Non-ionic Dyes in Silica Hybrid Materials as Coloured Coatings on Protein Fibers

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The paper presents experimental data regarding coloration of protein fibers using film building silica hybrids containing disperse dyes embedded or covalently linked into the inorganic network. Properties of the coatings are studied from the point of view of colour strength, fastness to light and washing and thermal stability in relation to their composition. The proposed method allows obtaining coloured protein fibers in a single step, with good uniformity and intensity using disperse dyes, which in dyeing practice are not intended to colour this type of fibers.

Keywords: silica hybrids, disperse dyes, protein fibers, thermal stability

Protein fibers are well represented by wool which is the second most important type of natural textile materials, from the production and applications point of view, after the cellulosic fibers. In contrast to cellulosic fibers, wool is the natural fiber with the most complex structure because is the epidermal product of some animals and contains insoluble structured proteins (keratins) constituted of 22 α-amino acids. In the structure of an amino acid exists two functional groups, one with an acid character (carboxyl) and the other one with a basic character (amino), groups that neutralize each other, intra-molecular protein macromolecules have an helicoidally space structure and are formed of polypeptide long chains in which the α-amino acids residues are connected by peptide groups, chains being linked each other by cysteine groups, electro valences, hydrogen bonds or van der Waals interactions. Polypeptide chains have at one end a free amino group and at the other end a carboxylic group.

Nanosols previously prepared for cellulosic supports [1-3] have the advantage of a great stability to storage, a good adherence to textile fibers and a short time of drying at moderate temperatures. The coatings obtained are easily applied under mild conditions and easy to modify their physical or chemical properties [4], which allow variation of the resulted properties in a very broad domain [5-10]. From the commercially point of view exists a wide range of precursors of organically substituted alkoxysilane type which allow practically unlimited possibilities to obtain variations in the composition of the synthesized materials [11,12].

The application of the hybrid silica coating materials on wool substrates in order to improve the properties of colouring obtained with different dyes, and also the study of the silica coatings influence on the colour of the wool fabric dyed with organic dyes in the usual manner of dyeing practice, has been subject of several publications in the literature [13,14].

The purpose of the experimental work carried out by applying nanosols colored with nonionic dyes, on proteic substrates are within the general objective pursued related to finding optimal compositions for subsequent application on mixtures of natural and synthetic fibers [15].

Structural differences of the coatings and their behaviour on protein fibers comparatively to cellulosic components raise new challenges in finding new components of the nanosols in order to obtain resistant and flexible coatings.

Experimental part

Materials and methods

The precursors used were of laboratory reagent grade and were obtained from Merck, Germany and Aldrich - USA. Hydrochloric acid (0.1 N), tetraethylortosilicate (TEOS), phenyltriethoxysilane (PhTES) diphenyldiethoxysilane (DPhDES), 3-glycidoxypropyltriethoxysilane, (GlyOPTES), vinyltriethoxysilane (VTES), 3-chloropropyltriethoxysilane (ClPTES), methyltriethoxysilane (METES), ethanol, tetrahydrofuran (THF) were used in the study without further purification. Disperse dyes: Disperse Red 1 (DR1), Disperse Red 5 (DR5), Disperse Red 17 (DR 17), Disperse Orange 5 (DO5), Disperse Brown 1 (DBr1) and their triethoxysilyl derivatives were previously obtained by us [16] and purified by extraction with toluene in a Soxhlet extractor, followed by recrystallization. The fabric used was 100% wool fabric with a specific weight of 220 g/m^2, ready for dyeing.

Preparation of the impregnation bath, impregnating-drying-crosslinking

A solution obtained from 3.25 mL of TEOS, 3.25 mL PhTES, 3.9 mL of a solution containing 1.7 g of disperse dye selected from those mentioned above in 100 mL of THF, 0.65 mL water, 2.35 mL of ethanol and a few drops of hydrochloric acid was stirred for 1 h at room temperature. The mixture was stirred vigorously at room temperature and used immediately for the impregnation of textile materials. A test sample of wool fabric of about 2 g was impregnated with an 80% degree of uptake in several successive passes, on a laboratory impregnation device Ernst Bentz, at a constant speed of 0.5 m / min and a pressure of 0.4 kg/cm^2. The coated materials were dried at room temperature for 2 h and then were subject to heat treatment at 120^{0}C for 1 h in a thermo-fixation oven.

