ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 1, pp. 220–229. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © V.G. Stokozenko, A.P. Moryganov, Yu.V. Nemanova, 2011, published in Rossiiskii Khimicheskii Zhurnal, 2011, Vol. 55, No. 3, pp. 107–116.

Generation of Redox Systems by Fiber Materials on the Reduction of Vat and Sulfur Dyes: Research and Practical Implementation

V. G. Stokozenko, A. P. Moryganov, and Yu. V. Nemanova

Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: vgs@isc-ras.ru

Received July 21, 2011

Abstract—An essential part of the processes of refinement of textile materials from natural cellulose fiber is based on redox reactions of the components of process solutions both with admixtures in the fiber and with cellulose. The reducing agents involved in these processes are used in the alkaline treatment of textile materials as antioxidants whose function is to prevent oxidative destruction of cellulose; reducing agents are also introduced into vat or sulfur dye compositions to convert these insoluble dyes into soluble leuco compounds.

DOI: 10.1134/S107036321301043X

INTRODUCTION

An essential part of the processes of refinement of textile materials from natural cellulose fiber is based on redox reactions of the components of process solutions both with admixtures in the fiber and with cellulose. The reducing agents involved in these processes are used in the alkaline treatment of textile materials as antioxidants whose function is to prevent oxidative destruction of cellulose; reducing agents are also introduced into vat or sulfur dye compositions to convert these insoluble dyes into soluble leuco compounds.

The effect of anthraquinone and nitrogen- and sulfur-containing reducers on the redox properties of alkaline solutions which are commonly used for the alkaline treatment and dyeing of cotton and flax textile materials has been considered in detail in the monographs [1–3]. Our literature analysis showed that so-called real reducers whose redox potentials in an alkaline medium are high and stable (about –1 V) cause no cellulose destruction. Moreover, such compounds as sodium boron hydride, sulfoxylic acid derivatives, for example, Rongalite, and certain aliphatic and aromatic amines are capable of stabilizing polysaccharides during alkaline treatment, by reducing the end aldehyde group and preventing depolymerization of polysaccharides with a reductive end group [4–6]. Along with the traditional view of strongly nucleophilic reducers (sodium sulfide, hydrazine, sodium stannite) as cellulose destruction inhibitors, there is quite a reasonable opinion that these agents can promote hydrolysis of the glycoside bonds in polysaccharides to form low-molecular compounds [7–10].

The above reducers are introduced into the compositions for treatment of textile fibers both individually and in mixtures with other compounds. However, certain chemical reactions (in particular, hydrolysis) in cellulose-containing substrates, that involve no reducers, can form compounds with reductive properties. Thus, the enhancement of the reductive activity of boiling agents during production and refinement of wood cellulose even in the absence of reducer additions has many times been mentioned. This effect is explained by the accumulation in the system of low-molecular products of the hydrolytic destruction of polysaccharide admixtures, which possess reductive activity [8, 10].

The research on the sodium hydroxide hydrolysis of substances associated with cellulose fiber, performed at the Krestov Institute of Solution Chemistry, showed that the accumulation in the system of the destruction products of polysaccharide admixtures increases the redox potential until it reaches the level of the leuco potentials of sulfur and certain vat dyes. These results were used as the basis to develop radically new technologies of dyeing of bast fiber with vat and sulfur dyes, which combines chemical modification of dyes with reducer formation.

Study of the Generation of Redox Systems on Alkaline Treatment of Cellulose Fiber Materials

To establish factors responsible for the generation of the redox potential in the sodium hydroxide – cellulose fiber system, we performed a potentiometric research in the course of treatment of raw and bleached cotton, bast (flax, hemp, jute), and cellulose hydrate (viscose) fibers, as well as microcrystalline cellulose.

As seen from Table 1, cellulose fibers of different origins have a specific effect of the redox potential of the fiber–alkaline solution system. In the presence of native cellulose fiber, the potential increases to about – 0.68 V, which is much higher than in the systems with raw cotton and jute fibers, as well as regenerated cellulose (viscose) fiber (–0.62 V). Further potential growth is caused by the addition of triethanolamine whose efficiency was noted in [11, 12].

Table 1. Redox potentials of the alkaline solution–fiber systems in the presence and in the absence of triethanolamine

Fiber	Redox potential, V	
	without triethanolamine	with triethanolamine
No fiber	0.60	0.62
Flax		
canvas	0.64	0.80
mechanically modified	0.67	0.82
Hemp		
canvas	0.66	0.82
mechanically modified	0.68	0.84
Dzhutovoe		
canvas	0.62	0.68
mechanically modified	0.63	0.71
Cotton canvas	0.62	0.68
Viscise	0.62	0.65

In terms of the strength of effect on the redox potential of the system, cellulose fiber can be ranked as follows: viscose < cotton < jute < flax < hemp.

