Alternative Hydrophobic Treatments Applied on Dyed Fabrics

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The product 3-chloro-2-hydroxypropyl stearate (CHPS) was used for durable hydrophobic finishing of cotton fabrics dyed with Reactive Blue 19, Vat Blue 4 and Direct Red 95. The hydrophobization compound used in this study was easy to synthesize, inexpensive and effective. The presence of CHPS on hydrophobic treated cellulose fiber was put into evidence by FTIR analysis. The hydrophobicity of treated sample was proved by water contact angles values and absorption times of the water drops. The best water water contact angle (150 degrees) and the best absorption time of water drop (180 min) were obtained for the samples treated with 60g/L CHPS. The effects of CHPS on chromatic parameters, colour fastness of dyed samples and comfort index (air permeability, hygroscopicity, rigidity) were evaluated.

Keywords: Hydrophobization, water contact angle, chromatic parameters, colour fastness, dyed cotton fabric

Hydrophobization is a finishing treatment applied to textiles to give them the ability to repel the water. Textile materials treated with hydrophobization agents may be used in the field garment, medical or technical [1].

Different ways conferring hydrophobic properties of textile materials include the use of waxes, aluminum and zirconium soaps, metal complexes, pyridinium compounds [2-3] or siliconic and fluorocarbon compounds [4-11]. However, some of these finishing treatments are expensive and have a poor durability, low permeability to air or present a risk for the human body and for the environment.

The modification of hydrophobicity for the textile materials by using of fluoropolymer repellent in combination with different monomers with reactive group or using of hybrid organic/inorganic materials elaborated through sol gel has also been studied [12-18]. The durable hydrophobic properties were also obtained by chemical reaction between cellulose hydroxyls and reactive groups of some hydrophobic compounds [19-22].

In this work CHPS was used as hydrophobizing agent due to its safety, availability, relatively low-cost and sustainability of the treatment. Since many textile materials that must be protected from water are colored, in this work we studied the effect of treatment with CHPS on the cotton materials dyed with the most commonly used classes of dyes (direct, reactive and vat dyes). The efficiency of the hydrophobization treatment, the colour measurements, the dyeing fastnesses and the comfort indices were evaluated.

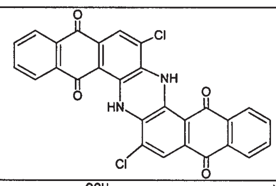
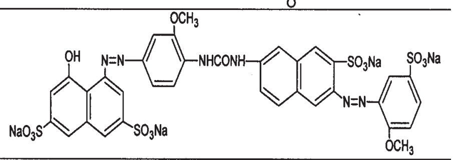
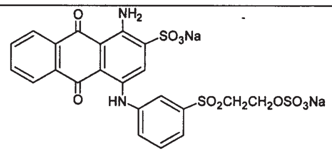
Experimental part

Materials and methods

Stearic acid, epichlorohydrin was purchased from Merck. Dyes presented in table 1 were purchased from Bezema Company (Bezathren blau RS), DyStar Company (Sirius licht scharlach BN) and Textilcolor AG Company (Tecofix Brill blau VSR). Another chemicals were purchased from Sigma-Aldrich Company and used without previous purification. Purolite A-520E catalyst was supplied by Victoria S.A. Purolite (Romania).

Desized, scoured and bleached 100% cotton fabric (170 g/m^2) was used in this study.

Table 1
DYES USED IN THIS STUDY

C.I. Generic name (Commercial name)	Structure
C.I. Vat Blue 4 (Bezathren blau RS)	
C.I. Direct Red 95 (Sirius licht scharlach BN)	
C.I. Reactive Blue 19 (Tecofix Brill blau VSR)	

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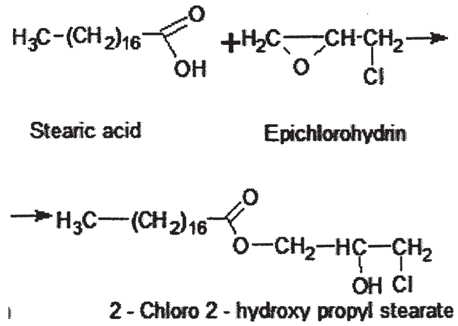
CHPS synthesis

