an increased affinity for the fiber, and when dyeing by continuous methods - a low affinity.

In this work, the value of the dye affinity was determined by the equilibrium sorption of active dyes by cotton fiber for 5 days at a temperature of 20 °C, from neutral solutions of dyes at a concentration of 2x10^-3 mol/L and a sodium chloride content of 30 g/L (bath modulus 1: 1000).

Affinity was calculated using the formula [4]:

\[ \Delta \mu^0 = \frac{RT}{\ln C_\infty} \left( z \cdot \ln [Na^+]_p - (z + 1) \ln V - z \cdot \ln [Na^+]_p - (z + 1) \right) \left( kJ \cdot mol^{-1} \right), \]

where: R is the universal gas constant (8.306 J/degmol); T - absolute temperature (293K); \( [Na^+]_p \) - concentration of sodium ions in solution; \( [Na^+]_p \) - equilibrium concentration of sodium ions in the fiber; \( C_\infty \) - the content of the dye in the fiber in the equilibrium state; \( V \) is the effective fiber volume (0.3 l/kg); \( z \) is the number of sulfogroups in the dye molecule.

2.2. Determination of the reaction rate constant (reaction activity)

Reaction activity with cellulose is a specific property of reactive dyes. On the one hand, highly reactive dyes can be quickly fixed on the fiber even at low temperatures, and on the other hand, such dyes are easily hydrolyzed, which reduces the degree of their fixation on the fiber.

The rate constant of interaction of dyes with cellulose fiber was determined from the kinetic curve of dye fixation during steaming. Seven samples of fabric were impregnated with dye solutions for 2-3 seconds (the content of dyes and sodium carbonate in dye solutions, 20 g/l) and one sample - with a solution containing only dye. The samples were steamed at a temperature of 100 °C for 1, 2, 3, 5, 10 and 25 minutes, washed (hot water and surfactant solutions) and dried. Based on the colorimetry of the obtained series of samples, the curves of the dependence of the color intensity on the duration of fixation were constructed.

The rate constant of interaction of dyes with cellulose was determined using the Beckman formula [5]:

\[ K_{cell} = \frac{\Delta C}{\Delta t [Scl]}, [min^{-1}], \]

where: \( K_{cell} \) is the constant of the rate of interaction of the dye with cellulose fiber; \( \Delta C \) is the amount of covalently fixed dye during the time \( \Delta t \), mg/g; \( \Delta t \) - time, min; \( [Scl] \) - concentration of the active form of the dye, substantively bound to the fiber, mg/g.

The content of the dye sorbed by the fiber during impregnation (C0) and fixed by the fiber for 1 minute (C1) was determined by the acid hydrosol method. The concentration of the active form of the dye under study (SCl) was determined as the product of the sorbed dye (C0) on the content of the active form of the dye in the technical powder.

2.3. Determination of the tendency to hydrolysis

Active dyes due to their chemical structure and the presence of active groups are able to easily interact with water (hydrolyze), which in turn leads to a decrease in the degree of fixation of the dye on the fiber.

The determination of the tendency of dyes to hydrolysis was carried out by analyzing the dyeing ability of dyes after their partial hydrolysis. Partial hydrolysis of dyes was carried out by adding sodium
hydroxide in increasing concentrations to dye solutions, followed by boiling these solutions from 30 sec to 30 min. The pH~10.5 was equalized and dyeing was carried out according to the pad-steam and pad-thermo-fixing methods.

In the steam method, the dye forms bonds with the fiber only due to highly and medium reactive groups; and with the thermo-fixing method - due to any active groups. This method makes it possible to separately analyze the hydrolysis resistance of groups with different accessibility.

The hydrolysis rate constant (Kg) was calculated by the formula:

\[ Kg = \frac{\Delta C}{\Delta t \cdot C}, [min^{-1}] \]

where: \( \Delta C/C \) - decrease in the degree of fixation of the dye on the fiber due to the hydrolysis carried out during \( \Delta t \) time.

2.4. Determination of the composition of dye solutions

The optimal content of TVV in the dyeing solutions was determined by dyeing cotton fabrics (twill) in laboratory dyeing installations using standard periodic and continuous methods. In the dyeing solutions, the type and concentration of alkaline agents were varied: the concentration of sodium bicarbonate and sodium carbonate was changed from 2 g/l to 35 g/l, sodium hydroxide 32.5% from 0.1 to 20 ml/l. In periodic dyeing, the bath modulus was set to 1: 2.5 and 1:10. When dyeing by the pad-steam method, the steaming temperature was 100-102 °C, with the pad-thermo-fixing method, the hot air temperature was from 150 to 180 °C. Dyeing was carried out at a concentration of dyes: 1, 2, and 4% by weight of the fabric (periodic method) and 5, 20, and 40 g/l (continuous methods).