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Measurements

FTIR spectra were recorded on a JASCO FT-IR 6300 spectrometer equipped with a Specac ATR Golden Gate (KRS5 lens) in the 400-4000 cm^{-1} (32 accumulations at a resolution of 4 cm^{-1}). Total colour differences in CIELAB system, using a 10 degrees standard observer and illuminant D65 and diffuse reflectance spectra were measured with a JASCO V570 UV-VIS-NIR spectrophotometer equipped with a JASCO ILN - 472 (150 mm) integrating sphere, using spectralon as reference. XRF analyzes were performed on a spectrometer PW4025 - MiniPal - Panalytical EDXRF. The measurements were carried out in an atmosphere of helium for 300 sec. without using a filter, at 20 kV and automatically adjusting the intensity of the current. Thermal analysis was carried out with an SDT Q600 instrument (TA Instruments) under an atmosphere of air or helium, at a heating rate of 10^{0}C/min. in alumina crucibles. The instrument was coupled to a Pfeiffer Thermostar mass spectrometer (0-300 amu, resolution of 1 amu). The light-fastness tests were carried out with a Xenotest 150 S+ (Atlas), in accordance with ISO B02.

Leaching tests

Coloured samples were tested in accordance with the standards for determining the change in color during 6 cycles of repeated washing. For this purpose, a washing solution similarly to those used in domestic washing was used under the conditions of ISO 105/C standard. Thus, tests were performed using a solution of 1% by weight sodium dodecyl sulfate at a temperature of 60^{0}C for 2 h, on a Linitest device type. The sample consisting of a piece of coloured wool fabric is placed between a piece of cotton and one of wool and are each sewn on the four sides. After washing, the specimen is rinsed with hot and cold water and allowed to air dry after un-sewn the specimen on three sides so that the fabric does not remain in contact with the accompanying materials. After drying, the samples are evaluated against the original colored fabrics.

Results and discussions

Impregnation bath compositions and resistance of the coatings

In order to obtain compositions for the impregnation baths some network modifiers have been used for both silica hybrids of class I and class II film-forming materials used in our previous works for coating cellulosic substrates. Due to structural changes operated on silica film-forming materials we can analyze the influence of different organic groups of the modifying agents on the dyestuffs used.

Analaysing the colours obtained with the same coating composition on the wool fibers comparatively to those produced on other types of fibers can be evaluated the influence of the substrate on the color obtained. Thus, from the analysis of the wavelength of absorption maximum obtained for coating compositions made of different types of silanes, mixed in different proportions, as in the case of those containing DO5 is obtained a hypsochromic effect of only 1-5 nm depending on the content of organic modified silanes. Such behaviour can be explained only by the existence of stronger interactions between the dye and the fabric, making the effect of the organic substituents in the silica network to have very little influence on the color of the dyes, as it can be seen from table 1.Regarding coating compositions obtained with different dyes it is obviously that a hypsochromic displacement of the absorption peak wavelength of about 10-18 nm takes place in the case of the coatings obtained with dyes covalently bonded on the network comparatively to those sequestrated into the inorganic network. The effect increases as the number of anchoring groups on silica network increase, due to steric hindrance on the lone pair electrons of the amino auxochromes of azo dyes. In order to obtain stronger adhesion forces between the coating and the substrate and to achieve a better compatibility of the organic dyes with the neighboring into silica networks was varied the composition of impregnating baths. In the same time another objective was to maintain into a reasonable range the stiffness of the coated material so that to be not affected significantly the original properties of the fiber.