The change of the redox potential is directly related to the content of natural admixtures in the fiber, the destruction degree of these admixtures, and, as a result, the content and composition of their destruction products. In the presence of mechanically modified bast fiber, the potential of the solution containing triethanolamine (up to –0.84 V) is higher than that of the solution containing the native fiber only. This difference can be explained in terms of a disturbance of the integrity of middle plates (structure-forming components of flax fiber), microcrack development, and detachment of fragments of complex fibers as a result of multiple mechanical exposure of the fiber in the breaker machine. Increased solid–liquid interface facilitates access inside complex bast fiber, which, in its turn, facilitates diffusion of the solution into the interfibrous space of the bast fiber bundle and dissolution of admixtures.

Kokorina [11] obtained evidence showing that substances associated with cellulose and responsible for the generation in the system of reducing agents and the increase of the redox potentials are hemiselluloses. Therewith, a correlation was found between the potential change and the content of hemicelluloses in the substrates. Viscose and cotton fibers contain almost no hemicelluloses (< 1%), and. As aresult, the redox potential in their presence changed only slightly (by 0.02–0.03 V). Complex flax, hemp, and jute fibers contain from 10 to 20% of these compounds, and in their presence the potential increases by 0.09–0.12 V.

The generation of redox systems in cellulose materials in alkaline solutions is much contributed no only by polysaccharide admixtures, but also by cellulose in itself [13–15]. Evidence for this suggestion is provided by the generation and rise of redox potentials in systems containing purified celluloses of different origins (Fig. 1).

The potential rise dynamics with the temperature rise from 20 to 100°C at a rate of 1°C/min shows that the reductive activity does not develop at low temperatures (~20–40°C) and any cellulose substrate and alkali concentration. As the temperature rises, a sharp potential jump is observed, after which the potential stabilizes in the range –0.54÷–0.80 V at 100°C. The upper potential levels are characteristic for systems containing raw fibers and lower potentials, for systems with bleached fibers. The potentials of all the systems persist at 100°C for no less than 60 min.

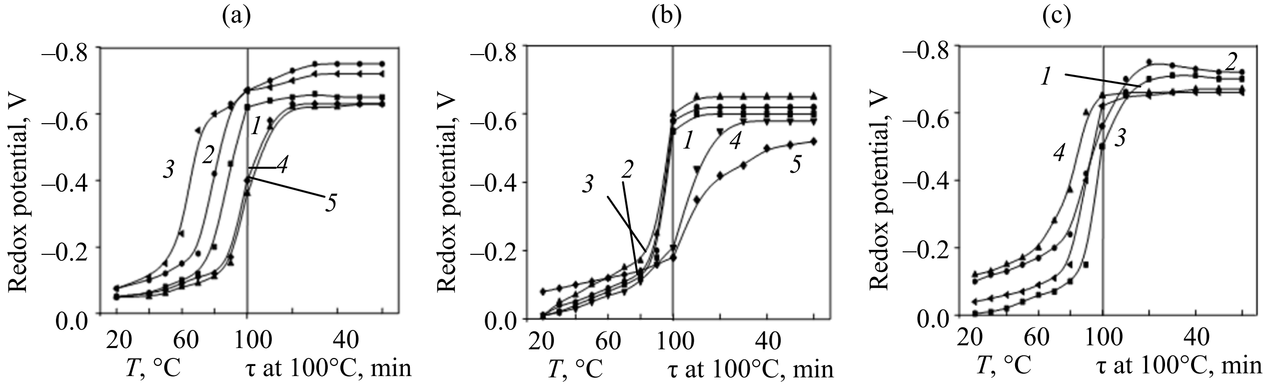

Fig. 1. Change of the redox potential of the cellulose–NaOH solution with temperature *T* and treatment time τ. Material: (a) Flux cellulose: (*1*, *2*, *3*) native fibers in the solutions with NaOH concentrations of 4, 10, and 20 g/l, respectively; (*4*, *5*) bleached fibers in the solutions with NaOH concentrations of 4 and 10 g/l, respectively; (b) cotton cellulose: (*1*–*5*) the same as in (a); (c): (*1*, *2*) microcrystalline cellulose and (*3*, *4*) cellulose hydrate in the solutions NaOH concentrations of 4 and 10 g/l, respectively.

The influence of alkali concentration on the conditions of redox potential generation is most pronounced in systems with native flax substrates (Figs. 1a and 1b, curves *1*–*3*). At the NaOH concentration of 4 g/l, the potential jump is observed at 80–100°C and, as the concentration is increased to 10 and 20 g/l, it shifts to lower temperatures: 70–80°C and 60–70°C, respectively. With bleached flax, no dependence is observed.

In the case of native cotton fiber, the NaOH concentration only slightly affects the temperature of redox potential generation. The potential jump at all NaOH concentrations occurs in the same temperature range, specifically 90–100°C.

The limiting potential values at 100°C in bleached flax systems scarcely depnde on NaOH concentration and equal –0.63 V (Fig. 1, curves 4 and 5), and if flax is replaced by cotton, higher potentials (up to –0.7 V) are observed at higher NaOH concentrations. It is important to note that, whatever was the composition and content of admixtures in cellulose substrates, redox potential was generated in all the studied systems. The difference is that, in the case of bleached fiber materials, the potential jump occurs at 100°C and reaches a maximum within 15 min with flax and 30 min with cotton.

