Effects of Cellulose Functionalization with Ethylenediamide Tetrakis(Ethoxylate-block-propoxylate) Tetrol

CEZAR-DORU RADU[1], OANA PARTENI[1*], IOAN GABRIEL SANDU[2], OANA BORHAN[1], ECATERINA VASLUIANU[1], ION SANDU[3,4]
[1]"Gheorghe Asachi" Technical University, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Mangeron Blv., TEX 1 Building, Iasi 700050, Romania
[2] "Gheorghe Asachi" Technical University, Faculty of Materials Sciences and Engineering, 69 Blvd. Mangeron, Iasi 700050, Romania
[3]"Alexandru Ioan Cuza" University, ARHEOINVEST Interdisciplinary Platform, 11 Carol I, Corp G demisol, 700506, Iasi, Romania
[4]Romanian Inventors Forum, 3 Sf. P.Movila 3 Str., L11, III/3, 700089, Iasi, Romania

The work determines the conditions for the treatment of some 100% cotton articles of clothing, meant to make them wrinkle-proof, simultaneously with a good water/perspiration absorbing capacity. Grafting with polyfunctional substances (with polar groups) creates the wrinkle recovery possibility, preserving the water absorbing capacity acquired after the desizing and alkaline cleaning). Ethylenediamide tetrakis(ethoxylate-block-propoxylate) tetrol (commercial denomination Tetronic 701) was used as polyfunctional agent of wettability and grafting. The influence of tetrol and catalyst concentrations, impregnation time, condensation duration and temperature was studied. The technology used for wrinkle-proofing was pad-dry-cure (impregnation – drying -condensation). At concentrations higher than 30%, tetrol forms ether bridges with cellulose at a condensation temperature of 160°C for 3 min. The grafting on cellulose was confirmed by FTIR analysis. The wrinkle-recovery angles, tensile strengths and water absorption increase with increasing tetrol concentration.

Keywords: wettability, wrinkle-proofing, Tetronic 701, grafting, FTIR

Before any chemical upgrading operation, every cotton textile must be properly prepared, because the cotton yarns have, besides the basic component (cellulose), their natural incrustations that need to be removed in an adequate proportion. The cotton natural incrustations: hemicelluloses (1-3%), wax (0.4-1.2%), pectins (0.4-1.2%), proteins (1-1.9%), mineral salts (0.7-1.6%), pigments (0.5-8%) have a negative influence. A large part of the morphological incrustations are removed during the alkaline or enzymatic scouring [1].

The waxes represent an important group of non-cellulose constituents of the cotton fibers, being considered for a long time the main cause of native cotton hydrophobia [2-4].

In order to explain the modus operandi of the chemical agents on the cotton waxes, it is necessary to know the individual components of the waxy compounds. Nowadays, the waxes' chemical composition is known in details. The waxes are esters of the monobasic superior acids with primary superior alcohols from the aliphatic series, in a mixture with free fat acids, free alcohols and paraffin hydrocarbons [5]. Alcohols with a number of 24-30 carbon atoms and the corresponding acids were identified, as well as the palmitic acids, stearic acids and oleic acids in proportion of 15-20% from all the component acids. Higher aliphatic hydrocarbons of the type $C_{30}H_{62}$ (triocontan) and $C_{31}H_{64}$ (hentriacontan) were also identified. It was found that, as the result of the preliminary cleaning stage, the entire quantity of wax existing in the fiber cuticle was removed [2, 3].

Still, the wax existing in the primary wall of the cotton fiber need not be entirely removed; the waxes presence in the fibers is favorable in the spinning and weaving processes; yet, during the finishing operations they hinder the reactive penetration inside the fiber, due to their hydrophobic properties.

Some researchers admit that only the waxy substances contribute to raw cotton hydrophobia, i.e. they determine a restricted adsorption and wetting [2, 4, 6]. Both the immature and over-mature cotton have a higher wax content than the cotton at its normal maturity (up to 1.4%, this fact having a big importance in equalization and penetration of chemical agents inside the fiber during the finishing process.

The waxes also have an influence on the physico-mechanical and chemical properties of the fibers [2].

In this work the tetrol induced wettability and wrinkle-proofing effects on the 100% cotton textile were tested. The tetrol chemical structure is illustrated in table 1. The treatments with tetrol are performed through the pad-dry-cure procedure, where concentrations of 10-50% tetrol and 2.5% catalyst ($MgCl_2$ or NaH_2PO_2) were used at padding. In order to determine the influence of the working parameters, the padding duration (3-10 min), condensation (3-10 minutes) and condensation temperatures (160-180°C) were varied.