Stearic acid (0.1 moles) was treated with epichlorohydrin (1.3 moles) in the presence of Purolite A-520E anion exchange resin (10g/100g reaction mixture) used as catalyst, at 90°C, 240 min. The final reaction mixture was vacuum filtered, washed with distilled water (70°C) and vacuum dried on a rotavapour. The main product resulted from reaction of epichlorohydrin with stearic acid 3-chloro-2-hydroxypropyl stearate was used as hydrophobizing agent. The yield 3-chloro-2-hydroxypropyl stearate determined by HPLC analysis was 70%. The obtaining reaction of 3-chloro-2-hydroxypropyl stearate (CHPS) is shown in chemical reaction 1.

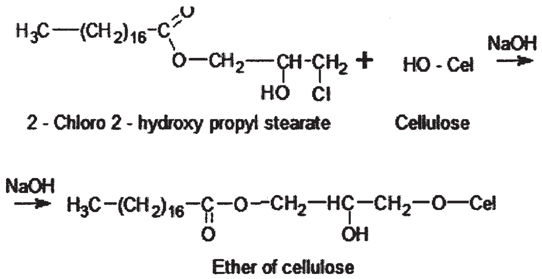


(1)

Working conditions

Dyeing cotton samples were performed with 3 classes of dyes: reactive dye (C.I. Reactive Blue 19), vat dye (C.I. Vat Blue 4) and direct (C.I. Direct Red 95), under the following conditions:

- *C.I. Vat Blue 4***:** 2% dye, 10 mL/L NaOH, 5 g/L $Na_2S_2O_4$, Hm 1:40, 60°C, 30 min.;
- *C.I. Direct Red 95:* 2% dye, 10% NaCl, Hm 1:40, temperature 100°C, 30 min.;
- *C.I. Reactive Blue 19:* 2% dye, 1g/L NaOH, 5g/L Na_2CO_3, 50g/L NaCl, Hm 1:40, temperature 60°C, 30 min.;



(2)

After dyeing, the samples were washed with cold and warm water, and the samples dyed with vat and reactive dyes were soaped with 0.5g/L Cotoblanc for 30 min at 80°C. Finally all the samples were dried at 80°C.

Hydrophobic treatment of cotton fabrics was performed with an emulsion obtained by mixing of the final product resulted from reaction with 2% aqueous solution of nonionic surface active agent at 70°C. Treating of cotton samples was carried out under the following conditions: padding with emulsion (at 70°C), padding with 10g/L NaOH, rolling, wrapping in polyethylene film, maintaining for 12 h at room temperature, drying for 20 min at 70°C, curing at 120°C, 20 min. In the presence of NaOH as catalyst, CHPS reacts with OH functional groups of cellulose resulting an ether linkage, as in chemical reaction 2.

After treatment, the products from the reaction mixture that do not show affinity for the cellulosic fiber (being only deposited on the fiber surface) were removed by washing with 2% Lavotan DSU (30 min at 70°C) and then by rinsing with cold and respectively warm distilled water.

Evaluation of hydrophobicity

Hydrophobicity of the samples treated with CHPS was proved by contact angles values and by the absorption times for a water drop placed onto fabric surface.

Static water contact angles of the sample surfaces were measured at 22°C in ambient air using an automatic contact angle goniometer equipped with a flash camera (Model DSA 100, Kreuss, Germany) applying a sessile drop method. For determination of water absorption time (according to AAATC Test Method 79) 10 droplets of water were poured with a micropipette on the surface of the treated samples from a distance of 2cm. The average volume of water droplet was about 30μL. The droplets were placed in different places on the surface of the fabric; the final result regarding the water absorption time by the fabric was considered as average of 10 measurements.

