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Kinetics of the Wool Chroming Process over Formation of Dyestuff Complexes

Abstract
The dyeing of wool with chrome-developed acid dyes is accompanied by the ejection of great quantities of three- and six-valent Cr-ions into the wastewater. This is in contravention of environmental protection regulations, and leads to the decreased application of wool dyed with such dyestuffs. The present work reports a study of the chroming process in presence of the sodium salt of dodecylbenzenesulphonic acid, which facilitates the dye-chrome complex formation. The quantity of residual six-valent Cr-ions in the bath decreases significantly when chroming according to the 50%-rule, while in the case of chroming with smaller amounts of $K_2Cr_2O_7$, it goes down almost to zero. A further evidence of this additive's positive effect is provided by the kinetic characteristics of the process in its initial step.

Key words: *chrome-developed acid dyes, effect of additives on chroming, kinetics of chroming.*

Introduction

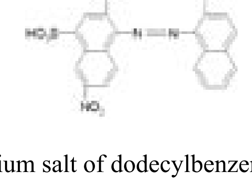
The dyeing of wool with chrome-developed acid dyes has been widely discussed. The advantages of these dyes in colouristics, especially in the cases of black and intensive colour shades, are well known. However, the technological procedure includes subsequent chroming which results in the ejection of great quantities of Cr-ions into the wastewater, a process which is subject to rigid limitations in all European countries. It has been found [1,2] that a significant decrease in the amount of three- and six-valent Cr-ions in the wastewater is achieved by working at low pH values (from 3.4 to 3.6) and with a stochiometrically calculated quantity of $K_2Cr_2O_7$. The first restriction connected with the introduction of greater amounts of H_2SO_4 or HCl affects fibre destruction, while the exact determination of $K_2Cr_2O_7$ quantity is not always possible. The effect of a number of mono- and dicarboxylic acids such as malic, tartaric, citric, lactic, oxalic, maleic acids etc. on the reduction of six- to three-valent Cr-ions has been studied [3]. According to Langman [1], the concentration of Cr-ions in the wastewater can be decreased by decreasing the $K_2Cr_2O_7$ concentration in the chroming bath; however, additional measures are required to exclude the retention of dichromate ions in the wool. The latter can be achieved through the addition of anions to the bath. They are able to block all positively charged groups in the wool which had been left unchanged during the dyeing procedure. The affinity of these anions should be close to that of the dichromate ion. The concepts just outlined have been used in developing a method for dyeing with subsequent chroming in the presence of Na_2SO_4. The concentration of Cr-ions in the wastewater can be brought down to a half or even one-third of its value following the 50%-rule [2]. There are a large number of papers [4-6] concerning the dyeing of wool with chrome-developed acid dyes and the corresponding possibilities for application; in contrast, very few deal with the kinetics of the process.

The present investigation is aimed at revealing the effect of the sodium salt of dodecylbenzenesulphonic acid (DDBS) on the kinetics of chroming which follows the dyeing of wool with Tomanolovo black AFD. Preliminary experiments [7] have shown that this additive facilitates the chroming process.

Experimental

Materials used

- Wool top of 60th quality;
- Tomanolovo black AFD (1:1):



- Sodium salt of dodecylbenzenesulphonic acid:

- Sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$);
- 1,5-diphenylcarbazide (C_6H_5-NH-NH-CO-NH-NH-C_6H_5);
- Potassium dichromate ($K_2Cr_2O_7$).