Experimental part

Materials

The 100% cotton cloth obtained from the IASITEX SA/ Romania presents the following characteristics: weight 100g/m², yarn count 17 Tex on weft and 19 Tex on warp. The fabric is enzyme desized and alkaline scoured. The ethylenediamide tetrakis(ethoxylate-block-propoxylate) tetrol (*Tetronic 701 is the commercial name)* was purchased from Aldrich Company, and the dyestuffs

* *email: oanaparteni@yahoo.com*

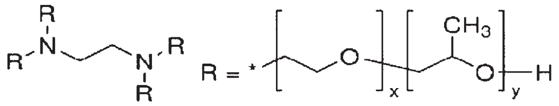
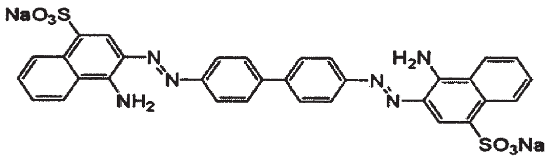
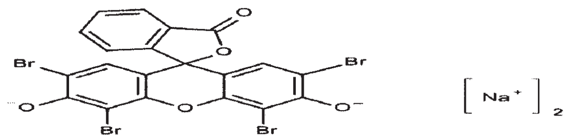
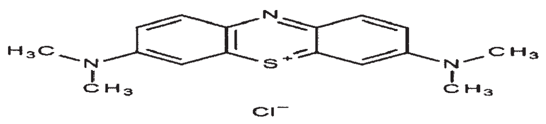
Name	Structures
Tetronic 701	
Congo Red *(C.I. 22120)*	
Eosin Y *(Acid Red 87 C.I. 45380)*	
Metylene Blue *(C.I. 52015)*	

Table 1
CHEMICAL STRUCTURES OF THE CHEMICAL REAGENTS USED

(C.I.221200, C.I. 45380 and C.I. 52015)- from the Merck Company. The chemical structures are illustrated in table 1.

Tetronic 701 is a surface active agent with poly(ethylene oxide)/poly(propylene oxide) linear di-blocks anchored on the molecule of a diamine situated in the molecule central position.

Ethylenediamide tetrakis(ethoxylate-block-propoxylate) tetrol is a polyol [7] that behaves like an amphoteric surface-active agent with hydrophilic and lipophilic groups. It has the molecular mass M_w = 3600 and is considered to be a compatible solvent with many chemical reagents, an antistatic agent and a good dispersant. At the same time, it is a good binder for linear and cross-linked polymers (polyesters, polyurethane, cellulose). It has the HLB number ranging between 1 and 7. The hydrophilic-lipophilic balance HLB is appreciated through numerical values and is used as a measure of the ratio between the hydrophilic/lipophilic groups. The products with HLB > 10 have affinity for water (i.e. they are hydrophilic), while those with HLB <10 have an affinity for oil. Tetronic 701 belongs to this last category, with affinity for fats, oils and waxes that exist in the 100% cotton cloth. It is a 100% active agent [3] and is not toxic, having a potential to be used in the textile chemical finishing to produce esthetical articles with a good handle and special properties of wettability, wrinkle proofing, easy care and anti-microbial properties.

Tetronic 701 was chosen with the aim to create a cleaner and more hydrophilic textile, able to work as a linking bridge for the future products that will be grafted.

Working procedure

The textile was prepared with the view to obtain a superior finish, through enzyme desizing – alkaline scouring, according to the following recipe [3]:

- enzime desizing (3g/L Beisol HTS; 1g/L NaCl; T= 100°C, t = 60 min) - warm washing;
- alkaline scouring (30g/L NaOH; 15g/L Na_2CO_3; 3g/L surfactant (Romopal); 9g/L sodium silicate; 15g/L reducing agent; T = 100°C: t = 60 min) - hot washing/warm washing/cold washing.

Taking into account that Tetronic 701 plays a double part (cleaning agent and bonding agent), we worked with increasing tetrol concentrations (at a constant catalyst concentration), in order to estimate tetrol influence on the cellulose textile material.

The magnesium chloride ($MgCl_2$) and sodium hypophosphite (NaH_2PO_2) were used as catalyst, in concentration of 2.5% as reported to the material mass for each sample.