In the case of wool fibers, bonds between the coating and the fabric hydrogen bonding and van der Waals forces predominantly ensure substrate. As the only groups capable of leading to hydrogen bonds are, on the one hand, amino and carboxyl groups in the structure of the substrate, and on the other hand, silanol groups of the hybrid silica matrices, the adhesion of the coatings to this type of textile fabric was relatively poor. This finding is of great importance from the viewpoint of obtaining coatings resistant to wet and dry cleaning processes. Thus, it can be seen from table1, the best resistance to washing is obtained for the hybrid coatings made from precursors that contain PhTES. This can be explained by the hydrophobic character of the silica hybrid coatings obtained with this type of modifying

Table 1
THE EFFECT OF NETWORK MODIFYING AGENT ON COATINGS RESISTANCE

Silanes content (%)		Dyestuff type and content (%)	Wavelength of the Vis absorption maximum (nm)	Light fastness (grade)	Washing fastness at 60^{0}C (grade)		
TEOS	Modifying agent (%)				Color changing	Staining on	
						wool	cotton
50	PhTES 50	DR1 0.5	503	5	2	3	4-5
50	PhTES 50	DR1-PTES 0.5	499	4-5	2-3	4	4-5
50	PhTES 50	DR5 0.5	521	3-4	2	2	3-4
50	PhTES 50	DR5-PTES 0.5	509	4	3	4-5	4-5
50	PhTES 50	DR17 0.5	514	4	2	2-3	4
50	PhTES 50	DR17-PTES 0.5	496	4	2-3	3-4	4
50	PhTES 50	DO5 0.5	466	4-5	2	3	4
50	PhTES 50	DO5-PTES 0.5	456	4	2-3	4	4-5
25	MeTES 75	DO5 0.5	459	4	2	1-2	3-4
50	MeTES 50	DO5 0.5	460	4	2-3	2	3-4
75	MeTES 25	DO5 0.5	459	4	2	1-2	3
25	VTES 75	DO5 0.5	458	4-5	1-2	2	2-3
50	VTES 50	DO5 0.5	457	4-5	1-2	2	3
75	VTES 25	DO5 0.5	463	4-5	2	2	2-3
25	ClPTES 75	DO5 0.5	460	5	2-3	2	3
50	ClPTES 50	DO5 0.5	459	5	3	2	3
75	ClPTES 25	DO5 0.5	463	5	2	2	2-3

agent, which finally leads to the stabilization of the coating to the water action in washing processes.

As it can be seen, especially in the case of staining on fiber of the same type for this coating the lowest resistance is obtained, whereas in case of staining on cotton fiber to which the dye has no affinity, it is obviously the result is better.

PhTES coatings is obtained with a precursor having a high adhesion to the textile substrate and it is quite clear in all the other cases detachment and migration to the surface of the accompanying material is due to the displacement of parts of the hybrid silica network from the coatings.

By comparing the washing behavior of the coatings obtained with hybrid of class I and class II it is observed the superior resistance obtained in the last case, especially when the coatings are obtained using PhTES as modifying agent of the silica network. This is due to an efficient immobilization of dyes in the inorganic network, in this case the leaching process being solely due to the oligomers and parts of the hybrid network displaced during the washing process.

Variations in color intensity of the hybrid coatings deposited onto fabrics were monitored after performing several successive washing cycles. From diffuse reflectance spectra recorded after each washing cycle it was found that both for hybrids of class I and class II there is a loss of color. Probably, in the first case this takes place by extraction of the dyestuff from the inorganic network, while in the second case the process can be explained only by detachment of oligomers from the hybrid network. The loss of coloring material continues at a slower rate in the case of hybrids of class I, whilst for hybrids of class II it is becoming smaller, as shown in figure 1. Analyzing the absorbance change for wool samples coated with hybrids of class I and class II, during successive washing processes, we can conclude that maintaining the parameters for obtaining the impregnation sols and of the impregnation operation are obtained colored coatings of equal intensity, as it can be seen in figure 1.

It is found that for DR1 chromogen the wavelength of the absorption maximum in the case of class I hybrid is situated at $\lambda_{max.}$=503 nm compared to $\lambda_{max.}$=499 nm recorded for the maximum absorption of the class II hybrid,probably due to steric hindrance caused by residues anchoring agent (NCOTEOS) with which was modified the dye. The emphasized decrease in intensity is recorded after the first washing cycle in both cases. After seven successive washes the loss of film-forming colored material from wool treated with the hybrids of class I and II is in the first case around 60%, while in the second case it is 35%, so as shown in figure 1.

Taking into account that the determination is based on quantification of the color of the substrate after washing, it is obvious that in the case of class I hybrids some of part of the dye is extracted from the inorganic network due to the surfactant micelles during the washing process. Values obtained raises serious questions about the effectiveness of the implementation of such colored coatings on protein fibers. It is noted that the loss of dye is important even in the case of class II hybrids which means that much material is lost by removing the whole hybrid material containing the dye covalently linked from the surface of the textile substrate.