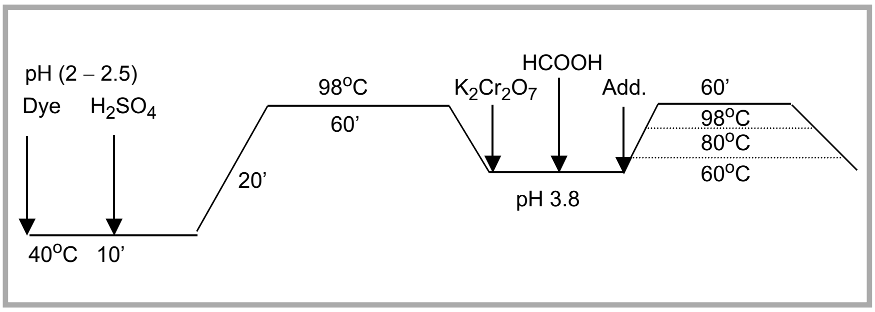


Figure 1. *Technological scheme of the dyeing.*

Procedure

5% dyeing with Tomanolovo black AFD of wool top was carried out at a 1:40 ratio in accordance with the technological scheme presented in Figure 1. The choice of the dye used in this investigation is determined by the following factors: on one hand, black, brown and dark blue dyes form usually metal complexes, while on the other only single representatives of the acid dyes provide these colours. The chrome-developed dyes give colours of higher resistivity towards water treatment, and especially towards light, when compared to acid dyes. This is due to the insertion of substituents to the keratin group into the metal complex. Other dyes have been studied as well, and the results obtained will be the subject of further publications.

The dyeing was followed by a temperature decrease to 333K. Half of the bath content was thrown away, and an equivalent quantity of water heated to 333K (or to 353K and 371K, respectively) was added. Next, solutions of $K_2Cr_2O_7$ and of the corresponding additive were also introduced. The pH value was adjusted to 3.8 by adding HCCOH. This value was chosen because it was found by us to be most suitable one for complex formation. Moreover, HCOOH is an effective reducing agent in respect to the required transformation of Cr-ions. No Na_2SO_4 was used during the dyeing procedure at this stage, because no irregular colouring was expected in the case of dark shades.

The chroming was carried out with 17%, 34% and 50%-presence of $K_2Cr_2O_7$ in reference to the dye mass. These quantities corresponded to 0.003 kg, 0.006 kg and 0.009 kg of Cr-ions respectively in reference to each kg of woollen fibres. The 50%-rule of chroming means that the $K_2Cr_2O_7$ quantity should be one-half of the dye mass, which in fact exceeds the stoichiometric mass. This old rule is found in some company cartels for chrome-developed dyes. The presence of 34% of $K_2Cr_2O_7$ corresponds to the stoichiometric quantity calculated in respect to Tomanolovo black AFD. The molar mass of the latter is 439.39 g mol^{-1}, while that of $K_2Cr_2O_7$ is 294.22 g mol^{-1}. The dye-chrome complex formation requires one molecule of the dye and one Cr-atom, which comes from $K_2Cr_2O_7$. Hence one half of the latter, i.e. 294.22/2=147.11 g mol^{-1} should be provided for the stoichiometric ratio. Then, in the case when 100 g of dye takes part in the complex formation, 33.48 g or 33.48% of $K_2Cr_2O_7$ will be required. The dye used was of 100% purity, and no correction of the amount calculated was introduced. No reliability percentage was used either. The values of $K_2Cr_2O_7$ quantity were chosen with the intention of elucidating the effect of the stoichiometric quantity, of a quantity higher than that (50%) and another one less than that (17%) of the colour characteristics of the samples dyed, on some physicochemical terms, as well as on the Cr-ions amount in the wastewater. The complex formed is of the type presented in Figure 2.

The aim of introducing anionic additives such as Na_2SO_4 and DDBS is to block most of the positively charged groups in the wool which are left free during the chroming procedure, and hence to hamper the deposition of dichromate ions there. The presence of a lower amount of Cr-ions in the bath and the blocking of the protonated amino groups presumes better interaction between the dichromate ions and the wool.

The exhaustion of Cr-ions was followed at 333K, 353K and 371K, correspondingly in the presence of 10% DDBS, 10% Na_2SO_4, and in the absence of any additive respectively. The DDBS concentration was determined in preliminary experiments. The temperature values were chosen in agreement with the fact that the reduction of six - to three-valent Cr-ions proceeded at temperatures higher than 333K. Moreover, the ions obtained participate in the complex formation [6]. This particular complex determines the high resistivity of the material towards water treatment. The quantity of the exhausted Cr-ions was estimated by the difference between the introduced and the residual six-valent Cr-ion concentration. The determination was carried out with diphenylcarbazide through colorimetration of the solutions at 540 nm. The kinetics of the exhaustion process were studied, and the corresponding kinetic curves were followed.