The influence of the tetrol concentration, catalyst concentration, padding and curing time was studied. The method used for wrinkle-proofing was the pad-dry-cure.The tested concentrations of Tetronic were: 10, 30, 41.9, 50% (table 2). We meant to obtain the maximum taking-up degree (Y_p). The treatment conditions are presented in table 2.

Sample code	Padding*		Padding time (min.)	Drying temperature (°C)	Drying duration (min.)	Curing temperature (°C)	Curing duration (min.)
	Tetronic 701(%)	Catalyst type					
W	Witness	-	-	-	-	-	-
1	10	$MgCl_2$	3	100	3	160	3
2	30	$MgCl_2$	3	100	3	160	3
3	41,9	$MgCl_2$	3	100	3	160	3
4	50	$MgCl_2$	3	100	3	160	3
5	50	NaH_2PO_2	3	100	3	160	3
6	50	$MgCl_2$	3	100	3	180	3
7	50	$MgCl_2$	6	100	3	160	3
8	50	$MgCl_2$	10	100	3	160	3
9	50	$MgCl_2$	6	100	3	160	6
10	50	$MgCl_2$	6	100	3	160	10

catalyst concentrations ($MgCl_2$ or NaH_2PO_2) were 2.5%, for all samples.

Table 2
TREATMENT CONDITIONS WITH TETRONIC FOR AN WOVEN FABRIC OF 100% COTTON

Methods and analyses

Infrared spectroscopic analysis

The ATR-FTIR analysis was carried out to reveal the Tetronic 701 presence onto the cotton fabric supports as the result of the process of simultaneous scouring and grafting. FT-IR analysis was carried out on a Multiple Internal Reflectance Accessory (USA) with ATR KRS-5 crystal of thallium bromide – iodide, having 25 reflections and the investigation angle of 45 degrees. This accessory device was attached to the Spectrophotometer FTIR Affinity-1 Shimadzu (Japan), the spectra registration was realized with 250 scans within the 1800÷600cm^{-1} range. After recording, the absorption spectra were electronically overlapped (using the Panorama software).

Taking-up degree (Y_p)

The taking-up degree was determined using the relation (1) [8]:

$$Y_p = 100 \cdot (W_a - W_b) / W_b \qquad (1)$$

Y_P = taking-up degree, [%]; W_a = cotton mass before treatment, [g]; W_b= cotton mass after wrinkle proofing treatment, [g].

Yellowness index (YI)

The yellowness index (YI) is the index that needs to be calculated in the case of prolonged exposure or of the treatment in the presence of some chemical agents [9] and/or of some catalysts of the acid salt type. The yellowness index was determined using the device Spectroflash SF300 Datacolor Spectrophotometer and the ASTM Method E313-73.

Fastness of the effects highlighted by tinctorial method

Testing the strength of the binding between the cotton fabric and the treatment substance (Tetronic 701) can be carried out by determining the losses recorded after a large number of repeated washings (5-10) [10], or through the tinctorial method. We preferred the tinctorial method to prove that Tetronic 701 remains covalently bound on the cotton fabric even under severe treatment conditions (at high temperatures required by the dyeing process).

The tinctorial tests were performed with three dyestuffs from three different classes: *Congo Red* (C.I. 22120, the class of direct dyestuffs), *Eosin Y* (Acid Red 87, C.I. 45380, the class of acid dyestuffs) and *Methylene Blue* (C.I. 52015, the class of cationic dyestuffs).

The three classes of dyestuffs were chosen taking into account the affinity of the two partners existing in any treated sample: cellulose and tetrol.

Dyeing with Congo Red was performed according to the classical procedure, in a neuter medium. The dyeing parameters were: temperature 90°C, time- 90 min.

Dyeings with Eosin Y (Acid Red 87) and Methylene Blue (C.I. 52015) respectively were performed only after previously carrying out the acidification operation (with acetic acid, *p*H = 4.5), time 30 min at 20°C, of the samples already treated with tetrol. The treatment is necessary for the protonation of the nitrogen atoms from Tetronic 701, thus conferring a cationic character to the treated cellulose. The intensity of the electrostatic interactions, of attraction (in the case of Eosin Y) or repulsion (in the case of the Methylene Blue dye) is reflected in the color strength values (K/S), which can justify the effects generated by the treatment with Tetronic 701.