FTIR analyses

FTIR analyses were carried out on a Multiple Internal Reflectance Accesory (SPECAC, USA) with ATR KRS-5 chrystal of thalium bromide-iodide, having 25 reflexions and the investigation angle of 45°. This accessory device was attached to the Spectrophotometer FTIR IR Affinity-1 Shimadzu (Japan); the spectra registration was realized with 250 scans in the 4000–2800cm^{-1} and respectively 1800 – 500cm^{-1} ranges.

Air permeability

The measurements for air permeability of treated and untreated samples were carried out on ATL-2 Metrimpex Hungary apparatus according to Standards ASTM D 737-96.

Hygroscopicity

Hygroscopicity (samples capacity to retain water vapours) was determined according to Standard EN ISO 12571:2000

Colour measurements

The colour measurements were performed using spectrophotometer Spectroflash 300^R from DATACOLOR for illuminant D65/10 using Micromath 2000^R software, according to ΔE^*, ΔL^*, Δa^*, Δb^*, ΔC^* and ΔH^* values as in literature [23-30].

Dyeing fastness

Colour fastnesses to washing and rubbing for the dyed samples (treated with CHPS and untreated) were appreciated according to the standard tests ISO 105-CO6:2010 and ISO 105-X12:2001.

Results and discussions

The ways in which the concentration of hydrophobizing agent (CHPS) and the nature of the dye influence the characteristics of the cotton fabric were studied:

Hydrophobicity of samples dyed and treated with CHPS

The hydrophobicity of the treated samples was evidenced by the values of the contact angle that the surface of the treated samples forms with water drop and through the time during which a drop of water placed on the surface of the fabric is completely absorbed by this. The results obtained are shown in the table 2.

The presence of water drops on the samples dyed and treated with CHPS is also illustrated by the photographic images shown in figure 1. The photographs were taken after 15 min for C.I. Direct Red 95, after 60 min for C.I. Vat Blue 4 and respectively after 5 min for C.I. Reactive Blue 19

Table 2
ABSORPTION TIMES AND CONTACT ANGLES OF THE SAMPLES DYED AND TREATED WITH CHPS

CHPS (g/L)	C.I. Vat Blue 4 AT* (min)	C.I. Vat Blue 4 CA** (degrees)	C.I. Direct Red 95 AT* (min)	C.I. Direct Red 95 CA** (degrees)	C.I. Reactive Blue 19 AT* (min)	C.I. Reactive Blue 19 CA** (degrees)
control sample	*the wetting times were less than 2s and the wetting angles could not be determined*					
20 g/L	90	117	15	66	5	28
40 g/L	120	135	90	124	50	59
60 g/L	180	150	115	140	105	123

** AT is the absorption time of water droplet (expressed in minutes);*
*** CA is the contact angle (expressed in degrees)*

