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SOL-GEL TECHNIQUE IN ECO-FRIENDLY COLORATION OF CELLULOSIC MATERIALS

Abstract. At this work, modified variant of sol-gel method is presented, which provides for carrying out of polycondensation not in the impregnation bath, but in the pores of cotton fibers. It is possible due to consistent impregnation in solution of precursor and colorant and catalyst of hydrolysis. The possibility of obtaining silica coating by this method has been proved by the results of scanning electron microscopy and energy dispersive analysis. An influence of treatment conditions on tensile properties and coloration intensity is studied. It was revealed that higher temperature of heat treatment leads to an increase of color fastness.

Key words: sol-gel, silica, sodium silicate, citric acid, cellulose, plant colorants, continuous dyeing, madder, chlorophyll

Introduction. The sol-gel technology is an effective method of introducing and fixing functional agents on the surface of substrates of various types. There are several advantages of using sol-gel technology in the functional finishing of textile materials, such as the possibility of high processing speed and the absence of damage to substrate materials. There are some papers about functional finishing of cellulose textile materials [1-16], which have proved the efficiency of fixing functional agents on the surface of cellulose fiber by using of a sol-gel method. The sol-gel technology implies obtaining functional coating on fiber, which consist metal (silica, aluminum, titan or zinc) oxide matrix and functional particles [17, 18]. Essential factors that limited using of sol-gel technology in mass production are the high cost of alkosilanes, which also requires the use of organic additives. At previous studies the existence of economically more advantageous ways of replacing alkosilanes by water-soluble silicates are explained. The most common water-soluble silicate is sodium or potassium liquid glass. There are several works about using of sol-gel method in dyeing of textile materials [19-21], where researchers applied an a colloidal sol-gel method with the use of aqueous solutions of sodium liquid glass (sodium silicate). Also, an eco-friendly method of dyeing involves the use of natural dyes. Application of plant colorants in textile materials dyeing is best known from antic period, however this type of dye implies the applying of a periodic dyeing method. So, in this research, extract of madder and chlorophyll copper complex choosen as colorants, these substances are commonly used in pharmaceutical and food industry. At this paper we suggest an environment-friendly 2 bath included continuous dyeing method of cotton fabrics, which is based on sol-gel process. General purpose of this research is development of safely and efficiently dyeing technology from economical point of view.

EXPERIMENTAL PART

Materials. 100% bleached cotton fabric, article 1030, with size 200x200mm and surface density of 147 g/m^2 was purchased from Blakit (“BCPA” JSC, Belorussia). As precursors of sol-gel process an aqueous solution of sodium silicate (liquid glass of Na_2SiO_3 in the mass ratio of water: Na_2SiO_3 equal to 9: 1) with a density of 1.36 g/m^3, and as a catalyst of hydrolysis, citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) were chosen. At the research extract of madder (purchased from Vifitech, Russia) and chlorophyll copper complex (purchased from Ecoplant, Russia) were selected as colorants. $AlK(SO_4)_2$ was used as a mordant.

Preparation of samples. Samples of cotton fabric with size 200x200mm and were washed in distilled water at 40 °C, dried in a oven and kept in a desiccators for 24 hours to conditional mass achievement. After this a dyeing solution was prepared (bath module is 5:1), which consisted colorant (2% o.w.f.), diluted in NaOH 1% (1/5 of required volume of dyeing solution) and water glass (50-100 g/l). At next, tissue samples were impregnated in bath with a dye solution. Impregnation was carried out at a temperature of 65-70 °C for one minute, followed by padding. After this, the dyed samples were immersed in second bath, containing an aqueous solution of citric acid (20 - 50 g/l) at a temperature of 65-70 °C for one minute, followed by padding. After, cloths were dried at a temperature of 70-80 °C for 5 minutes and heat treated by heat at temperatures of 120-160 °C. Further, samples were washed with solution, which consist a surfactant (2 g/l) at 50 °C, and rinsed in distilled water.

Research methods. The color stability determination of dyed samples carried out, the PT-4 device and the gray standards scale were used in accordance standart «ГОСТ 9733.27-83» "Textile materials. Method of testing the color fastness to friction". The color intensity K/S of samples calculated according to equation from reflection coefficient R, which measured on a CarlZeiss spectrophotometer. The fact of the coating existence is one of the reasons of changing mechanical properties in comparison with the original fabric. Determination of the tensile strength of the fabric was carried out on a tensile machine RT-250M in accordance standart «ГОСТ 3813-72». "Textile materials. Fabrics and piece goods. Methods for determining tensile properties". For studying of sample’s surface morphology scanning electron microscopy used (SEM).