Wrinkle recovering angles (WRA)

The wrinkle recovering angles are determined according to the DIN 53890 standard. The Metrimpex FF 01 apparatus was used to determine the wrinkle-recovering angles along the warp and weft directions respectively, as the average of 10 measurements. The measurements were performed both on dry and wet samples.

Tensile strength

The tensile strength for the untreated fabric and for the sample treated with tetrol was measured according to the standard test DIN EN 13934-1. The determinations were carried out in the weft and warp direction using the apparatus ZWICK ROELL 2005 Germany 2008.

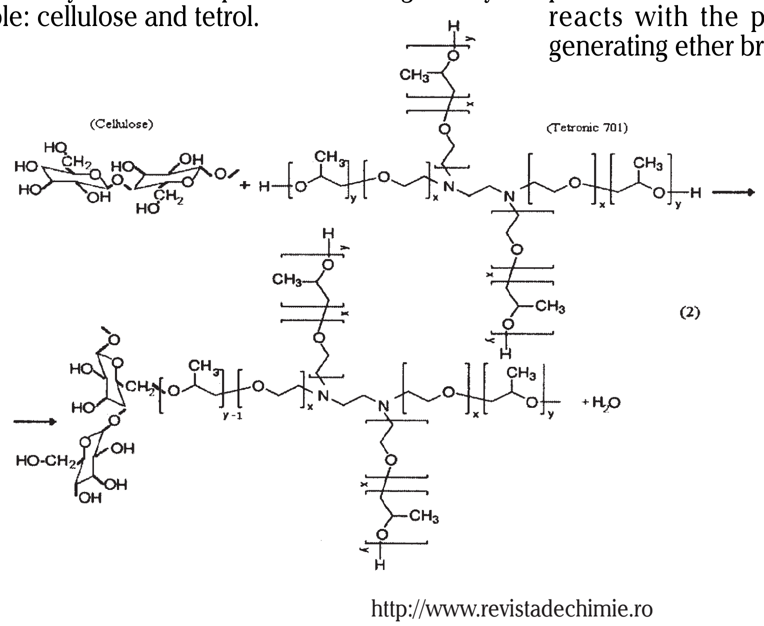
Water absorption through capillarity

The samples treated with tetrol had the following dimensions: 25x200mm. The 0.2% Eosin Y solution was poured in the apparatus vat up to the indicated mark. The samples were fixed in their upper end from the support from the top of the apparatus, while the other end was immersed in the solution from the vat till 30mm depth. The level up to which the solution rose on the material during each 5 min interval was measured during one hour. Twelve measurements were carried out for each sample, until the rise level became constant. The capillarity absorption was tested on 22 samples, because two identical specimens were used for each sample.

Results and discussions

Mechanism

At high temperature during the condensation and in the presence of an acid generating salt ($MgCl_2$), Tetronic 701 reacts with the primary OH groups from cellulose, generating ether bridges, according to the scheme 1.



Scheme 1

Table 3
CHARACTERISTICS IR FREQUENCIES OF CELLULOSE

IR (cm^{-1})	Assignments	Intensity*
3339	OH stretching	s
2916	CH_2 antysimetric stretching	w
2855	CH stretching and CH_2 symmetric stretching	w
1630	(Highlights the water presence)	m
1438	CH_2 deformation	m-w
1370	CH deformation	m-w
1338	OH deformation	w
1317	CH_2 (from C_6) deformation	m-w
1239	OH bending	m
1160	asymmetric bridge oxygen (C-O-C) Stretching	m
1053	C-O stretching of C_3-OH	m-s
1028	C-O stretching of C_6-OH	s
892	Glucose ring stretching	m
663	OH deformation out-of-plane	w

s-strong ; w-weak; m-medium.