3. Results and discussion

Figure 1 shows the values of the affinity and rate constants of interaction with cellulose fiber dyes belonging to six groups: I - dichlorotriazine (active with the "X" index), II - vinyl sulfone (active with the "T" index), III - monochlorotriazine (active without index); and bifunctional: IV - LS cybacrons, V drimerens HF and VI - tsemaktiv BF - HF drimarens and VI - BF cement assets.

![Figure 1. Indicators of the affinity and accessibility of reactive dyes in relation to cellulose fibers.](image_url)

It can be seen from figure 1, each group of dyes is represented by a wide range of values of affinity and reaction activity. Dichlorotriazine dyes are close in terms of reaction activity, but differ significantly in affinity; vinyl sulfone dyes, on the contrary, have low affinity values, but differ significantly in
reaction activity. The studied groups of bifunctional active dyes are similar in properties to vinyl sulfone, although some brands have high reaction activity (usually black) or high affinity (dark blue). The highest affinity values are for HF drimarens, on the whole, somewhat lower for BF tsemactivs and LS cibachrons.

The level of reaction activity in dyes is maintained across all applications, so this indicator can be used to predict dyeing conditions in ways that were not described in the company catalogs. Table 1 shows the concentration of alkaline agents recommended for dyeing materials of cotton fiber according to the periodic, pad-steam and pad-thermo-fixing methods.

Table 1. Concentrations of alkaline agents in dye baths for dyeing cotton fabrics in medium tone (g/l, ml/l).

| Characteristics of the dyes | Method of dyeing         |
|-----------------------------|---------------------------|
| Activity of the reactivity | Periodic                  | Plusone-zaparno | Plusone-thermo-fixing |
|                             | I          | II         | I        | II        | III       | I       | II         |
|                             | the tempera- | Na₂CO₃     | Na₂CO₃+  | NaOH     | NaHCO₃   | Na₂CO₃  | NaOH       | NaHCO₃   | Na₂CO₃  |
|                             | ture of the  |            | 32.5%    |           | 32.5%    | 32.5%   | 32.5%     | 32.5%    | 32.5%   |
|                             | dyeing      |            |         |           |         |         |           |         |         |
| 1 high                      | 40°        | 10-15      | -        | -        | 5        | -       | -         | 10       | -       |
| 2 high                      | 40°        | 15-20      | -        | -        | 10       | -       | -         | 15       | -       |
| 3 high                      | 40°        | 20-25      | -        | -        | 15-20    | -       | -         | 20       | -       |
| 4 average                   | 60°        | -          | 5        | 0.2-0.5  | 5        | -       | -         | 10       | -       |
| 5 average                   | 60°        | 15         | -        | 20-30    | -        | -       | -         | 13-15    | -       |
| 6 average                   | 60°        | 20         | -        | 30-35    | -        | -       | -         | 15-17    | -       |
|                             | 60°        | -          | 5        | 1.5-2.5  | -        | -       | 5-10      | -        | 18-20   |
| 7 moderate                  | 60°        | 25-30      | -        | -        | -        | -       | 10-15     | -        | 20-22   |
|                             | 60°        | 25-30      | -        | -        | -        | -       | 10-15     | -        | 20-22   |
|                             | 80°        | -          | 5        | 3-4      | -        | -       | -         | 20-22    | -       |
| 8 moderate                  | 60°        | 4-5        | -        | 1.8-2    | -        | -       | 25-30     | -        | 23-25   |
|                             | 80°        | 20         | -        | 1.8-2    | -        | -       | 25-30     | -        | 23-25   |
| 9 low                       | 80°        | 20-30      | 1-2      | -        | -        | -       | -         | -        | 25-30   |
| 10 lowest                   | 80°        | 25-30      | 3-6      | -        | -        | -       | -         | -        | 30      |
The table shows the optimal concentration of sodium bicarbonate, sodium carbonate, caustic soda (32.5%) or their mixtures for dyeing into medium tone. When dyeing according to the periodic method: dye concentration - 2%, bath modulus M = 1: 2.5; dyeing temperature T = 40 °C, 60 °C or 80 °C. When dyeing using the pad-steam method: the concentration of the dye in the dye bath is 20 g/l, the steaming temperature is 102-105 °C, the steaming time is 2 minutes. When dyeing by the pad-thermo-fixing method: the concentration of the dye is 20 g/l, the fixing temperature is 160-170 °C, the fixing time is 1.5-2 minutes.

The average indicators of the rate constant of hydrolysis determined during dyeing by the steam method are presented in table 2.