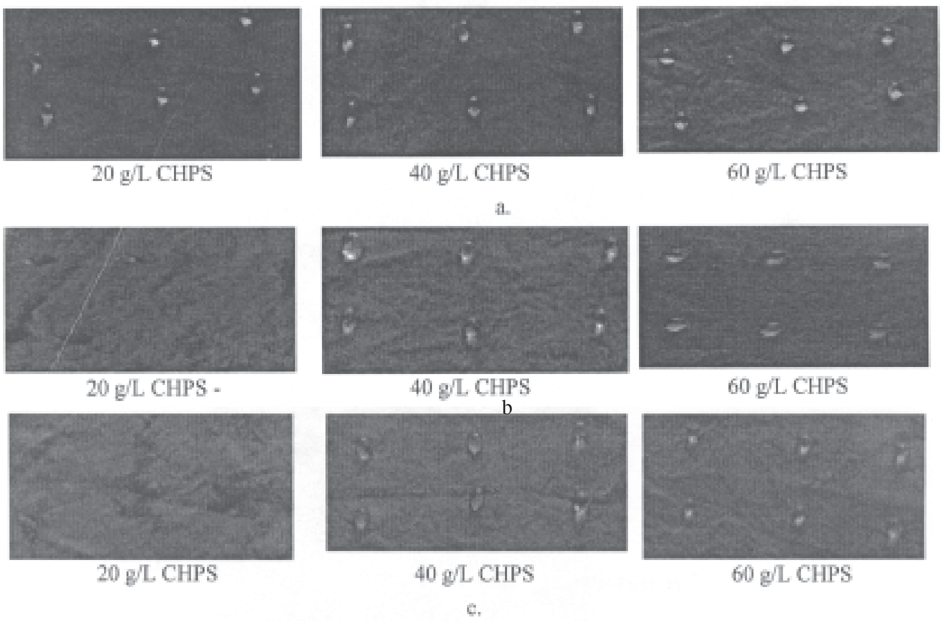


Fig. 1. Photographs of the water droplets placed on the surface of samples treated with CHPS: a. dyed with vat dye; b. dyed with direct dye; c. dyed with reactive dye

since the placement of the water drops on the surface of the samples.

Analyzing the obtained results one notice that the best hydrophobizing effect was obtained for the samples treated with 60g/L CHPS. As far as concerns the nature of the dye, the best results were obtained for the samples dyed with vat dye and the worst results were obtained for the samples dyed with reactive dye. The higher values for the wetting angles and the absorption times of the water drops obtained for the samples dyed with vat dye can be explained by the reduced affinity of this dye toward water due to the lack of the solubilized groups

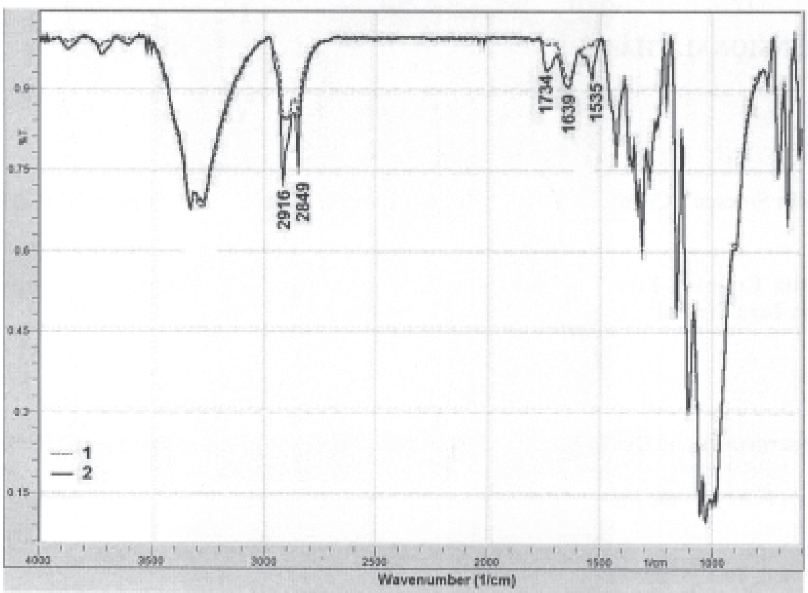
FTIR analysis

The analysis of the IR spectra showed the presence of CHPS onto the dyed cotton fabric (fig. 2).

The chemical interactions between CHPS and cotton fabric are highlighted by the absorption bands from the characteristic spectra (table 3).