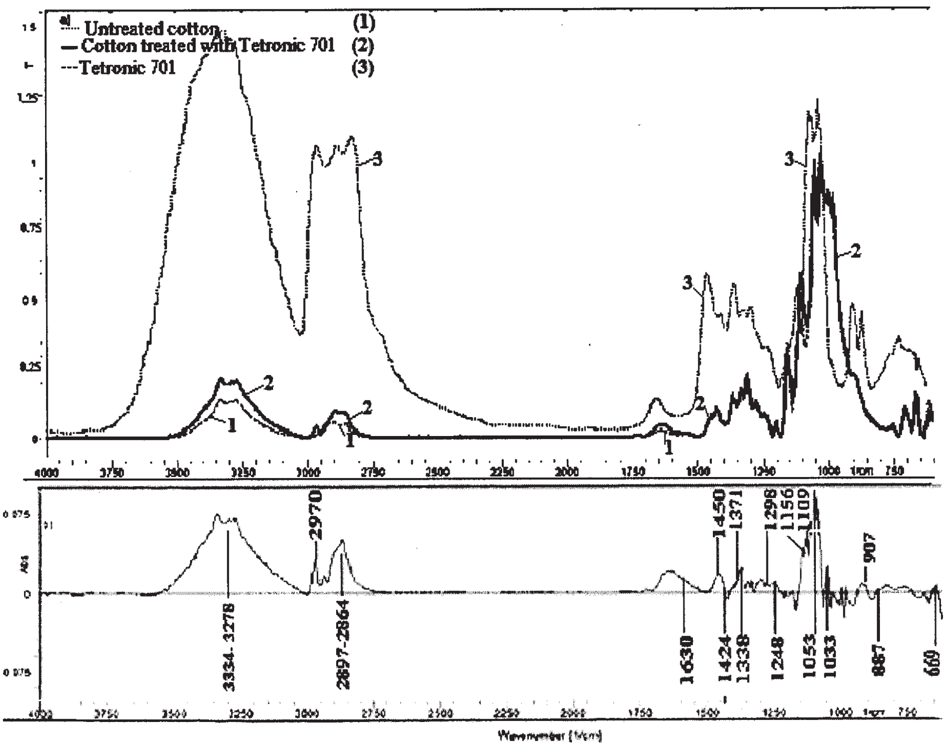


Fig. 1. IR spectra: a) overlapping spectra; b) substraction of witness spectrum from the spectrum of cotton fabric treated with Tetrol

FT-IR spectroscopic analysis

The effects acquired after the treatments performed either with natural or with synthetic polymers can be relieved through FT-IR analysis [11, 12].

Tetronic 701 plays the part of solvent for waxes and fats from the fabric, and of binder able to create covalent bridges between the cellulose and other substances (wrinkle-proofing agents). Tetronic 701 in bound on the cotton fabric by means of the terminal OH groups as follows: the cellulose OH groups (as a rule, those attached to C number 6), that reacts with the OH groups from tetrol remove the water during the condensation reaction produced at 160°C, necessary for cross-linking. The FT-IR analyses confirm the tetrol cross-linking to cellulose (fig. 1). The frequencies characteristic to the vibrations of the untreated cellulose sample [13, 14] are presented in table 3.

The spectra confirming the existence of an ether-type covalent bond realized between Tetronic 701 and cellulose are presented in figure 1.

Tetronic 701 has the following functional groups: four terminal OH groups, four methoxy groups, four ethoxy groups and two tertiary amine groups (table 1). Figure 1 presents the spectra of the textile treated with Tetronic 701 which preserves the cellulose characteristics, but besides these also appear the vibrations characteristic to the functional groups from Tetronic 701. In order to relieve the spectral differences of the sample treated with Tetronic 701, as compared to those of the untreated witness, the method of spectral subtraction was used, whose description is given in literature [15]. In figure 1b the spectrum afferent to the witness was subtracted from that of the treated sample, in order to reveal the effects created only by Tetronic 701. One can notice positive values almost within the entire studied IR range (4000-600cm^{-1}), which confirms the presence of tetrol as substance grafted on cellulose.

The IR frequencies characteristic for the textile treated with Tetronic 701 are illustrated in table 4. The ether bridges between tetrol and cellulose are confirmed by the positive values from 1156 and 1033cm^{-1} (asymmetrical and symmetrical C-O-O vibration).

Taking-up degree (Y_p)

Tetrol passage from the treatment solution into the textile material after the pad-dry-cure (impregnation/ drying/condensation) treatment can be appreciated by means of the taking-up degree [16]. The values obtained for the taking-up degree after condensation *(Y_p)* are presented in figure 2.