Regarding light fastness, it is largely influenced by the structure of the chromogen, but in this case the values obtained using the same chromogenic structure on protein substrate are less sensitive and are not influenced by the type or quantity of hybrid network modifier. It also finds that there are no significant differences in terms of light

Colour differences in the CIELAB system, as can be seen from table 2, are mainly determined by differences in lightness, darkness of the shades obtained being greater if in the structure of the hybrid material are present aromatic nuclei, which interact with the dyestuff molecules. Shifting of the hue to red occurs, when the volume of the organic substituent from the hybrid network is smaller (MeTES). This is due to the establishment of hydrogen bonding interactions between the auxochromes from the dyestuff molecules and the silanol groups of the silica network, which cannot be shielded by the low-volume of organic substituent grafted onto silica network.

Structural characteristics of the coated materials

FTIR ATR spectra show characteristic bands of constituents of the coating material together with those specific of the protein substrate. As can be seen from figure 2, the most important absorption bands in the spectrum belong to the wool fiber. The intense band located at 1634

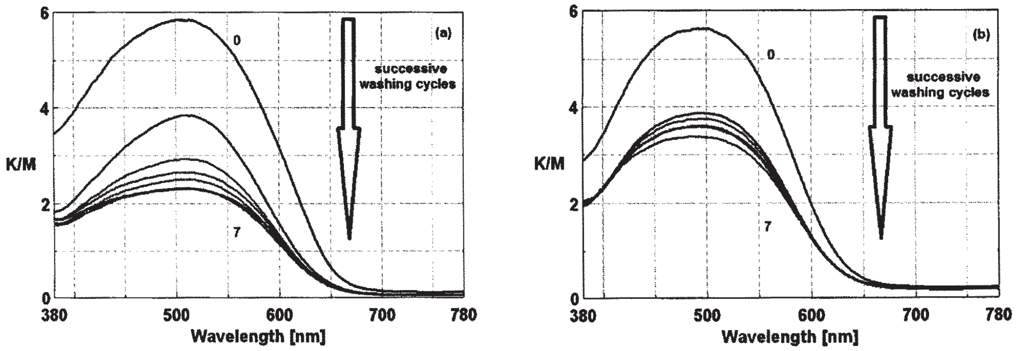

Fig. 1. Changes in the K/S values during successive washes of wool coated with silica hybrids obtained from TEOS/PhTES containing: (a) DR17 and (b) DR17-PTES

Table 2
COLOUR DIFFERENCES OF THE COATED TEXTILE MATERIALS

Coating composition	D65 Illuminant / 10^0 standard observer												
	Tristimulus values			Trichromatic coordinates		CIELAB values			Color differences				
(DO5/TEOS/)	X	Y	Z	x	y	L	a	b	ΔL	Δa	Δb	ΔE_{ab}	ΔH
ClPTES	18.62	15.55	10.19	0.4197	0.3506	46.38	21.74	16.33	-46.83	22.30	16.90	54.55	9.30
MeTES	16.76	13.89	8.85	0.4243	0.3515	44.07	21.70	16.50	-49.14	22.26	17.08	56.58	9.31
VTES	19.66	16.36	10.47	0.4229	0.3519	47.45	22.48	17.32	-45.76	23.04	17.89	54.27	9.50
PhTES	18.15	15.60	11.39	0.4022	0.3456	46.44	19.03	12.97	-46.77	19.59	13.55	52.48	8.54