The lower temperature of redox potential generation in native flax systems is apparently explained by the initiation of hemicellulose hydrolysis. However, this does not explain the rise of the potential to–0.6 to –0.65 V in the systems containing bleached fiber materials, since flax no longer contains hemicelluloses after the bleaching process, while cotton intrinsically scarcely contains hemicelluloses.

The redox potential generated in solutions in the presence of cellulose substrates completely purified from hemicelluloses (cellulose hydrate and high-purity microcrystalline cellulose) follows the same characteristic trends (Fig. 1c), as bleached cotton and flax systems: Potential jump at –0.5 to –0.6 V at 80–100°C and stabilization at 100°C. In view of the fact that microcrystalline cellulose contains no admixtures, the potential rise can be associated with no other reason than the hydrolysis of cellulose, initiated by OH-catalyzed hydrolysis of cellulose in itself.

The obtained results together with published data allowed us to suggest form in the dyeing and modification cycle of a labile reductive complex with a potential of not lower than –0.8 mV and comprising hemicellulose destruction products and cellulose. The structure of this complex can hardly be established because of its complexity, diversity of alkaline hydrolysis products and their speciation in the surrounding phase, as well as in the vicinity of the fiber and in its capillary structure. Based on published data, we can suggest that the activity of this complex is underlain by the end groups of reductive polysaccharides [16].

Evidence showing that the systems in study contain a labile reductive complex comes from the UV spectra of the solutions obtained after the alkaline treatment of purified cotton and flax cellulose samples (Fig. 2). The spectra show well-defined maxima in the same absorption region (280–290 nm) as reductive sugars. Similar spectra were obtained for other celluloses.

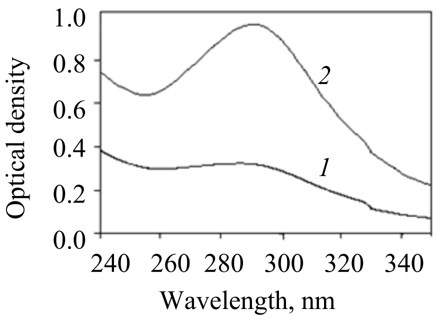

Fig. 2. Differential UV spectra of the solutions obtained on alkaline treatment of (*1*) cotton and (*2*) flax cellulose. Treatment conditions: 100°C, time 60 min, NaOH concentration 0.1 M.

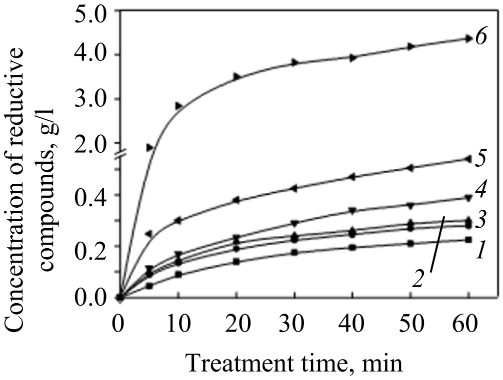

Fig. 3. Kinetics of the accumulation of reductive compounds on alkaline treatment of (*1*) cotton, (*2*) flax, (*3*) hemp, and (*4*) wood celluloses, (*5*) cellulose hydrate, and (*6*) microcrystalline cellulose. Treatment conditions: 100°C, NaOH concentration in the solution 0.1 M.

The formation dynamics of labile reductive complexes in solutions under the action of NaOH on cellulose materials are shown in Fig. 3.

There is a great difference in the yields of reductive compounds on the alkaline treatment of plant (cotton, flax, hemp, and wood) and industrially (chemically) produced celluloses (cellulose hydrate, microcrystalline cellulose), implying that the latter are more susceptible to hydrolytic destruction. Thus, after 60-min alkaline treatment, as little as 0.2 g/l of sugars pass from cotton cellulose into solution; in the case of cellulose hydrate, the respective value increases to 0.52 g/l, and it reaches a maximum of 4.4 g/l in the microcrystalline cellulose.

The reductive activity of the systems in study was confirmed by the results of a spectrophotometric kinetic study of the transition of vat dyes into the leuco form [11]. It was shown on an example of indigo and polycyclic dyes that the system containing a labile reductive complex as completely reduces bromindigo dye as the alkaline rongalite solution.

Role of Nucleophilic Reagents in the Activation of Redox Systems

The modeling of dyeing of flax and flax semi-finished products (rove, yarns) in laboratory and pilot plant the new alkaline reagent–reductive complex systems offer definite advantages over dye solutions containing traditional reductive agents, there are some disadvantages (in particular, incomplete reduction of certain dyes having a high leuco potential) which can hardly be eliminated.

The fact that the hydrolytic transformation of polysaccharides in an alkaline medium are promoted by reagents with enhanced nucleophilic activity (sodium sulfide, hydrazine hydrate) was taken into account in choosing catalysts for enhancing the reductive power of dyeing systems.

Comparison of the nucleophilic constants of anions showed that sodium sulfide whose anion SH^- has the highest nucleophilicity (5.1 against 4.2 for OH^-) [17] should exhibit a high reactivity toward cellulose.