Results and Discussion

The concentration of Cr-ions in the bath decreases because of the formation of a complex with the dyestuff. This proceeds over approximately 30 min. An equilibrium value is then reached. The kinetics of the complex formation reaction can be followed, providing a proper kinetic variable is chosen. In this study, the quantity of Cr-ions exhausted from the woollen fibres is used as a kinetic variable. It is designated by *c* and is expressed in kg of Cr-ions per kg of woollen fibres. Its variation with time was followed at all the temperature values studied. Figure 3 show the kinetic curves obtained in the case of Cr-ion exhaustion in the absence and presence of additives at 371K. The form of the corresponding curves referring to temperature values of 333K and 353K is similar.

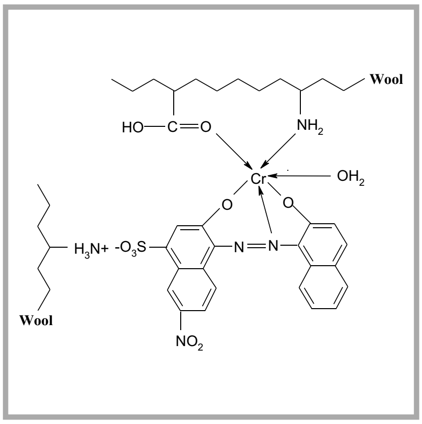


Figure 2. *The dye-chrome complex formed.*

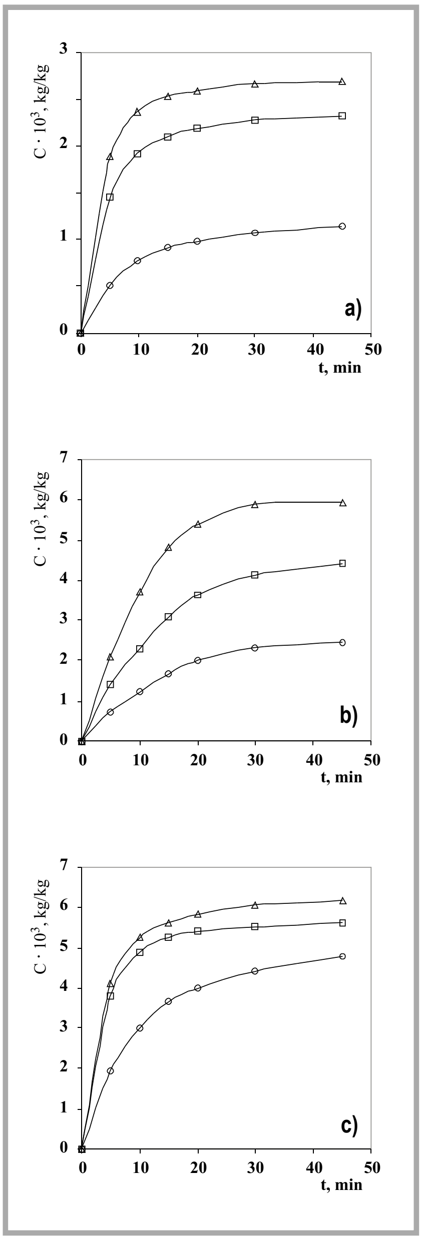


Figure 3. Kinetic curves obtained in the study of Cr-ion exhaustion from woollen fibres dyed with Tomanolovo black AFD; chroming at 371K: a - with 17% of $K_2Cr_2O_7$; b - with 34% of $K_2Cr_2O_7$; c - with 50% of $K_2Cr_2O_7$; o - without an additive, □ - in presence of sodium sulphate, △ - in presence of DDBS.

It is found that the complex formation can be described by an exponential kinetic equation of the type:

$$v = v_o \exp(-\chi c) \quad (1)$$

where:
v_o - the initial rate,
χ - a kinetic coefficient characterising the inhomogeneity of the surface [8].

Its approximate integral form is derived by taking into consideration that

$$v = -dc/dt,$$

$$c = \chi \ln(v_o/\chi) + \chi \ln t \quad (2)$$

Table 1. Values of the kinetic coefficient χ calculated on the basis of data obtained in the presence of different concentrations of $K_2Cr_2O_7$ at different temperatures in the absence and presence of additives (Na_2SO_4, DDBS).