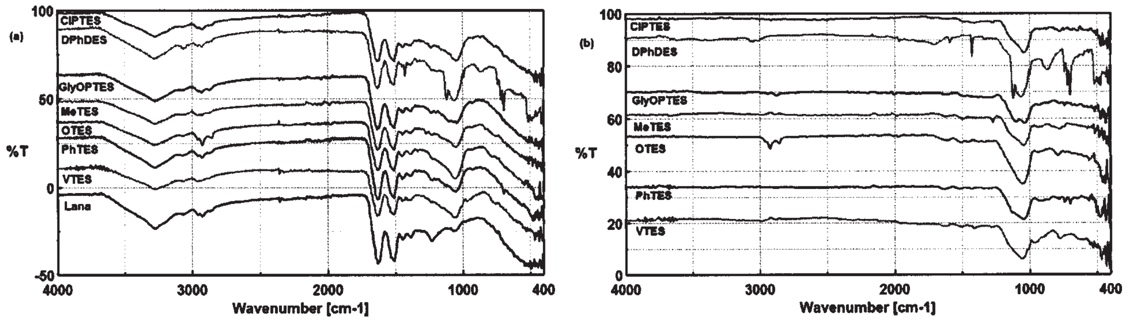

Fig. 2. FTIR spectra of wool fabrics coated with nanosols (a) and of the coatings obtained by subtracting the substrate pattern (b)

cm^{-1} correspond to the stretching vibration of the carbonyl group of the amide linkages (amide I), at 1511 cm^{-1} is situated an intense band corresponding to the deformation vibration of the C-N-H amide groups (amide II), whereas at 1234 and 1055 cm^{-1} are identified absorption bands amide III and IV corresponding to C-N stretching vibration. Another important band characteristic for protein fibers is determined by the swinging vibrations of methylene and methyl groups, located at 1450 cm^{-1}.

It should be noted that in the FTIR spectrum of the wool fiber also appear the corresponding bands of symmetric and asymmetric stretching vibration of methylene groups located at 2925 cm^{-1} and 2869 cm^{-1} respectively, while at 3275 cm^{-1} is situated an absorption band due to intermolecular hydrogen bonding of the amide groups.

Analyzing FTIR spectra obtained by substraction it was found the presence of the characteristic absorption bands for each type of coating material depending on the modifying agent used. The doublet situated at 2924 and 2854 cm^{-1} is assigned to asymmetric respectively symmetrical stretching vibration of CH_2 group due to the presence of OTES as modifying agent. At 1336 cm^{-1} was observed a band corresponding to deformation of OH group, and around 1100 and 1052 cm^{-1} are found bands which are attributed to the stretching vibration of Si-O-Si. Also, at 964 cm^{-1} must be mentioned a characteristic band of silanol groups.

For coatings containing VTES the stretching vibration of C = C groups is found at 774 cm^{-1} overlapped with the corresponding out of the plane vibration of the C=C-H. In the case of coatings containing ClPTES, the stretching vibration of the C-Cl bond is situated at 774 cm^{-1}, whereas in the case of PhTES the out of the plane deformation vibration of CH groups belonging to the aromatic ring was placed at 740 cm^{-1}. In the case of hybrid film building materials containing MeTES the band located at 777 cm^{-1} corresponds to Si-CH_3 bond deformation while GlyOPTES modified silica coatings exhibit a band at 926 cm^{-1}, which is due to the symmetric stretching vibration of the epoxy ring.

XRF analysis of the wool fibers coated with hybrid materials shows the presence of silica on the surface of the textile material, the amount depending on the composition of the coating material. The results obtained show that the silica situated at the surface of the textile material was in the range of 6 to 6.9%. The highest value was recorded for coatings obtained from VTES and TEOS at a 1:1 molar ratio after 4 successive passes on the impregnation machine, and the lowest is recorded for the composition obtained from GlyOPTES and TEOS at a 1:1 molar ratio (fig. 3).

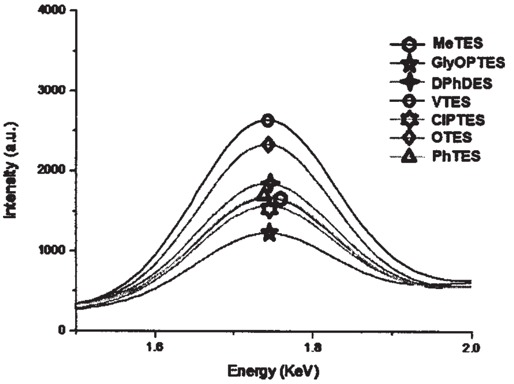

Fig. 3. The silicon content on the surface of the wool fabric determined by XRF

Thermal stability of the coated protein fibers

Analyzing by thermogravimetry the protein support samples coated with silica nanosols it is found that the decomposition pattern of the protein support in the temperature range considered typically consists of four oxidative decomposition steps. The first step is the removal of water from the textile, which in this case is around 9-10% of the total mass loss. In the case of film-coated wool material, this stage is about 6% of total mass loss and is due to the hydrophobicity of the coating materials, as it can be seen in figure 4.