The choice of sodium sulfide as a reagent able to increase the redox potential of dyeing systemswas also motivated by its high delignifying activity in the chemical modification of bast fiber with increased lignin contents (hemp and jute fibers). The efficiency of sodium sulfide in the chemical modification of these fibers was established in [18].

The data in Table 2 evidence a strong effect of sodium sulfide on cellulose hydrolysis. In the presence of sodium sulfide, the amount of low-molecular reductive cellulose destruction products which have passed into solution after 10-min treatment increases 18–42-fold.

The potentiometric research showed that the sharp potential jump at 80–100°C, observed in the flax fiber–sodium hydroxide system (Fig. 1) and associated with the hydrolysis of hemicellulose and, in part, cellulose is no longer observed in the presence of sodium sulfide. The fact that the potential gradually rises within the entire temperature and time range appears to be explained by deep and vigorous

Table 2. Assessment of the effect pg sodium sulfide on the formation of reductive compounds on cellulose hydrolysis

Cellulose	Concentration of reductive compounds in the solution, g/l	
	alkaline treatment (10 min)	alkaline sulfide treatment (10 min)
Cotton	0.04	1.44
Flax	0.08	3.34
Wood	0.18	3.30

hydrolytic destruction and saturation of the system with reductive hydrolysis products. At 100°C, the potential is higher than –0.85 V, which allows reduction of virtually all dyes, except for certain policyclic dyes whose leuco potentials are higher than –0.9 V.

Thus, by purposefully controlling parameters of the hydrolytic destruction of polysaccharide components of cellulose fiber in an alkaline medium one can ensure formation a complex of reductive agents with a redox potential high enough to reduce vat and sulfur dyes.

Engineering aspects of the use of redox systems in combined chemical modification and dyeing of bast fiber with vat and sulfur dyes. The technology combining chemical modification of bast fiber (primarily flax fiber) with their dyeing with vat and sulfur dyes is of practical interest for the production and processing of new types of fibers from bast raw materials, as well as for finishing of textile articles.

Unlike the classical reduction of these dyes with sulfur-containing compounds, which occurs in solution, in the systems in study the reduction of dyes is initiated at the fiber–solution interface and then, as the reducing agents diffuse from the fiber to the environment, the reduction process extends to the entire volume of the dye bath. Evidence for this mechanism is provided by visual observations on the reduction of vat dyes: Their transition to the leuco form is initiated in the border diffusion region of the flax fiber and then is continued in the liquid phase [11, 19, 20]. Figure 4 illustrates the principal difference between traditional vatting and vatting by our proposed technology.

Similar processes can occur in sulfur dyeing of cellulose materials.

According to [11], an important problem to be solved in developing the engineering design of the combined chemical modification and dyeing process is to pay due attention to the system “ignition” stage. The “ignition” time should correspond to the time required to remove the most part of admixtures from the fiber. During this time, along with the separation of complex fiber bundles into elemental fibers (elementarization), most reductive compounds responsible for the generation of redox potential in the diffusion layer at the fiber –solution interface are passing to the solution. Fast temperature rise may lead to low-quality dyeing because of the premature reduction of the dye, caused by the formation of reductive compounds with high redox potentials.

As hemicellulose destruction products are accumulated in the system, the redox potential increases to reach the level of the leuco potentials of certain vat dyes. Therewith, as noted above, dye reduction is

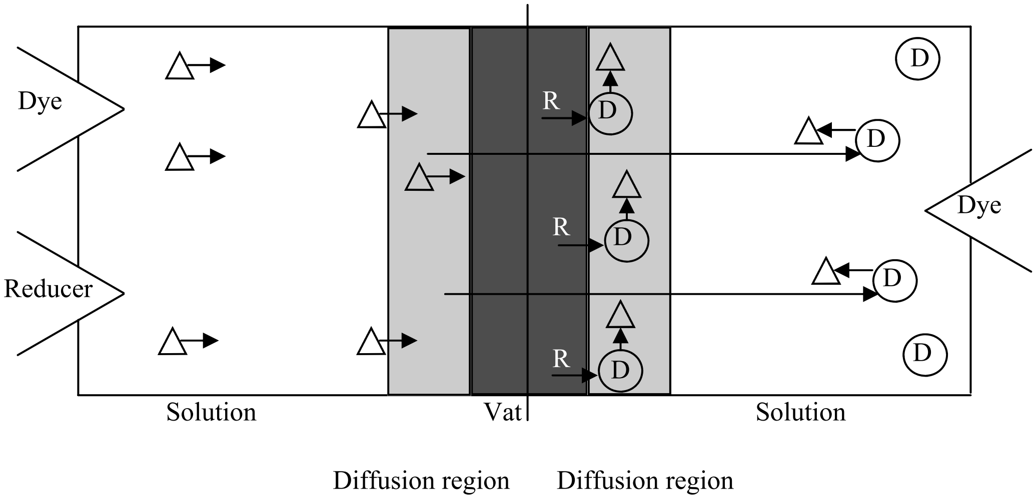

Fig. 4. Process schemes of vat and sulfur dyeing with (left) traditional reducers and (right) redox systems. (R) Reducer; (D) dye, and (Δ) leuco form of the dye.

initiated after all admixtures have been removed from the fiber, and, as a result, the fiber is first purified and modified and then, an only then, it is dyed. Such an effect is impossible to obtain with traditional sulfur reducers. The discovered regularities of the formation and solution of reductive compounds and vat dye reduction involving these compounds formed the basis for the combined modification–vatting process for flax fiber, developed in 2001–2002 at the Institute of Solution Chemistry of the Russian Academy of Sciences [20].

