

Intensifikators Increases of Fixing of Dyes

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Abstract

In the article it's investigated the possibility of producing high-quality color on natural silk by reactive dyes using intensifiers which contain heterocyclice tertiary amine, in order to increase the permeability (availability) of the fibers relative to the dye, the dye diffusion into the fiber. It's revealed the increase in efficiency of using reactive dyes for dyeing in the presence of an enhancer, the degree of dyes utilization increases by10-14%, the rate of dyeing. It's offered the mechanism which shows how the intensifier acts on dyeing process.

Keywords: Intensifier, fiber, natural silk, reactive dyes, fixation catalyst, functional groups, dyeing, oligomer, sorption, desorption, concentration.

Introduction

Excipients intensifying the fixation dyes, accelerate the diffusion of the dye into the fiber by reducing the affinity of the dye to the fiber, improve permeability (accessibility) of the fibers relative to diffusible dye by swelling or rupture of intermolecular bonds, increase the dispersion of the dye, catalyst, speed up the chemical transformations of the dye underlying the fixing dyes.

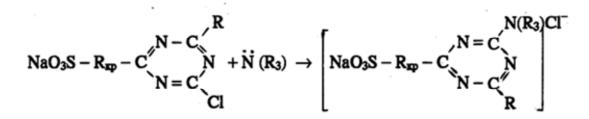
It's been studied and uses in practice catalysts for monochlortriazine reactive dyes (MChTA) for coloring the products from cellulose fibers [1]. Tertiary amines are more effective enhancers in dyeing products from cellulosic fibers by MChTA dyes that increase the electrophilic of the carbon atom of the active site of the dye. The best results provide a non-symmetric dimetyl hydrazine and cyclic trietilendiamine. It's shown the accelerating effect of trietanolamine in dyeing products made of viscose and polyamide fiber by chlorpiridinie dyes. It's effectively to use enzyme preparations of cellulolytic action in the technology of the final softening trim of linen and semi-linen bleached and dyed fabrics [2]. Infusion of flame retardancy to textile fabric made by modification by phosphorous-containing compounds [3]. It was found that low-temperature dyeing of wool by acid and reactive dyes with using concentration as intensifiers redokssistem (0.0075 ... 0.0600) mol/l contributes to obtaining stronger and more intense colors [4-6]. The theoretical backgroundsfor finding substances, that intensifies the process of dyeing of wool materials at a lower temperature, lies in the fact that these substances must either increase the accessibility of the fibers or to activate the dye, and the better - act in the indicated directions simultaneously. For this purpose it can be used redox systems [7]. Using intensifiers allows you to shorten the duration of dyeing, reduce the fixing temperature, the use of MChTA-dyes in periodical and plusine-impregnation ways to print cellulosic materials by these dyes, to eliminate the process of steaming, facilitate the subsequent washing [1].

Result and Discussion

The role of intensifiers is to increase the reactivity of the dye by increasing the positive charge in the atoms participated in the formation of a covalent bond with the functional groups of the fibers. The positive charge on the reaction center of the dye may be increased by replacing the halogen on the



quaternary ammonium group. In practice, this way is implemented with insertion into the bath as enhancers of certain tertiary amines:



The quaternary ammonium salt of the dye

Positive state of charge in the area of atoms C and Namplifies the displacement of the electron pair towards Cl increases. Due to the fact that the reaction mechanism of reactive dyes with cellulose, proteinaceous and polyamide fibers are identical, the tertiary amines may be used as intensifiers also for natural silk. It's explored the possibility of intensifying the process of dyeing of natural silk with reactive dyes by certain substances containing a hetero cyclic tertiary amine.

Dyeing process was carried with active bright red 5 SCh under the following conditions: dye - 0.5 g/dm³, acetic acid (98%) - 1.6 g/dm³, intensifier - 3 g/dm³, dyeing time - 60 minutes, dyeing temperature - 60° C, the bath module - 1:50. After the dyeing it should follow the thorough washing to remove the adsorbed dye. The obtained data is presented in table 1.

Name TAS	Quantity of dye on a fiber		
	g/kg	%, of using	
Benzimidazol	15.5	62.0	
Epychlorgidrinbenzimidazol	16.5	66.0	
Without the catalyst	13.0	52.0	

Table 1 Influence of nature intensifications on degree of using active bright red 5 SChj

From the results shown in table 1. It can be seen that the degree of utilization of the dye in the presence of intensifiers increases on 10-14%. The mechanism of the catalytic action of the studied textile auxiliaries can be explained by the structural features of the heterocyclic - imidazole, which is a part the molecule. Imidazole core represents a closed system with conjugated double bonds and has aromaticity. Easily movable single π -electron cloud of thering is displaced towards nitrogen connected with carbon by double bond.

Apparently, benzimidazole and also oligomer obtained on its basis, and also epichlorhydrin react with active bright red 5SCh, forming a more reactive complex with the quaternary nitrogen. Imidazole and its derivatives easily form hydrogen bonds, therefore they formmolecular association. Benzimidazole can form a complex with silk in solution with dyes, binding by hydrogen bonding by uncharged amino groups of the fiber. Procrastination of a proton from nitrogen of an amino group of silk raises its nucleophilicity, thereby accelerating reaction: dye-fiber





It has been studied the kinetic of silk dyeing process by active bright red 5SCh with and without an addition of an intensifier - oligomer - epychlorgidrinbenzimidazol (fig. 1). As can be seen, the rate of dyeing increases in dyeing in the presence of the intensifier, the number of fixed-dye silk is sharply increases with increasing duration of the process.