Another step of the decomposition profile of the wool fibers situated at about 270^{0}C, represents about 40-45 % of the total weight loss and is due to thermal decomposition of the macromolecular chains, firstly by destruction of sulfur chains and decarboxylation , followed by breaking of the peptide bonds. The processes that take place lead to the release of carbon dioxide, carbon monoxide, water, hydrogen sulfide, and formation of tar residue. For coated materials, this stage has the thermal decomposition peak located at 276- 286^{0}C and represents 15-40% of the total mass loss. It should be noted that in the case of coatings obtained with ClPTES and OTES decomposition occurs in two steps, the second step having the maximum of thermal decomposition at 320- 360^{0}C. The effect of ClPTES addition in the coating composition is to protect the substrate from oxidative thermal decomposition; the temperature corresponding to the maximum speed of thermal decomposition is shifted to a higher value with 10^{0}C.

The third stage of the wool fabric thermal decomposition consists of the oxidative decomposition of the tar previously formed, that takes place at about 530^{0}C, and is about 30-40% of the total weight loss. In the case of all coated materials, this stage is present in the range 529-540^{0}C and

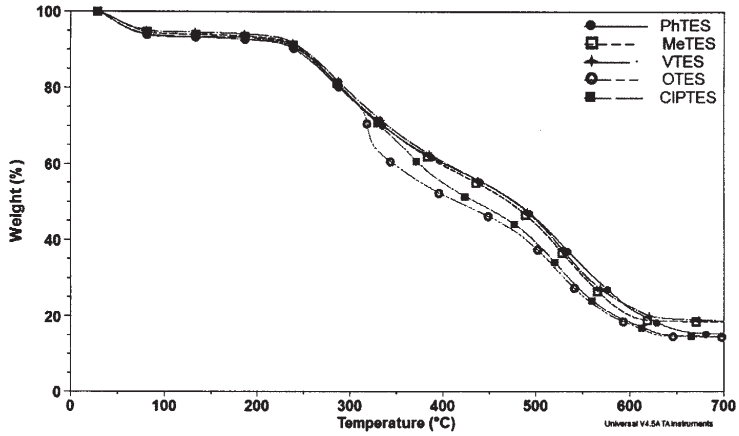

Fig. 4. Thermogravimetric curves of wool fibers coated with hybrid materials

Table 3
RESULTS OF THERMOGRAVIMETRIC ANALYSIS

Sample		Temperature range (°C)						Residue
		RT-150	150-330	330-440	440-605	605-700		
Wool	Weight loss (%)	9.32	42.8	44.55		3.05		0.29
	T $_{max.}$ (°C)	45.8	276.9	526.7		645		
TEOS/OTES 50/50	Weight loss (%)	6.7	14.65	29.62	31.07	3.49		14.47
	T $_{max.}$ (°C)	45.1	277.7	319.6	522.8	615.7		
TEOS/MeTES5 0/50	Weight loss (%)	6	36.59	29.19		9.62		18.6
	T $_{max.}$ (°C)	50.1	279	529.1		559.4		
TEOS/VTES 50/50	Weight loss (%)	5.38	37.19	35.13		3.49		18.81
	T $_{max.}$ (°C)	47	279.8	528.7		603		
TEOS/ClPTES 50/50	Weight loss (%)	6.55	23.46	20.28	31.76	3.29		14.66
	T $_{max.}$ (°C)	44.6	286.8	366.9	523.9	617.6		
TEOS/PhTES 50/50	Weight loss (%)	6.41	35.3	30.36		8.14	4.16	15.63
	T $_{max.}$ (°C)	44.5	278	530.4		586.4	625.6	

represents about 10-15% of the total weight loss, based on the organic groups initially grafted onto the inorganic silica network. The last stage, which corresponds to complete combustion of highly condensed materials obtained from aromatic residues, is situated at 615-645°C and represents 3-5% of the total mass loss. This is confirmed by the similar behaviour of the coating obtained using PhTES, which has a characteristic step of decomposition located at 625°C and that corresponds to such a process.