Testing at textile enterprises gave evidence for the efficiency of redox systems. The developed technology provides deep and level dyeing of fibers both over their cross-section and over the bulk pack. This is just the reason for the lack of dye flaking off during processing of dyed flax fiber in spinning and weaving shops (flaking off is a big problem associated with processing of dyed cotton fiber). Along with high dyeing characteristics, modification endows the dyed flax fiber with improved technical characteristics (linear density ~ 2 tex, average length ~ 45 mm, curvature, and water repellency), which allows such fiber to be successfully processed in textile manufacturing [21].

Development of the Technology of a Combined Process Involving Chemical Modification and Vat or Sulfur Dyeing of Fibers

The process of generation of redox systems on alkaline treatment of fibers formed the basis for the following radically new dyeing technologies:

– technology of chemical modification of flax fiber, combined with their sulfur dyeing;

– technology of chemical modification of technical bast (hemp and jute) fiber, combined with their sulfur and vat dyeing.

Combined Process of Chemical Modification of Flax Fiber and Its Sulfur Dyeing

Sulfur dyes have a limited application in the flux industry because of the narrow color palette. However, the continuing effort of major firms on improving commercial forms of dyes, extending the color palette, and developing progressive dyeing technologies is maintaining the interest of producers in their use. Thus, the environmental safety of the dyeing was proposed to be enhanced by replacing the traditional sodium sulfide reducer by mono- and oligosaccharides (glucose, fructose, isomaltose, isomaltulose, etc.) [22, 23].

The complex of reductive compounds, formed in the course of the chemical modification of flax fiber by carbohydrate hydrolysis can compare in efficiency with the above compounds in the reduction of sulfur dyes. Introduction of triethanolamine into the modifying compositions favors, along more active fiber purification, better fixation of the dye, more level dyeing, and higher fastness of color to wet treatments. Evidence for this suggestion was obtained by laboratory modeling of one-stage chemical modification and sulfur dyeing processes.

Quite an important issue of the process of dyeing combined with chemical modification is the order of introduction of the sulfur dye into the solution. Initially, the working solutions have an increased alkalinity (up to 5 g/l NaOH), which adversely affects the dye and the quality of dyeing [24]. Analysis of the dynamics of the solution alkalinity variation during chemical modification of fibers showed that NaOH is partially bound by carbohydrate destruction products, and, as a result, its content is decreased to a level corresponding to the regulations for the dyeing process (1–2 g/l) [18]. By controlling the time parameters of the process, the subsequent one-stage fiber dyeing and elementarization can be accomplished, when the alkali concentration in the working solution is safe in terms of the quality of dyeing.

The combined process of chemical modification and sulfur dyeing of flux fiber can be constructed similarly to the process developed previously for vat dyes [11, 20].

The results obtained on dyeing of flux fiber provide evidence for the suggestion that sulfur dyes can be converted into the leuco form by the reductive systems generated on alkaline treatment of the fiber. The color obtained under such conditions compares in intensity to the flux color obtained in the presence of sodium sulfide (fastness to dry friction ~ 5, to wet wiping 4, and to soap and soda solutions at 40 and 100°C 4–5). Thus, the complex of reductive hydrolysis products of polysaccharide compounds, including cellulose and components of modifying solutions, can constitute a competitive alternative to the traditional sodium sulfide reducer.

The vigorous fiber breaking processes that, along with dyeing, occur in the dyeing and modifying solutions provide fibers similar in technical characteristics to a modified flax fiber (Table 3).

Table 3. Technical characteristics of sulfur-dyed modified flax fiber

Parameter	Value for modified fiber		
	dyed with Sulfur Black	dyed with Sulfur Brown	undyed
Linear density, tex	2.1	2.1	2.1
Average fiber length, mm	51.2	52.0	52.4
Pecentage of fibers, %, with the length, mm			
< 15.0	18.0	17.2	18.0
15.1−60.0	74.5	76.2	77.2
> 60.1	7.5	6.6	4.8
Curvature (crimp/cm)	2−4	2−4	2−4

Assessment of the Possibility of Combining Chemical Modification and Vat and Sulfur Dyeing of Bast Fiber

The above-described data, as well as the data obtained by Konycheva et al. [18, 25] who developed the technology of chemical modification of hemp and jute fibers, have formed the basis for research on the possibility of combining, in one stage, modification of bast fiber and its vat or sulfur dyeing.