One can see from figure 2 that the taking-up degree depends on the treatment conditions, namely: utilized tetrol concentration, impregnation time, curing temperature and duration. From the analysis of the values of taking-up degree, one can notice that this registers corresponding values both when the treatment is performed with

Table 4
IR CHARACTERISTICS FREQUENCIES OF
WOVEN FABRIC TREATED WITH TETROL

IR(cm^{-1})	Assignments	Intensity*
3334-3278	OH stretching	s
2970	CH stretching (from metoxi)	w
2897-2864	CH stretching / CH_2	w
1630	(Highlights the water presence)	m
1450	CH bend, CH_2/CH_3 (asimetric)	m-w
1424	CH_3 def. simetric	m
1371	CH bend, CH_3	m-w
1338	OH deformation	w
1298	C-O stretch (from etoxi and cellulose)	m-w
1248	OH bending and C-N stretch	m
1156	Asymmetric bridge oxygen (C-O-C) stretching-from cellulose	m
1109	C-O stretching	m
1053	C-O stretching of C_3-OH	m-s
1033	C-O stretching of C_6-OH	s
907	C-Skeletal, metoxi	m
887	Glucose ring stretching	m
669	OH deformation out-of-plane	w

**s-strong ; w-weak; m-medium.*

increasing tetrol concentrations (the cases of 10, 30, 41.9, 50% in the treatment solution, and $MgCl_2$), and when the impregnation time is bigger (the case when the impregnation lasts 6 min at a concentration of 50% tetrol and $MgCl_2$).

Yellowness index (YI)

It was noticed that the treatment performed with Tetronic 701 determines a slight yellowing of the samples, especially after condensation. This fact certifies the occurrence of the reaction between textile and tetrol, a reaction that has as a secondary effect either a color change as the result of the presence of nitrogen on the cotton surface, or an alteration of the structural integrity of the cotton cellulose by yellowing the treated sample.

The values of the yellowness index are presented in table 5.

Table 5
THE VALUES OF
YELLOWNESS INDEX

Sample code*	Yellowness index YI
W	11.58
1	15.64
2	15.31
3	17.11
4	16.77
5	13.56
6	13.96
7	17.65
8	16.99
9	17.89
10	17.92

Fastness of the treatment effects relieved through dyeing

Dyeing with Congo Red (C.I. 22120)

The cellulose from the cotton cloth has a high affinity for direct dyestuffs, as well as a certain substantivitity for the cationic dyestuffs.

Figure 2 illustrates the performances obtained with Tetronic 701 within this study, namely: on the one side, it is a cleaning agent that determines the dissolution of a percentage from the waxes existing in the cotton cloth, and on the other side, it plays the role of binder between cellulose and the wrinkle proofing agents that will be subsequently applied. The waxes removal from cotton implies an increase of the cleaning degree, therefore an increased degree of white. Dyeing the samples with a more advanced degree of white than the witness results in

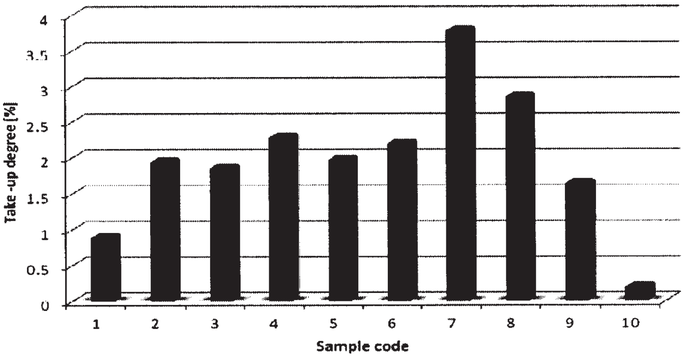


Fig. 2. Influence of treatement conditions on take-up degree (the treatment conditions of 10 tests have been illustrated in table 2)

producing lighter colours (fig. 3) than of the witness (samples 2 - 5). The concentration of 30% Tetronic 701 (sample 2) determines a significant wax removal, resulting in smaller K/S values than for the witness. The increase of tetrol concentration (41.9 - 50%) implies the increase of the colour intensity. This fact proves that Tetronic 701 was grafted on cellulose (samples 3 and 4), thus contributing to the increase of the number of OH groups able to form bonds with the direct dye.

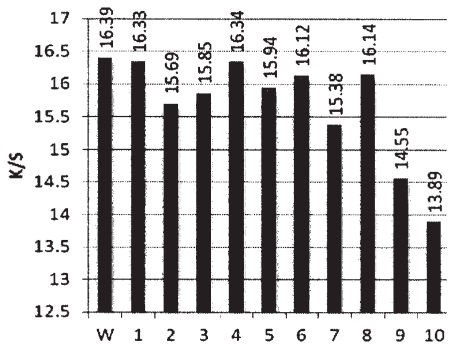


Fig. 3. The K/S values of samples dyed with Red Congo (for the wavelength, λ = 510nm). Samples have the same codes as in table 2.