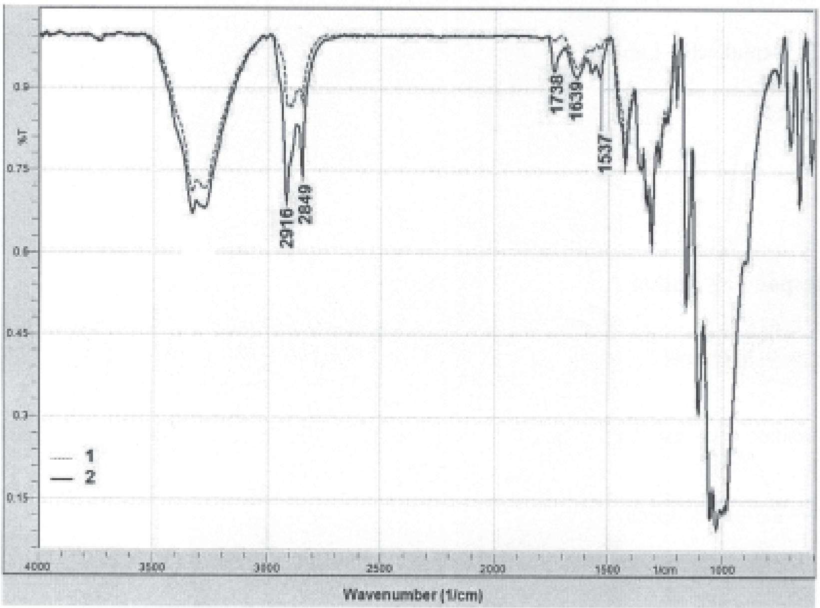
Evaluation of the comfort properties

The effect of hydrophobization treatment on the comfort index of the textile materials were appreciated by determination of air permeability, higroscopicity and rigidity (table 4).

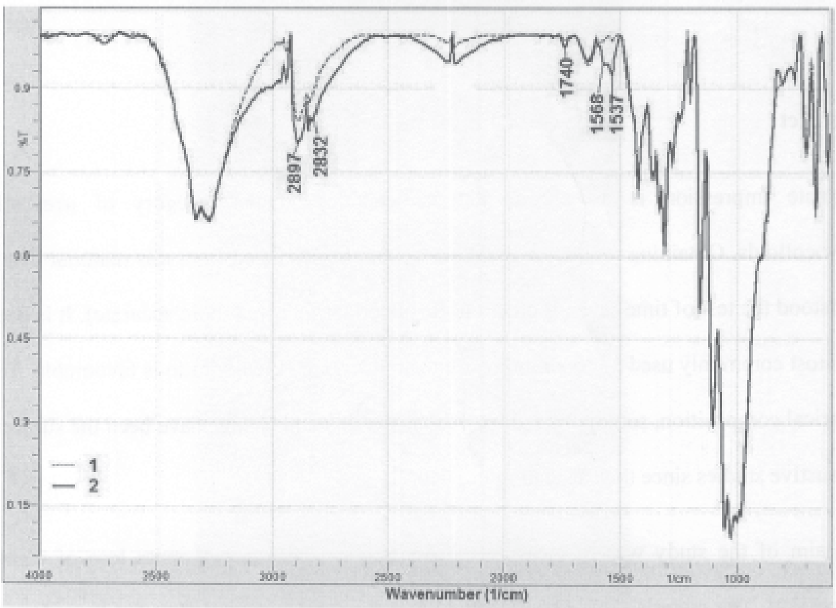


a. samples dyed with vat dye

Fig. 2. FTIR spectra of dyed cotton fabrics: 1. control sample (dyed but witout CHPS treatment) ; 2. sample dyed and treated with CHPS



b. samples dyed with direct dye



c. samples dyed with reactive dye

Fig. 2. FTIR spectra of dyed cotton fabrics: 1. control sample (dyed but witout CHPS treatment) ; 2. sample dyed and treated with CHPS

Table 3
CHARACTERISTICS PEAKS OF FUNCTIONAL GROUPS

IR Vibration Frequency			attributed to:
Reactive Dye	Vat Dye	Direct Dye	
2897 cm^{-1} 2832 cm^{-1}	2916 cm^{-1} 2849 cm^{-1}	2916 cm^{-1} 2849 cm^{-1}	asymmetric and symmetric stretching vibration of CH_3 and CH_2 groups from the hydrocarbonate chain of CHPS
1740 cm^{-1}	1734 cm^{-1}	1738 cm^{-1}	C=O stretching vibration from the esteric group of CHPS
1639 cm^{-1} 1537 cm^{-1}	1639 cm^{-1} 1535 cm^{-1}	1639 cm^{-1} 1537 cm^{-1}	-CON< stretching vibrations from amide groups (formed by reaction of CHPS with NH_2 and respectively NH functional groups from the structure of the dyes)

Air permeability

The air permeability was calculated as mean of 10 determinations. By applying of CHPS one notice a slightly decrease of the air permeability values compared to the ones of the untreated samples due to reduction of the interstices from the fibers of fabric.