The study of the dynamics in the change of the redox potential during treatment of bast fiber with various modifying compositions gave the following results (Fig. 5).

It was found that the change of the potential in the hemp fiber –sodium hydroxide–triethanolamine systems follows the same trends as in the system with flax fiber. The labile reductive complex formed in the solution can reduce sulfur dyes and some vat dyes (with the leuco potentials less than–0.8 V); addition of sodium sulfide can further increase the potential to –0.86 V.

A different pattern is observed when hemp fiber is replaced by jute fiber. In the latter case, the maximum redox potential is no higher than –0.71 V. Sodium sulfide can only increase the potential to –0.76 V. Such potentials are sufficient to reduce sulfur dyes, but vat dyes are unlikely to be actively reduced under these conditions.

The low redox activity of the system generated in the presence of jute fiber appears to be associated with the specific morphology and chemical composition of this fiber. The close packing of jute fibers in bundles retards sorption and diffusion processes and makes the internal structure of fibers hardly accessible for reagents. Moreover, the high degree of lignification of jute fiber (> 15% vs. 4–6% for flax and hemp fibers [18]) and strong chemical bonds between lignin and the carbohydrate complex prevents destruction of the latter and passage of monomer fragments into solution. Evidence for this reasoning is provided by the lower rate of accumulation in the solution of reductive

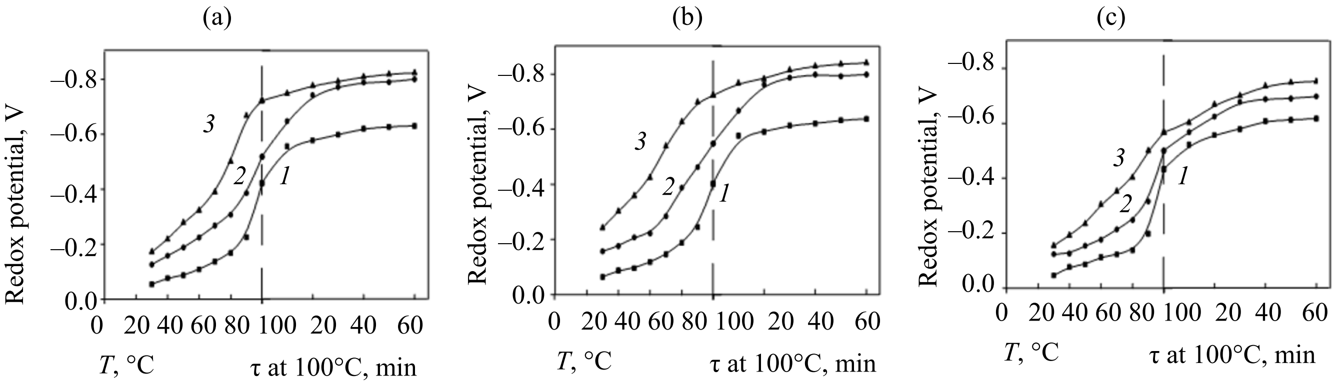

Fig. 5. Temperature and time dependences of the redox potential of the alkaline solutions on fiber treatment in the presence and in the absence of modifying additives. Fiber: (a) flux; (b) hemp, and (c) jute. Additive: (*1*) none; (*2*) triethanolamine, and (*3*) sodium sulfide.

Table 4. Concentration of reductive substances in the solution on treatment of bast fibers

Fiber	Concentration (treatment time 60 min), g/l	
	alkali solution	alkali sulfide solution
Flax	0.034	0.24
Hemp	0.038	0.34
Jute	0.018	0.08

polysaccharide destruction products on alkaline treatment with sodium hydroxide of flax fiber compared with hemp and jute fibers (Fig. 6).

The essential difference in the amounts of reductive compounds formed on NaOH hydrolysis of jute fiber, on the one hand, and flax and hemp fibers, on the other, shows that the carbohydrate complexes of the latter fibers are more susceptible to hydrolytic destruction. After 60-min alkaline treatment of jute fiber, as little as 0.018 g/l of its destruction products pass to solution, whereas the respective values for flax and hemp fibers are 0.032 and 0.038 g/l.

As seen from Table 4, sodium sulfide promotes hydrolytic processes in the carbohydrate part of fibers. In the presence of sodium sulfide, the yield of reductive sugars increases 7 times with flux fiber and 9 times with hemp fiber. With jute, sodium sulfide to a lesser extent promotes accumulation of the low-molecular fraction in the solution (4.5 times), which agrees with redox titration data: The concentration of reductive compounds and their composition do not generate a redox potential sufficient for vat dye reduction.

Thus, the assessment of the redox properties of the bast fiber –modifying solution system gives us grounds to suggest that, along with flax fiber, simultaneous vat dyeing and chemical modification is only possible with hemp fiber. With jute fiber, these two processes can be combined into one stage only in the case of sulfur dyes.

One-stage processes involving chemical modification and vat (polycyclic and indigo) and sulfur dyeing of hemp and jute fibers in alkaline solutions containing triethanolamine and sodium sulfide were modeled at the laboratory scale. Sulfur dyes were also used for dyeing flax fiber (to avoid fiber destruction [18], the process was performed without sodium sulfide additions). The results of vat dyeing provided evidence showing that the combined process is suitable for hemp fiber and unsuitable for jute fiber (Table 5).