RESULTS AND DISCUSSION

The result of color intensity determination is represented in table 1. The intensity measurement of samples, which were colored by madder extract, clearly show, that K/S value decreased versus high temperature of treatment, and reduced with higher citric acid concentration. This fact can be explained by the destruction of the colorant. K/S value of samples, which were colored by chlorophyll, has shown direct proportional dependability from temperature of heat treatment,

Table 1 – K/S value of colored and uncolored samples

№	$C_{water\text{-}glass}$ ($C_{W.G.}$), g/L	C_{acid}, g/L	Temperature of treatment ($T_{T.H.}$), °C	K/S value	
				Colored by madder	Colored by chlorophyll
1	100	50	160	0.46152	0.24114
2	100	50	120	0.51376	0.23454
3	100	20	160	0.64314	0.19837
4	100	20	120	0.69955	0.18875
5	50	50	160	0.50088	0.20763
6	50	50	120	0.51779	0.19399
7	50	20	160	0.56889	0.18180
8	50	20	120	0.57339	0.17998
0	Untreated, uncolored			0.009713	

water-glass concentration and acid concentration. Therefore, next conclusions can be made: copper complex of chlorophyll has good thermal stability, in comparison with madder extract; increasing of intensity with the highest temperature and concentration of the liquid glass contributes to better fixation of the dye.

For identify patterns of color fixation from treatment parameters, PT-4 device and the gray standards scale were used. Result of color fastness test is shown in table 2.

Table 2 – Results of testing the color fastness to wet/dry friction

№	$C_{W.G.}$, g/L	C_{acid}, g/L	$T_{T.H}$, °C	Colored by madder		Colored by chlorophyll	
				dry	wet	dry	wet
1	100	50	160	5	4	5	4-5
2	100	50	120	5	3-4	5	4-5
3	100	20	160	5	3-4	5	4-5
4	100	20	120	5	3-4	5	4-5
5	50	50	160	5	4	5	4-5
6	50	50	120	5	4	5	4-5
7	50	20	160	5	4	5	4-5
8	50	20	120	5	4	5	4-5

It's clearly shows, that increasing temperature of thermal fixation leads to best color fixation results. But high treatment temperature can injure cellulosic fibers. So, heating in temperature 120-160 °C of fabric is one of the reasons of changing mechanical properties in comparison with the original fabric, tensile strength had been measured consequently. Testing results are shown in table 3.

Table 3 – Tensile strength of the treated and untreated samples

Number of regime	$C_{W.G.}$, g/L	C_{acid}, g/L	Tensile strength, N	
			$T_{T.H}$=160 °C	$T_{T.H}$=120 °C
Colored by madder extract				
1	100	50	388	462
2	100	50	458	497
3	100	20	365	488
4	100	20	411	452
Coloured by chlorophyll copper complex				
1	100	50	281	284
2	100	50	311	333
3	100	20	260	306
4	100	20	358	428
Untreated	0	0	232	232
Non-coloured, treated by $AlK(SO_4)_2$	0	0	0	409

It can be seen, that with decreasing of treatment temperature and acid concentration and increasing of water glass, the tensile strength has been enhanced.

Thus, optimal parameters of treatment can be chosen depend on color rubbing test results and K/S value. So, results of research are shown, that $C_{water\text{-}glass}$= =100 g/L, C_{acid}= 20 g/L and $T_{T.H}$ =120 °C are better parameters for sol-gel dyeing by madder extract. $C_{water\text{-}glass}$= 100 g/L, C_{acid}= 50 g/L and $T_{T.H}$ =160 °C are better parameters for sol-gel dyeing by chlorophyll copper complex.

For studying of surface morphology of treated and untreated samples SEM/EDX method was used. Images of fibers structure are shown on figure1. Surface images and EDX analysis is proving existence of silica oxide gel coating.