The class of dyes used in dyeing of the cotton samples also affects the air permeability. The lowest air permeability values were obtained for the samples dyed with the vat dye and the highest air permeability values have been achieved for the samples dyed with direct dye. The differences that arise are probably due to different spatial configurations of the three dyes (table 4).

Higroscopicity

The hygroscopicity of the samples treated with CHPS decreases with the increase of CHPS concentration due to the presence of the hydrophobic chain from CHPS on the surface of the cotton fabric. The highest values of hygroscopicity were obtained for direct dyes, followed by reactive dyes and respectively vat dyes. The results obtained can be explained by the different numbers of polar groups and respectively sulfonic groups contained by the three dyes (table 4).

Table 4
EVALUATION OF THE COMFORT PROPERTIES

Dye	CHPS (g/L)	Air permeability (m^3/ min · m^2)	Higroscopicity (%)	Rigidity (cm)
C.I. Vat Blue 4	control sample	26.66	17.02	4.2
	20	26.11	15.61	4
	40	25.72	15.38	4
	60	25.02	14.87	4.3
C.I. Direct Red 95	control sample	31.11	19.01	4.2
	20	30.03	17.29	3.9
	40	29.43	16.83	4
	60	28.61	16.21	4.2
C.I. Reactive Blue 19	control sample	29.71	18.08	4.2
	20	29.55	16.41	4
	40	28.61	16.11	4
	60	26.93	15.78	4.2

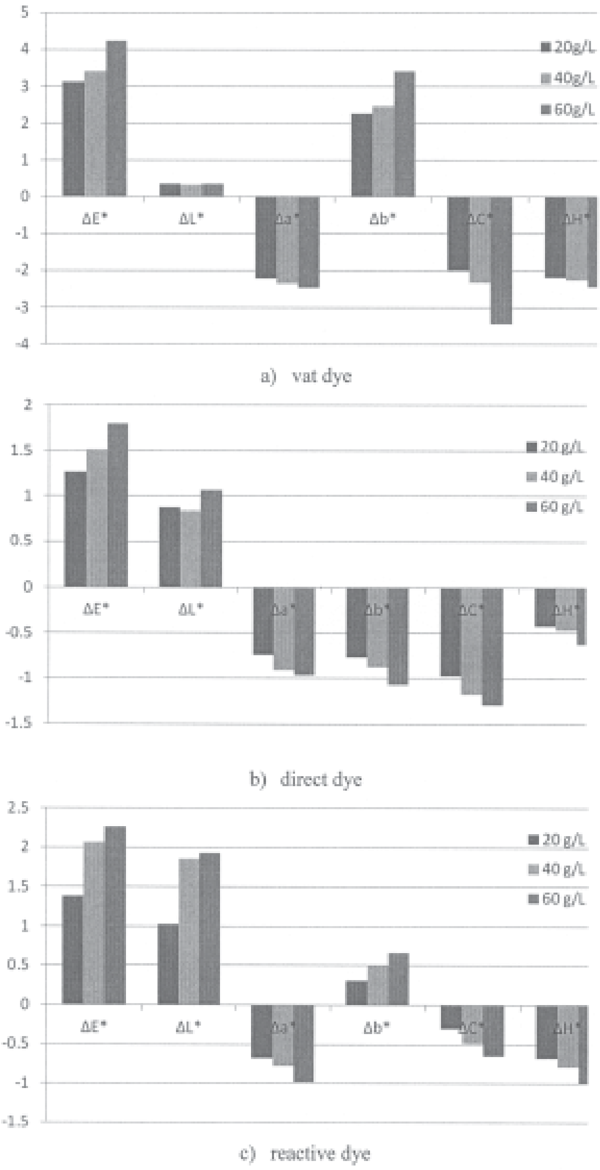


Fig. 3. Change in color difference of dyed and hydrophobized samples

Rigidity

The rigidity of the treated and untreated samples was appreciated using Paramount Fabric Stiffness Tester. The method consists in measuring the free length of the fabric that bends under its own weight by the intersection with a 45° sloping plane. The experiments were accomplished on warp direction; the values obtained represented the media of five measurements for each sample. The results obtained are shown in table 4.