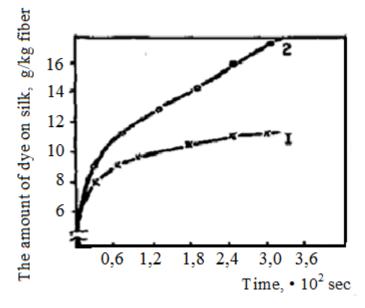


Fig. 1.Kinetic process of the dyeing of silk by active bright red 5SCh - 0,5 g/dm³, temperature - 85°C: 1 - without the catalyst 2 - in the presence of the catalyst, 3 g/dm³

It is also possible to increase the efficiency of the silk dyeing process with reactive dyes by the creation of conditions, which conducive to the maximum sorption of the dye by fiber. According to the accepted theory of fixation reactive dyes, the sorption of the dyeby fiber is a mandatory stage, preceding the true chemical reaction. The role of the sorption consists in the location of dye molecules in close proximity and in favorable steric position to the active centers of fiber, which they will then react with [1, p.53]. Deformation of the electron cloud of the dye molecule happens when dye sorption by fiber occurs, and it goes into a state similar to the state of the active by catalyst complex, which is more reactive and easily enters in the subsequent reaction with the fiber, than the dye molecule in adsorbed condition.

In order to improve efficiency of using of the dye and increasing of intensity of dyeing on silk, it was conducted researches at the possibility of increasing the sorption of the dye by fiber. When silk is dyed withacid dye baths, an anionic dye is sorbed on active centers of the fiber with the forming of a monolayer, that is, there is a Langmuir character of sorption, which is realized by ionic bond.

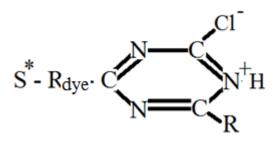
The quantity of sorbed dye will be proportional to the number of amino groups of ionized silk, whosevalue will increase with a decrease of pH-dyeing solution. The research of the effect of concentration of acetic acid on degree of using bright red 5SCh and durability of dyeing were performed with dyeing of silk samples according to the following regime: dye -0.5 g/dm³, the concentration of acetic acid varied in limits - 1-20 g/dm³, dyeing temperature - 60°C, dyeing time -1 minute.

Flushing in sodium bicarbonate solution (Na_2CO_3) with concentration of 1 g/dm^3 , temperature of 25°C and during 10 minutes follows then, Flushing in a sulfanol solution - 2 g/dm³ for 20 min., at a temperature of 95°C and 2 times in cold water. The number of fixed dye was determined by the method of A.I.Sokolov,by dint of colorimetry of sulfuric acid solutions of colored fibers. The results are shown in table 2.

The concentration of	Quantity of dye on a fiber		durability of color in	
acetic acid g/dm ³	g/kg	degree of using of dye, in %	points	
1	6.4	25.6	5/5/4	
5	9.4	37.6	5/5/4	
10	10.2	40.8	5/5/5	
15	13.6	54.4	5/5/5	
20	20.8	89.2	5/5/5	

Table 2 Influence of concentration of acetic acid on degree of using of active bright red 5SCh.

As it's seen from the results shown in table 2, the amount of dye on the fiber increases with increasing of the acid concentration. Increasing of the fixation of the dye on silk is a consequence of increasing of sorbed its amount, also it happens by the addition of heterocycle to the nitrogen, and thereby by its electrical attracting action:



Uncharged amino groups participate in the covalent fixation of reactive dyes with silk. Therefore, it is advisable to conduct the alkali treatment aftercompletion of the sorption of acidic dye baths. Recharging of protein fibers happens at this treatment, ionic bonds between the dye and the fiber break, and conditions are created for the completion of the chemical reaction of fixation. As a result, part of the dye desorbs in solution, enter electrolyte in alkaline solution to decrease it's desorption.

In order to determine the optimal concentration of the electrolyte, dyed silk in dye bath with compound: active bright red 5SCh– 1,5 g/dm³, acetic acid – 2,5 g/dm³, electrolyte - 10 g/dm³, for 10 min. at 80°C, is treated with a solution of soda with concentration of 1 g/dm³ with an additive 0,5,10,15,20,25 g/dm³ NaCl, treatment temperature 20-25°C, time -10 min. Liquor in the dyeing process and during subsequent processing is 1:50. Then the samples are treated with a solution of sulfanol - 2 g/dm³ at reflux for 2 times during 10 min., flushing with hot and cold water for 5 minutes. The amount of immobilized dye is determined by the residual bath. The results are presented in figure 2.

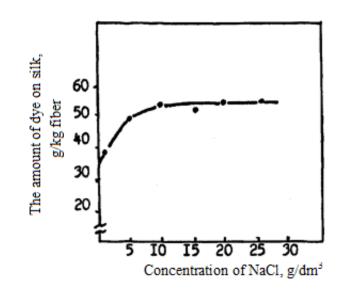


Fig.2. The influence of electrolyte concentration in the compound of the alkaline solution on fixation of active bright red 5SCh on silk.

Apparently from figure 2, amount of the fixed dye increases to concentration NaCl- 10 g/dm³, and the growth is 20 g/dm³. Thus, based on these results, we recommend to add electrolyte NaCl in alkaline solution of 10 g/dm³.

Conclusions

It's developed an effective technological regime of dyeing with reactive dyes in the presence of etilenchlorgidrin. It's found an increase in the degree of utilization of dyes from 4.2 to 50% due to the additional fixation of sorbed part of the dye. It's proposed themechanism of action of etilenchlorhydrin on the dyeing process. Comparing the color characteristics of samples,dyed with reactive dyes from dye solutions containing etilenchlorgidrin and without it, show that the change of the color tone is not essential and is $0 \div 3$ nm, color intensity for all dyes increases, color variation improves, smoothness dyeing and color purity, except black W [8].

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