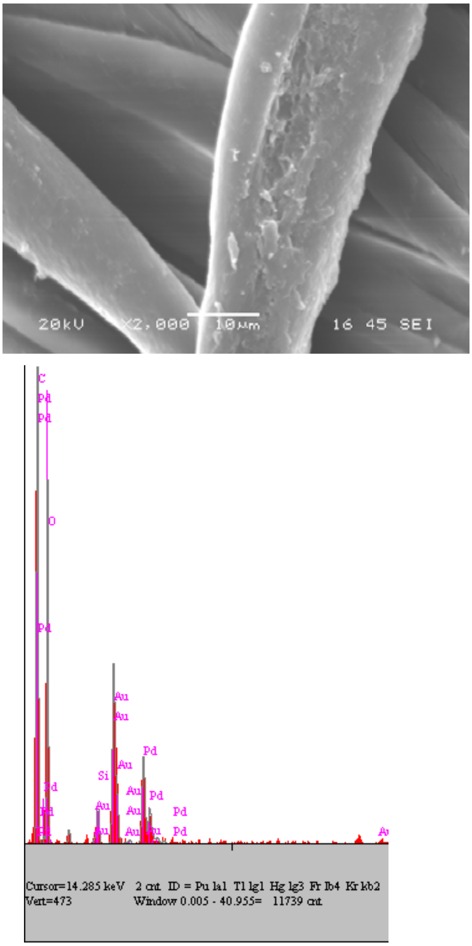
Conclusion.

1. The proposed coloring technology based on double-bath impregnation sol-gel method allows to obtain barrier silica coatings, where natural dye is included, it has been proved by images of SEM/EDX method.

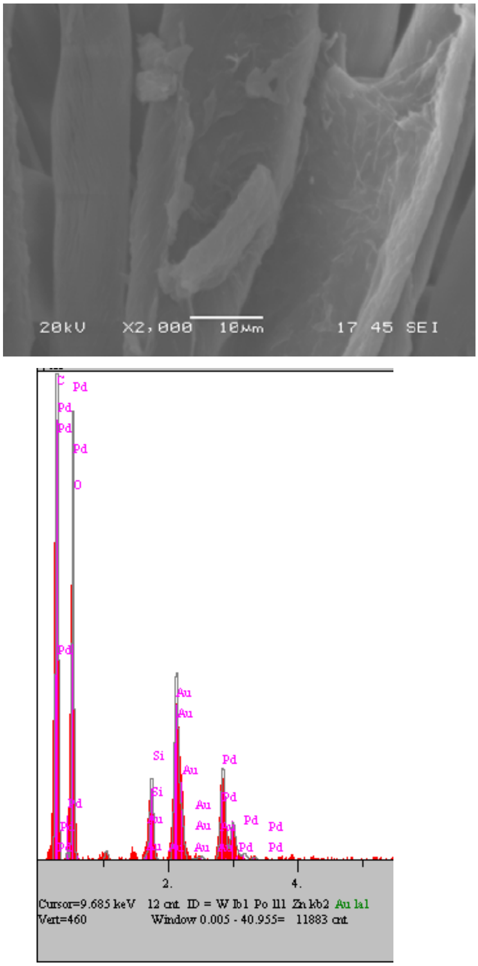
2. The general advantages of this coloring method is that reaction of polycondensation doesn't proceeds in the bath, It occurs in the pores of cotton fiber, therefore present method makes it possible to increase the storage time of using solution up to several days without gelling and that the solution can be recycled and reapplicated again.

3. At work an eco-friendly natural colorants and environment safely fixation method of dyes through sol-gel process, applying of water-soluble precursor and non-mineral acid, was used.

4. It was found that $C_{W.G}$ = 100 g/l, C_{acid}= 20 g/l and $T_{T.H}$ =120 °C are better parameters for sol-gel dyeing by madder extract. Then $C_{W.G}$ = 100 g/l, C_{acid}= 50 g/l

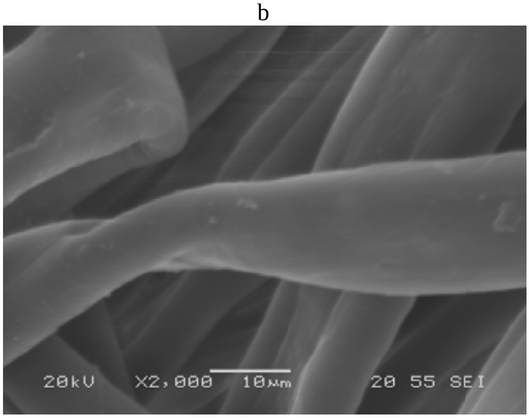


a



b

Figure 1 –
SEM images of samples:
a – colored by chlorophyll,
b – colored by madder extract,
c – untreated cotton sample



c

and $T_{T.H}$ =160 °C are better parameters for sol-gel dyeing by chlorophyll copper complex.