Table 5. Results of vat dyeing of bast fibers by the combined technology

Dye	Relative dye content of the fiber[a], %		
	flax	hemp	jute
Dyeng with triethanolamine			
Vat Bright Green SD	108.4	112.5	42.3
Vat Bright Violet KD	111.4	115.6	45.4
Bromoindigo	114.4	116.8	66.8
Thoindigo Red S	114.7	118.2	61.2
Dyeing with triethanolamine + sodium sulfide			
Vat Bright Green SD	112.8	117.0	54.5
Vat Bright Violet KD	116.8	119.0	53.6
Bromoindigo	117.0	121.2	72.8
Thoindigo Red S	119.2	120.8	68.2

[a] The dye content of fibers dyed by traditional technologies is taken to be 100%.

The technology combining modification, dyeing, and elementarization of complex fibers allows intense and fast dyeing of hemp fiber, as evidenced by a higher dye content of the fiber compared to the fiber after suspension dyeing. High-quality dyeing can be

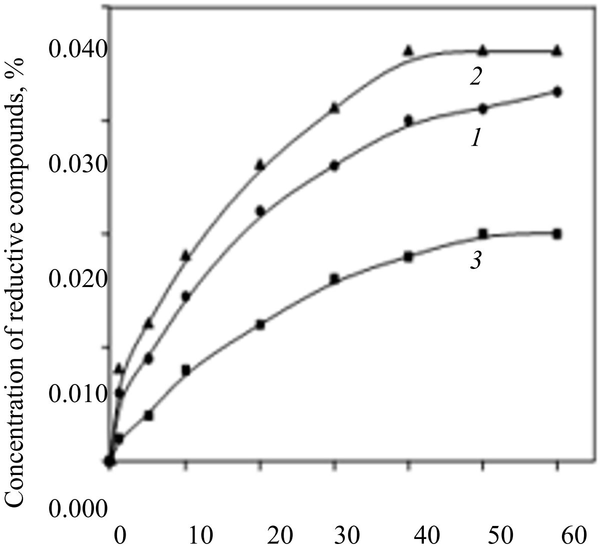

Fig. 6. Kinetics of passage of reductive substances into solution on the treatment of (*1*) flux, (*2*) hemp, and (*3*) jute fibers with a NaOH solution (0.1 M).

Table 6. Color characteristics of sulfur-dyed bast fibers

Fiber	Combined technology		Traditional batch technology	
	brightness, %	color strength , %	brightness, %	color strength, %
Flax	28.1	26.8	27.9	26.4
Hemp	16.2	59.6	18.0	52.0
Jute	21.8	37.9	24.5	26.7

obtained even if no other additive but triethanolamine is used. The composition of triethanolamine and sodium sulfide increases the dye efficiency by 4–5%.

The parameters of color fastness to dry friction and wet wiping (about 3–4) and soap and soda solutions at 40 and 100°C (4) provide evidence for satisfactory dye fixation not only on the surface, but also in the bulk of the fiber, which guarantees the lack of dye flaking off on mechanical exposures. The latter fact is quite important for further processing of dyed fibers in the spinning and weaving industry.

To assess the quality of sulfur dyeing, along with the above-mentioned fastness parameters (4–5), color characteristics were determined on a Kolorist complex (Table 6). Unlike vat dyes, the leuco forms of sulfur dyes show affinity to all fibers in the one-stage dyeing process. Therewith, deep dye penetration into the fiber structure and sufficiently full dye utilization are provided.

The results of color strength assessment assessment of hemp and jute fibers demonstrate a clear advantage of the combined dyeing–modification technology over the traditional one: The color strength of modified fibers is higher by 15–40% that the respective value for the fiber died by the batch technology.

The attained level of technical parameters of modified dyed fibers shows that the proper choice reagents for dyeing and modifying solutions favor more efficient fiber elementarization. The parameters of dyed fibers fit the requirements for modified flax fiber (linear density 2.6 tex, average length 43 mm, 15–60-mm-long fiber group for joint processing with cotton, wool, and/or chemical fibers up to 60%).

Like modified flax fiber, dyed hemp and jute fibers are of great interest for mélange production. Mélange fabrics from such fibers can be recommended for fabrication of outwear clothing, for example, jeans. Melange yarns with a high linear density will find application for fabrication of articles with voluminous knitted drawings and diverse coloristic decoration to meet the fashion trends for the season autumn–winter 2011.

CONCLUSIONS

The discovery of the possibility for and ways to the generation of redox systems directly in the cellulose substrate by means of targeted regulation of hydrolysis of cellulose and associated compounds opens up broad possibilities for the development of environmentally friendly and economically efficient technologies in the textile industry.