$K_2Cr_2O_7$ concentration, %	Temperature, K	$\chi \cdot 10^4$		
		In absence of an additive	In presence of Na_2SO_4	In presence of DDBS
17	333	2.8	3.6	6.5
	353	3.4	7.2	8.2
	371	3.6	8.2	8.6
34	333	7.7	11.4	15.2
	353	9.6	13.5	18.5
	371	10.0	15.0	20.0
50	333	12.5	14.0	16.1
	353	13.0	15.6	19.3
	371	13.8	17.4	20.2

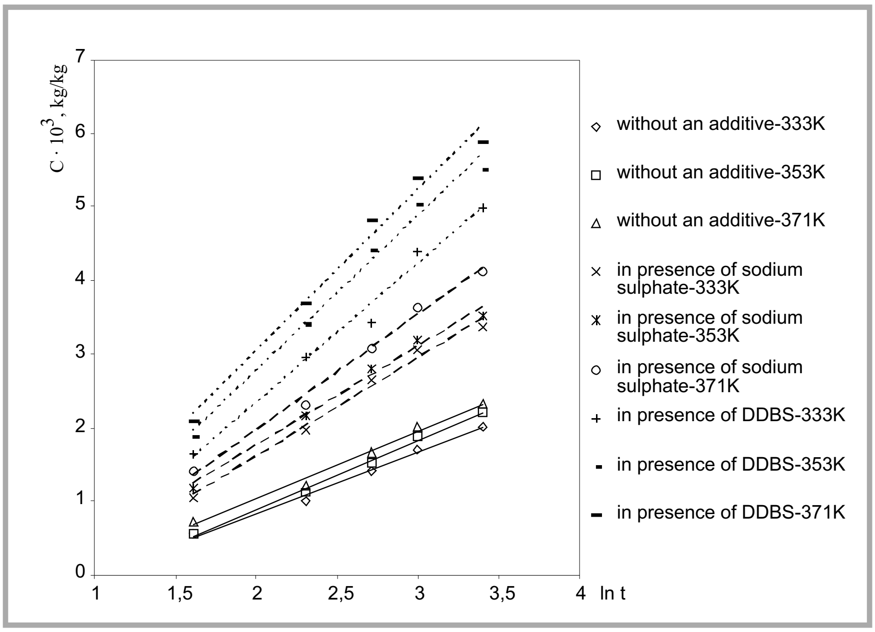


Figure 4. Plots of the exhausted Cr-ion concentration vs ln t during chroming with 34% of $K_2Cr_2O_7$.

All the experimental data obtained agree with equation (2). This is verified by the linear plots of c vs. ln t. Some of these, referring to the experiments with 34% concentration of $K_2Cr_2O_7$ at all temperatures studied, are presented in Figure 4. The values of χ calculated from the slope of the linear plots indicated above are summarised in Table 1. As can be seen, χ-values depend on the temperature and the presence of the additives. Further discussion of the dependencies observed will be presented [9].

The initial rate of the process was investigated further because this time interval presents a definite interest. The effect of the initial concentration of $K_2Cr_2O_7$ was followed at a constant temperature. It was found that the initial rate does not vary regularly with the increase in concentration. This is most probably because the number of the dyestuff molecules not bonded in a complex decreases, while the quantity of free Cr-ions in the bath increases with the increase in the initial concentration of $K_2Cr_2O_7$. That is why the initial rate average value was calculated. The latter has the meaning significance of the constant of the process rate during the initial step. The values obtained at all temperatures studied are presented in Table 2.

It is seen from Table 2 that the chroming rate increases with the temperature increase, as is expected. Higher rates are found in the case of the presence of Na_2SO_4 or DDBS in the chroming bath. The presence of these additives most probably facilitates the reaction of complex formation.

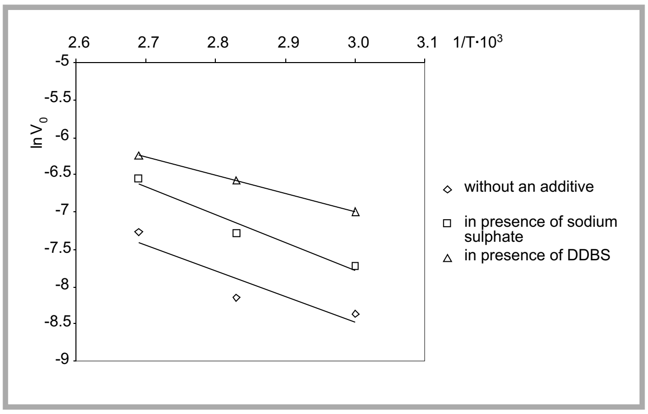


Figure 5. Temperature dependence of the initial rate.