Therefore, the process can be carried out on common industrial dyeing machines. General disadvantage is possibility of coloring hydrophilic fibers only. Results of this research can be used as basic for development of eco-friendly sol-gel dyeing technology.

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Резюме

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ЗОЛЬ-ГЕЛЬ ТЕХНИКА
В ЭКОЛОГИЧНОМ КРАШЕНИИ ЦЕЛЛЮЛОЗНЫХ МАТЕРИАЛОВ

Описан двухванный золь-гель метод крашения целлюлозных текстильных материалов. Предложен экологически безопасный способ крашения целлюлозных текстильных материалов с применение натуральных красителей растительного происхождения (экстракт марены красильной и медного комплекса хлорофилла). Предложенный способ состоит в последовательной пропитке образцов хлопчатобумажной ткани сначала в прекурсоре золь-гель процесса, а затем в катализаторе гидролиза, с последующей сушкой и термической обработкой. Исследовано влияние концентрации прекурсора золь-гель перехода и катализатора гидролиза на колористические и прочностные свойства полученных образцов. Выявлено, что оптимальными параметрами для крашения являются: концентрация жидкого стекла $C_{W.G}$ = 100 г/л, концентрация лимонной кислоты C_{acid} =50 г/л и температура термообработки $T_{T.H}$ = 160 °C для хлорофилла и $C_{W.G}$ = 100 г/л, C_{acid} = 20 г/л and $T_{T.H}$ = =120 °C для марены красильной. Для исследования поверхности обработанных волокон применен метод электронной микроскопии, по результатам которого доказывается наличие кремнеземного покрытия. Результаты исследования могут быть применены в отделочном производстве текстильных целлюлозосодержащих материалов.

Ключевые слова: золь-гель, кремний, натрия силикат, лимонная кислота, растительные красители, непрерывное крашение, марена, хлорофилл.

Резюме

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ЦЕЛЛЮЛОЗДІ МАТЕРИАЛДАРЫН ЭКОЛОГИЯЛЫҚ
БОЯУ КЕЗІНДЕГІ ЗОЛЬ-ГЕЛЬ ТЕХНИКАСЫ

Мақалада целлюлозалық тоқыма материалдарын бояуға арналған екі ванналық золь-гель әдісі сипатталған. Зерттеудің нәтижелері бойынша өсімдік табиғи бояғыштар (бояғыштың сығындысы және хлорофилдің мыс кешені) қолданылатын целлюлоздық тоқыма материалдарын бояудың экологиялық қауіпсіз әдісі ұсынылған. Ұсынылған әдіс алдымен золь-гель процесінің прекурсорларында мақта-мата үлгілерін сіңіріліп, содан кейін гидролиз катализаторында сіңіріліп, кейін кептіру және термиялық өңдеуден тұрады. Алынған үлгілердің түсі мен беріктігі қасиеттеріне золь-гельдік гидролиз катализаторының прекурсорлық концентрациясының әсері зерттелді. Өңдеу параметрлерінің текстиль материалының физико-механикалық қасиеттері, бояу интенсивтілігі мен беріктілігі зерделенген. Нәтижесінде, келесі оптимальді параметрлер анықталған: хлорофилл мыс комплексі үшін - натрий силикат концентрациясы $C_{W.G}$ = 100 г/л, лимон қышқылы концентрациясы C_{acid} = 50 г/л және термоөңдеу температурасы $T_{T.H}$ =160 °С; бояуринмен бояу процесі үшін - $C_{W.G}$ = 100 г/л, C_{acid} = 20 г/л and $T_{T.H}$ = 120 °С. Сонымен қатар электронды микроскопия әдісін қолдана отырып функционалды жабын мен бояғыштың бекітілгені зерделенген. Зерттеу нәтижесі целлюлозалы текстиль материалдарын өңдеу өндірісінде пайдалауға болады.

Түйін сөздер: золь-гель, кремний, натрий силикаты, лимон қышқылы, өсімдік бояғыштар, үздіксіз бояу, бояурин, хлорофилл.