The curing temperature and NaOH used during treatement with CHPS can lead to a slight stiffening of the fabric, reflected by the larger bending lengths as compared to the bending length of the control sample, while the CHPS gives softness to the fabric due to the orientation of the hydrophobic moiety toward the outside of the fiber surface. The explanation may be that the samples treated with a high concentration of CHPS (60g/L) have the same rigidity or are less rigid as compared with the unhydrophobized sample.

Colour measurements of samples dyed and treated with CHPS

Since by treatement with CHPS the colour of the dyed samples can change, the chromatic parameters against the control samples (dyed but without CHPS treatment) were determined. The obtained values are shown in figure 3.

The differences that appear in the colour measurements are influenced by the structures of the dye used in dyeing processes.

Effect of hydrophobic treatment on dyeing fastness

Effects of hydrophobization treatment with CHPS on dyeing fastnesses are shown in tables 5 and 6.

Analysing the obtained results one notice that the fastenesses to washing and dry rubbing of the samples dyed with the three dyes does not change by the application of the treatment with CHPS. As far as concerns the fastnesses to wett rubbing there is a slight improvement of these parameters for the samples dyed with reactive and vat dyes and treated with CHPS (20-60g/L).

Table 5
COLOUR FASTNESS TO WASHING

CHPS (g/L)	*C.I. Vat Blue 4*			*C.I. Direct Red 95*			*C.I. Reactive Blue 19*		
	Colour change	Staining		Colour change	Staining		Colour change	Staining	
		C*	W**		C*	W**		C*	W**
Control sample	4	4-5	5	4	4-5	5	4-5	4-5	5
20	4	4-5	5	4	4-5	5	4-5	5	5
40	4	4-5	5	4	4-5	5	4-5	5	5
60	4	4-5	5	4	4-5	5	4-5	5	5

*C = staining on cotton; **W = staining on wool

CHPS (g/L)	C.I. Vat Blue 4		C.I.Direct Red 95		C.I. Reactive Blue 19	
	Dry rubbing	Wet rubbing	Dry rubbing	Wet rubbing	Dry rubbing	Wet rubbing
Control sample	4-5	4-5	4-5/5	4-5	4-5/5	4-4/5
20	4-5	4/5	4-5/5	4-5	4-5/5	4-4/5
40	4-5	4-5/5	4-5/5	4-5	4-5/5	4-5
60	4-5	4-5/5	4-5/5	4-5	4-5/5	4-5

Table 6
COLOUR FASTNESS TO RUBBING

Conclusions

A hydrophobization process by chemical fixation of CHPS on the dyed cotton fabric was accomplished. CHPS is easily synthesized, inexpensive and effective. The presence of CHPS on treated cotton fabric was confirmed by FTIR analysis and by the photographic images. Effectiveness of the hydrophobic treatment performed with CHPS is proved by the high values of the wetting angles and through long period of time that the water droplet can stay on the surface of the treated fabric. The values for the air permeability and hygroscopicity are influenced by the concentration of CHPS used to hydrophobic treatment and by the nature of dyes used in dyeing of the cotton fabrics. The colour fastnesses to washing and to rubbing were not influenced by the CHPS concentration; their appreciations were very close by the control sample.