The establishment of factors controlling the generation in the fiber of “alternative” carbohydrate reducers and ways to enhancing their efficiency in the modification and refinement of cellulose materials, as well as the practical implementation of the new technologies meet the requirements of green chemistry, a modern research field, the main strategy of which is “careful selection of raw materials and process schemes, so that the use of hazardous substances is completely excluded” (Principle no. 7: “A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable”) [26].

REFERENCES

1. Mel’nikov, B.N., Zakharova, T.D., and Kirillova, M.N., *Fiziko-khimicheskie osnovy processov otde-lochnogo proizvodstva* (Physicochemical Principles of Finishing Processes), Moscow: Legkaya i Pishchevaya Promyshlennost’, 1982.
2. Peters, R.H., *Tekstil’naya khimiya (ochistka tekstil’nykh materialov ot zagryaznenii)* [Textile Chemistry. Vol. II: Impurities in Fibres; Purification of Fibres), Amsterdam: Elsevier, 1967.
3. Krichevskii, G.E., *Khimicheskaya tekhnologiya tekstil’nykh materialov* (Chemical Technology of Textile Materials), Moscow: Ross. Zaoch. Inst. Tekst. Legk. Prom-sti, 2000–2001, vols. 1–3.
4. Pestovskaya, E.A., *Razvitie teorii i sovershenstvovanie tekhnologicheskih processov mokrogo pryadeniya l’na* (Development of Theory and Improvement of Technological Processes of Wet Flax Spinning), Ivanovo: Ivanov. Gos. Tekst. Akad., 2010.
5. Fengel, D. and Wegener, G., *Wood Chemistry, Ultrastructure, and Reactions*, Berlin: Walter de Gruyter, 1984.

6. Shevchenko, S.M. and Deineko. I.P., *Khim. Drev*., 1983, no. 6, pp. 3–32.
7. Bennaser, El'-Manaa, Kiryushina, M.F., Sultanov, V.S., Zarubin, M.Ya., et al., *Ibid.,* 1988, no.4, pp. 70–73.
8. Orlovskaya, G.M. and Bazhenskii, V.L., *Zh. Prikl. Khim*., 1975, no. 4, pp. 865–868.
9. Zarudskaya, O.L., Dobrynin, N.A., Moskvin, B.V., and Nagrodskii, I.A., *Khim. Drev*., 1978, no. 4, pp. 7–10.
10. Chudakov, M.I., Mel'chakova, N.A., and El'nitskaya, Z.P., *Ibid.*, 1976, no. 4, pp. 3–5.
11. Kokorina, L.Yu., *Cand. Sci. (Tekh.) Dissertation*, Ivanovo, 2002.
12. Kokorina, L.Yu., Gubina, S.M., and Stokozenko, V.G., *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Tekst. Prom-sti*, 2002, no. 1, pp. 58–61.
13. Gubina, S.M. and Stokozenko, V.G*., Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol*., 2007, vol. 50, no. 12, pp. 96–99.
14. Stokozenko, V.G., Gubina, S.M., and Ermolaeva, N.A., *Ibid*., 2008, vol. 51, no. 6, pp. 33–35.
15. Gubina, S.M., Stokozenko, V.G., Petrenko, V.E., and Korablev, D.B., Abstracts of Papers, *IX Mezhd. konf. "Problemy sol'vatatsii i kompleksoobrazovaniya v rastvorakh"* (IX Int. Conf. "Problems of Solvation and Complex Formation in Solutions"), Ples, 2004, p. 369.
16. Dudkin, M.S., *Gemitsellyulozy* (Hemicelluloses), Riga: Zinatne, 1991.
17 Kochetkov, N.K., Bochkov, A.F., Dmitriev, B.A., Usov, A.I., Chizhov, O.S., and Shibaev, V.N., *Khimiya uglevodov* (Carbohydrate Chemistry), Moscow: Khimiya, 1967.
18. Konycheva, M.V., *Cand. Sci. (Tekh.) Dissertation*, Ivanovo, 2011.
19. Stokozenko, V.G. and Nemanova, Yu.V., *Tekst. Prom-st'*, 2008, nos. 7–8, pp. 30–33.
20. RF Patent no. 2190052, 2001; *Byull. Izobret*., no. 27.
21. Kokorina, L.Yu., Stokozenko, V.G., and Denisenko, V.P., *LegPromBizne*s, 2001, no. 9, pp. 9–10.
22. DE Patent no. 2178473, 2002.
23. Shukla, S. R. and Pai Roshan, S., *Indian J. Fibre Text. Res*., 2004, vol. 29, no. 4, pp. 454–461.
24. *Otdelka khlopchatobumazhnykh tkanei: Spravochnik* (Finishing of Cotton Fabrics: Reference Book), Mel'nikov, B.N., Ed., Ivanovo: Talka, 2003.
25. Konycheva, M.V., Stokozenko, V.G., Titova, Yu.V., and Moryganov, A.P., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2010, vol. 53, no. 6, p. 82.
26. Lunin, V.V. and Lokteva, E.S., *Zelenaya khimiya v Rossii: Sb. nauch. trudov* (Green Chemistry in Russia: Coll. Scientific Papers) Moscow: Mosk. Gos. Univ., 2004, pp. 10–23.