### Table 2. Average values of hydrolysis rate constants of active dyes.

| Kinds                      | Subgroups         | Groups           | Hydrolysis rate constants, min⁻¹mol⁻¹ | Ch⁺max | Ch⁻ | Ch⁺ap | Ch⁻ap | Ch⁺min/Ch⁻ap |
|----------------------------|-------------------|------------------|---------------------------------------|--------|-----|-------|-------|--------------|
| Mono-functional dyes       | Highlyreactive    | Active X         | 0.60                                  | 0.22   | 1.00| 0.35  |       |              |
|                            | Mediumreactive    | Active T         | 0.46-0.57                             | 0.33-0.62| 0.77-0.95| 0.37-0.46|       |              |
|                            | Lowreactivity     | Activewithoutanindex| 0.24                                  | 0.31   | 0.40| 0.88  |       |              |
| Bifunctional dyes          | Heterobifunctions| Tsemaktiv        | 0.40                                  | 0.31   | 0.82| 0.43  |       |              |
|                            |                   | Drimarene        | 0.50-0.53                             | 0.18-0.29| 0.83-0.88| 0.40-0.42|       |              |
|                            |                   | Cibachrone       | 0.38                                  | 0.23   | 0.55| 0.64  |       |              |

Monochlorotriazine dyes are the most resistant to hydrolysis, dichlorotriazine and vinyl sulfone dyes are the least stable.

The values obtained in the course of the experiments were compared with the values of the dyes basic properties indicators. As a result of the mathematical processing of experimental data, approximate indicators of the significance of the properties of dyes (the degree of the corresponding indicator in the formula for the dependence of the intensity of the color on the indicators of properties) were determined when dyeing cellulose-containing materials by periodic and continuous methods.

In the work, the studied active dyes were divided according to the values of affinity - into 5 levels and according to the values of reaction activity - into 10 groups (figure 1).

Dyes with high affinity values allow for a more intense color with a periodic dyeing method; at the same time, dyes with low affinity values guarantee better color uniformity, although they require higher temperatures or electrolyte concentrations. Low reactive dyes with low affinity values (group III) are recommended mainly for printing; and those with higher affinity values are more suitable for dyeing by the pad-thermo-fixing method.

Table 3 shows the significance of the main indicators of dyes for all dyeing methods. When using the selection method, the most important indicator is the resistance of dyes to hydrolysis. In continuous dyeing methods, especially in pad-drying-thermo-fixing, the significance of this property on the dyeing results falls. Also, in these dyeing processes, the dye affinity and reactivity are reduced.

### Table 3. Significance of indicators of properties of active dyes in various dyeing technologies.

| Properties          | Method of dyeing |
|---------------------|------------------|
|                     | Periodic         | Plusone-zaparno | Plus-drying-steaming | Plusone-thermo fixation |
| Reactivity          | 1.0              | 0.9             | 0.7                  | 0.4                      |
| Resistance to hydrolysis | 1.4            | 0.8             | 0.5                  | 0.2                      |
| Affinity            | 1.0              | 0.6             | 0.5                  | 0.6                      |
The use of dyes with different affinity in the same dyebath can lead to uneven colors along the length of the lot and to the decrease in the selectivity of the least significant dyes. If the dyes have different reaction activity, then such a composition will give unstable, non-reproducible colors, giving different shades at the slightest fluctuations in the technological conditions of their use.

From those groups in which dyes have a wide range of properties, it is possible to select brands suitable for various coloring methods: from dyeing by exhaustion to printing. These groups include, for example, Russian active dyes with the "T" index. On the other hand, not all dyes in such groups can be considered compatible in coloring processes.

Dyes belonging to the same group or to the closest two groups can be considered compatible: they give reproducible, even colors; there are general optimal dyeing conditions for dyes. Brands of dyes belonging to the same group, and at the same time known in practice of dyeing as incompatible, may be an example. As can be seen in Figure 1, active golden yellow 2KX (#2) and active bright blue KX (#5) (from Group I) differ significantly in terms of affinity; when they are used in one dyeing bath in periodic and pad-steam dyeing methods, the color is very often uneven. Active black 4CT (No. 14) and active yellow light-resistant 2CT (No. 2), belonging to the group of vinyl sulfone with the T index (group II), differ greatly in reaction activity; this pair of dyes produces the most unrepeatable, unstable colors.

At the same time, Figure 1 shows that many groups of dyes have overlapping areas; dyes found in such areas can be used for dyeing in one dye bath.

Thus, using the presented table 1 and the exact data on the optimal concentrations of alkaline agents for one group of dyes, it is possible to determine the conditions for dyeing by these dyes using two other methods. It is necessary to clarify that this work was not aimed at assessing all the advantages and disadvantages of the range of active dyes. So, it has not yet determined such important indicators as smoothing and coloring ability, extinction coefficient, tendency to hydrolysis, compatibility of dyes in groups, sensitivity to changes in dyeing conditions and, finally, economic characteristics.

4. Conclusions
The ratio of the main physicochemical, chemical and technological properties of active dyes has been determined. The investigated active dyes were distributed by levels in accordance with the values of
their main indicators, which will make it possible, in practical application, to select dyes from different groups and classes, and different manufacturers for their use in one dye bath. c) The optimal concentrations of alkaline agents have been determined, which will allow using the obtained summary data and bearing in mind the dyeing conditions for at least one of the presented methods, to determine the dyeing conditions for these dyes by other methods.

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