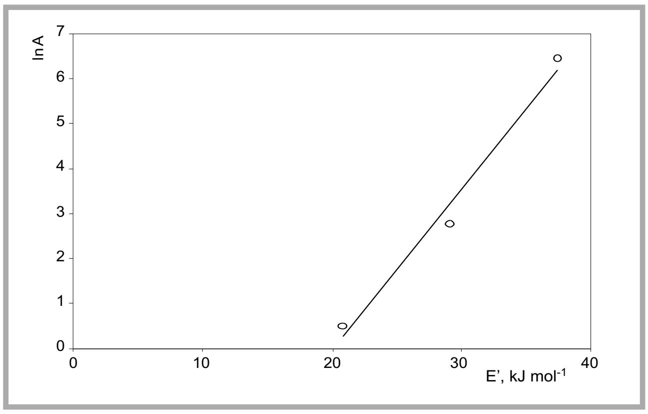


Figure 6. Dependence of the pre-exponential factor on the apparent activation energy.

The temperature dependence of the initial rate interpreted as a rate constant was analysed in correspondence with the Arrhenius equation:

$$k = A \exp(-E^{\neq}/RT) \qquad (3)$$

where all the symbols have their usual meaning. This was done on the basis of data obtained in the absence of an additive and in the presence of Na_2SO_4 or DDBS (Figure 5). The values of lnA and $E^{\neq}$ calculated on the basis of all experimental data are presented in Table 3.

The lower values of the apparent activation energy during chroming in the presence of Na_2SO_4 or DDBS (Table 3) result from the energetic facilitation of the process. The latter proceeds at a higher rate because of the determining effect of the energetic factor. The usage of DDBS facilitates chroming through the decrease in the apparent activation energy of the reaction, which is probably connected with the surface-active properties and the anionic character of this additive (Figure 6).

The quantity of the exhausted Cr-ions is greatest in the case of chroming proceeding in the presence of DDBS. The results on the colour stability after washing at 313K are very good, which shows that the quantity of $K_2Cr_2O_7$ can be decreased even to that under the stochiometrically determined level.

There is a correlation between lnA and $E^{\neq}$ known as the compensating effect (Figure 6). It is described by

$$\ln A = \ln A_0 + b\,E^{\neq} \qquad (4)$$

where A_0 and b are empirical constants. The presence of the compensating effect shows that the additives used do not change the mechanism of the chroming process of wool dyed with an acidic dyestuff undergoing chroming.

Table 2. Values of the initial rate average values calculated for experiments carried out at different temperatures in the absence and presence of additives (Na_2SO_4, DDBS).

Temperature, K	$v_o \cdot 10^4$, kg of Cr-ions/kg of fibres		
	In absence of an additive	In presence of Na_2SO_4	In presence of DDBS
333	2.3	4.4	9.0
353	2.9	6.8	13.9
371	7.0	14.1	19.3

Table 3. Values of the pre-exponential factor and of the apparent activation energy obtained in kinetic studies in the absence and presence of additives.

Chroming bath	ln A	E, kJ mol^{-1}
In absence of an additive	6.44	37.4
In presence of Na_2SO_4	2.77	29.1
In presence of DDBS	0.51	20.8

Conclusions

The data obtained in this study lead to the following conclusions:

- The presence of Na_2SO_4 or DDBS in the chroming bath leads to a decrease in apparent activation energy, which energetically facilitates the process of dyestuff-chrome complex formation. The effect of DDBS is the greatest.
- The mechanism of chroming remains unchanged irrespective of the additives used, as is verified by the compensation effect observed.
- The studies carried out show that Cr-ions are completely depleted when the process of chroming is carried out with 17% and 34% of $K_2Cr_2O_7$ and an additive of Na_2SO_4 or DDBS respectively.
- The application of chroming baths containing less than 50% of $K_2Cr_2O_7$ in the presence of Na_2SO_4 or DDBS as additives leads to a drastic decrease in Cr-ions in the wastewater without any change in the quality of dying with Tomanolovo black AFD.

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