The color characteristics of the samples treated with Tetronic 701 and dyed with Congo Red are relieved in table 6.

The color differences ΔE* were examined using the spectrophotometer Spectroflash SF 300 type DataColor; they were estimated by means of the values of the variables ΔL*, Δa*, Δb*, ΔC* and ΔH* that have the following meanings: ΔE* is the color difference between the examined sample and the witness, i.e. the distance between the corresponding positions in the CIELAB space; ΔL* is the brightness difference; ΔC* is the saturation difference; Δa* and Δb* represent the chromatic

Table 6
CHROMATIC CHARACTERISTICS AT THE DYEING WITH RED CONGO

Sample code *	Chromatic characteristics					
	ΔE*	ΔL*	Δa*	Δb*	ΔC*	ΔH*
W	-	-	-	-	-	-
1	1.693	1.070	1.069	0.761	1.301	0.176
2	3.367	2.099	2.269	1.334	2.629	0.127
3	2.807	1.452	2.143	1.087	2.402	-0.030
4	3.343	2.257	2.223	1.066	2.464	-0.084
5	4.284	2.242	3.237	1.688	3.651	-0.005
6	3.703	2.080	2.451	1.838	3.026	0.479
7	3.281	2.091	2.160	1.314	2.523	0.159
8	2.831	1.532	2.161	0.999	2.377	-0.114
9	3.254	2.662	1.753	0.657	1.858	-0.227
10	4.011	3.321	2.227	0.322	2.127	-0,733

• samples have the same codes as in Table 2.

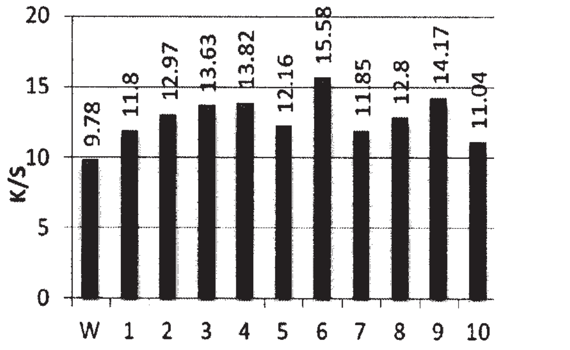


Fig. 4. Colour strength of samples treated with tetrol and dyed with Eosin Y(samples have the same codes as in table 2)

Table 7
CHROMATIC CHARACTERISTICS OF SAMPLES DYED WITH EOSIN Y

Sample code*	Chromatic parameters					
	ΔE*	ΔL*	Δa*	Δb*	ΔC*	ΔH*
W	-	-	-	-	-	-
1	4.556	-3.265	2.073	-2.409	1.222	-2.934
2	5.266	-3.405	3.152	-2.490	2.234	-3.338
3	6.589	-4.234	3.816	-3.305	2.650	-4.297
4	6.825	-3.006	3.847	-4.769	2.307	-5.677
5	4.941	-2.781	3.367	-2.311	2.491	-3.236
6	7.180	-5.110	4.993	-0.717	4.510	-2.259
7	5.644	-3.096	3.305	-3.369	2.140	-4.206
8	6.674	-2.520	4.222	-4.512	2.733	-5.542
9	5,653	-0,562	4,356	-4,715	2,451	-5,642
10	4.850	-0.812	1.745	-4.452	0.351	-4.769

samples have the same codes as in table 2.

parameters: red green for "a" and yellow blue for the parameter "b"; ΔH* is the hue difference [14, 17 - 24].

One can notice that all the samples from 1 to 10 had the lightness difference ΔL* > 0, which means that the witness dyed more intensely. The samples 1 - 10 are lighter than the witness. It is known that lightness difference $\Delta L^* = L_{sample} - L_{witness}$. The values ΔC* > 0 indicates the colour saturation between the dyed samples and the witness. The chromatic parameters indicate the colour variation toward red (through the positive values for Δa*), and a tendency to yellow (through the positive values of Δb*) respectively [25 - 31]. The positive values of Δb* show that by dyeing with Congo Red, some samples are more yellow than the witness (when Δb*>0), while others are bluer than the witness (those with ΔH*<0). Data from table 6 indicate that all the samples are lighter red than the witness, but with a minor variable yellow component, as compared to the red component.