References

1.FERERO, F., PERIOLOTTO, M., SANGERMANO, M., BIANCHETTO, SM., J. Appl. Polym. Sci., **107**, 2008, p.810.
2.SATO, Y., TOMIJI, T., TOKINO, S., NIU, S., UEDA, M., MIZUSHIMA, H., TAKEKOSHI, S., Text. Res. J., **64**, no. 6, 1994, p. 316.
3.SCHUYTEN, H.A., WEAVER. J.W., FRICK, JR. J.G., DAVID REID, J., Text. Res. J. **22**, no. 6**,** 1952, **p. 424.**
4.NISHI, K., JEONG, D.S., TOKUYAMA, T., ITAZU, T., MIYAJI, Y., WAKIDA, T., Sen-I Gakkaish, **61**, no.11, 2005, p.309.
5.PERIYASAMY, S., KHANNA, A., Melliand International, **1**, 2008, p.54.
6.THUMM, S., SIELEMANN, D., STAINICA, C., JIANG, L., Melliand International, **3**, 2008, p. 180.
7.CERNE, L., SIMINIC, B., Text Res J, **74**, no.5, 2004, p.426.
8.GADKARI, R.G., Colourage, **47**, no. 10, 2000, p.15.
9.LAMMERMANN, D., Fluorocarbons in textile finishing. MelliandTextilberichte, **72**, E 380, 1991, p. 949.
10.GROTTENMÜLLER, R., MelliandTextilberichte, **79**, no. 10, E 195, 1998, p. 743.
11.OTTO, P., MelliandTextilberichte, **72**, no. 5, 1991, p. 378.
12.MAHLTIG, B., BOTTCHER, H., J Sol–Gel Sci Technol., **27**, no. 1, 2003, p.43.
13.MAHLTIG, B., AUDENAERT, F., BÖTTCHER, H., J Mater Chem., **15**, 2005, p. 4385.
14.FIR, M., VINCE, J., ŠURCA VUK, A., VILCNIK, A., JOVANOVSKI, V., MALI, G., OREL, B., Acta Chim Slov, **54**, 2007, p.144.
15.QUAN, Z., QINWEN, G., YULIANG, G., CHARLES, Q. Y., LI, S., Ind Eng Chem Res., **50**, no. 10, 2011, p. 5881.
16. PIPATCHANCHAI, T., SRIKULKIT, K., J Sol–Gel Sci Technol., **44**, 2007, p.119.
17.LIHUI, X., WEI, Z., XU, B., ZAISHENG, C., Appl Surf Sci., **257**, no. 13, 2011, p. 5491.
18.SENTHELKUMAAR, S., THAMIZ SELVI, R., Melliand International, **2**, 2008, p. 110.
19.DANKOVICH, T.A., HSIEH, Y. L., Cellulose, **14**, no.5, 2007, p. 469.
20.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**, no.4, 2013, p. 241.
21.BERCU, E., SANDU, I.,RADU, C.-D., VASILACHE, V., TOMA, V., Mat. Plast, **50**, no. 3, 2013, p. 215.
22.BERCU, E., SANDU, I.,ALDEA, H.A., VASILACHE, V., TOMA, V., Rev.Chim. (Bucharest), **64**, no. 10, 2013, p. 1121.
23.SANDU, I., SANDU, I.C.A., SANDU, I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.
24. SCHANDA, J., Colorimetry, Wiley-Interscience John Wiley & Sons Inc., 2007, p. 56.
25. SANDU, I.C.A., LUCA, C., SANDU, I., Rev. Chim. (Bucharest), **51**, 2000, p. 532.
26. SANDU I., LUCA C., SANDU I.C.A., CIOCAN, A., SULITANU, N., Rev.Chim. (Bucharest), **52**, 2001, p. 485.
27. SANDU, I.C.A., LUCA, C., SANDU, I., POHONTU, M., Rev. Chim.,(Bucharest), **52**, no. 7-8, 2001, p.409.
28. ATODIRESEI G.V., SANDU, I.G., TULBURE, E.A., VASILACHE, V., BUTNARU, R., Rev. Chim. (Bucharest), **64**, no. 2, 2013, p. 165.
29. BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., ALDEA, H.A., Mat. Plast., **49**, no. 4, 2012, p.270.
30. RADU, C.-D., BERCU, E., SANDU, I., FOIA, L.G., Mat. Plast., **51**, no. 1, 2014, p. 104.

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