Residue at 700°C varies depending on the composition and amount of coating material deposited on the fiber and represent 15-20% of the total mass loss, as can be seen from table 3.

Conclusions

Analyzing colored wool fabrics using as impregnating compositions nanosols of the type shown was revealed that coloration of the protein fiber can be achieved in a single step, with good uniformity and satisfactory intensity.

Changing the inorganic network it is very easy to modify the nuances obtained, the deviation is towards red. The disperse dyes used in the process produce colouration at standard intensity at a concentration of about 0.5 %.

The thermal fixing of the coatings at a temperature of 120°C for 1/2 to 1 hour is sufficient to obtain hybrid networks stable to washing processes. Under these conditions, the coatings obtained are sufficiently intense and uniform, but resistances to washing of this type of substrate are fair.

During performing successive washing tests, takes place the removal of the coating material in much higher quantities than in the case of the cotton substrates.

After six successive washes, the loss of coloured film-forming materials from the surface of the wool substrate treated with the hybrids of the class I and II, estimated from the diffuse reflectance spectra, is situated in the first case around 60 %, while in the second case it is about 35 %.

The best compatibilization of the non-ionic dyes with the inorganic silica network is obtained by the use of network modifiers containing aromatic residues, but thermal stabilization is more accentuated when ClPTES was used to obtain coating compositions.

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References

1. RADITOIU, A., AMARIUTEI, V., RADITOIU, V., GHIUREA, M., NICOLAE, C.A., WAGNER, L.E., Rev. Chim. (Bucharest), **63**, 2012, p. 612
2. RADITOIU, A., RADITOIU, V., AMARIUTEI, V., GHIUREA, M., NICOLAE, C.A., GABOR, R., FIERASCU, R.C., WAGNER, L.E., J. Optoelectron. Adv. Mat., **14**, 2012, p. 846
3. RADITOIU, A., RADITOIU, V., AMARIUTEI, V., NICOLAE, C.A., GABOR, A.R., FRONE, A.N., FIERASCU, R.C., GHIUREA, M., WAGNER, L.E., HUBCA, G., Mat.. Plast., **50**, 2013, p. 241
4. RADITOIU, A., RADITOIU, V., GABOR, R., NICOLAE, C.A., GHIUREA, M., HUBCA, G., U.P.B. Sci. Bull. Ser. A, **75**, 2013, p. 285
5. MAHLTIG, B., FIEDLER, D., BÖTTCHER, H., J. Sol-Gel Sci. Technol., **32**, 2004, p. 219
6. MAHLTIG, B., J. Text. Inst., **102**, 2011, p. 455

7. HRIBERNIK, S., SMOLE, M.S., KLEINSCHEK, K.S., BELE, M., JAMNIK, J., GABERSCEK, M., Polym. Degrad. & Stabil., **92**, 2007, p. 19578. VEITH, S.R., PERREN, M., PRATSINIS, S.E., J. Colloid. Interf. Sci., **283**, 2005, p. 495
9. BERENDJCHI, A., KHAJAVI, R., YAZDANSHENAS, M.E., Nanoscale Res. Lett., **6**, 2011, p. 594
10. MESSAOUD, M., HOUMARD, M., BRICHE, S., ROUSSEL, F., LANGLET, M., J. Sol-Gel Sci. Technol., **55**, 2010, p. 243
11. MIN, L., XIAOLI, Z., SHUILIN, C., Color. Technol., **119**, 2003, p. 297
12. LATTHE, S.S., IMAI, H., GANESAN, V., KAPPENSTEIN, C., RAO, A.V., J. Sol-Gel Sci. Technol., **53**, 2010, p. 208
13. CHENG, T., LIN, T., BRADY, R., WANG, X., Fibers Polym., **9**, 2008, p. 521
14. CHENG, T., LIN, T., FANG, J., BRADY, R., Textile Res. J., **77**, 2007, p. 923
15. ALONGI, J., CIOBANU, M., TATA, J., CAROSIO, F., MALUCELLI, G., J. Appl. Polym. Sci., **119**, 2011, p. 1961
16.WAGNER, L., RADITOIU, V., RADITOIU, A., ARDELEANU, P., AMARIUTEI, V., RADULY, M., Rev. Chim. (Bucharest), **60**, no. 5, 2009, p. 444

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