Dyeing with Eosin Y (Acid Red 87, C.I. 45380)

Dyeing with Eosin Y of the treated and protonated samples is possible due to the electrostatic attraction between the positive groups from the treated textile (acquired at the level of nitrogen atom) with the negative carboxylic and hydroxyl groups of the acid dye.

The colour strength (K/S) of the examined samples offers indications on the treatment efficiency, namely, the higher the efficiency of Tetronic 701 bond with cellulose, the higher will be the K/S values. If Tetronic 701 was not bound with cellulose, it would have been completely removed at the first washing. If Tetronic 701 would only had the role of solving the fats from cotton, once increasing its concentration the colour strength should diminish, which did not happened. The fact that colour strength increased confirms the accomplishment of the bond with the cotton cloth (fig. 4).

As the dye concentration was the same for all dyeing operations, the lightness differences ΔL* < 0) (table 7) can explain the completion of the reaction of covalent bonding of tetrol agent with the cotton fabric through pad-dry-cure technology preceding the dyeing. All the samples treated with Tetronic 701 and dyed with Eosin Y are darker than the witness, because they dyed more intensely than this.

The values ΔC* > 0 indicate that dyeing with Eosin Y chromatic characteristics increase. The chromatic parameters Δ**a*** and Δ**b*** indicate the colour variation toward red (through the positive values for Δ**a***), and a tendency to blue (through the negative values of Δ**b***). The negative values of Δ**H*** show that all the samples are bluer than the witness.

Data from table 7 shows that all the samples are more chromatic coloured in a more intense red than witness, but with a smaller portion of yellow.

Dyeing with Methylene blue (C.I. 52015)

Methylene blue is a cationic dye that has a certain affinity for cotton fabric, since this has a negative charge in the dyeing medium.

Dyeing with a cationic dye implies an acid medium (*p*H = 4.5 by means of the acetic acid). At the contact with the acid medium, the sample treated with Tetronic 701 can get cationized due to protonation phenomenon from the level of the nitrogen atom. An electrostatic repulsion occurs between the cationized samples and the cation of the basic dye, rejection indicated by the colour intensities, poorer than those of the witness (fig. 5), and by the values of the colour differences from table 8.

Another explanation is based on the cleaning role played by Tetronic 701 for cotton. Under the action of Tetronic 701, the amount of pectins remained in the cotton decreases, which results in colour intensity diminution after dyeing with a cationic dyestuff, also as the result of a more

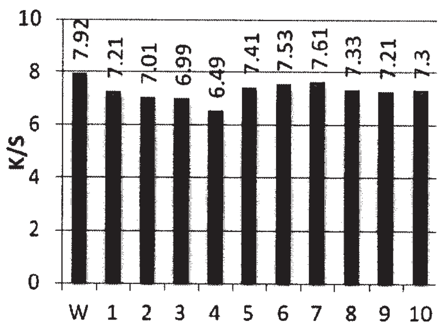


Fig. 5. Colour strength of samples dyed with Methylene Blue. Samples have the same codes as in table 2.

Table 8
COLOUR DIFFERENCES AND ITS COMPONENTS FOR SAMPLES DYED WITH METHYLENE BLUE

Sample code*	Chromatic characterictics					
	ΔE*	ΔL*	Δa*	Δb*	ΔC*	ΔH*
W	-	-	-	-	-	-
1	2.188	1.531	-0.901	1.278	-1.016	-1.188
2	3.961	2.610	-2.472	1.665	-0.934	-2.830
3	3.794	2.558	-2.384	1.472	-0.778	-2.691
4	4.703	3.461	-2.470	2.010	-1.263	-2.923
5	2.744	1.607	-1.779	1.336	-0.829	-2.065
6	1.992	1.122	-1.432	0.811	-0.423	-1.591
7	1.646	1.233	-0.787	0.754	-0.540	-0.947
8	2.506	1.635	-1.569	1.068	-0.632	-1.790
9	2.965	2.072	-1.811	1.103	-0.597	-2.035
10	4.656	3.104	-3.175	1.401	-0.460	-3.440

** samples have the same codes as in table 2.*

Sample codes*	WRA (on warp)		WRA (on weft)		Dry WRA	Wet WRA
	Dry samples	Wet samples	Dry samples	Wet samples	W+F**	W+F**
W	92	96	90	82	182	178
1	98	96	92	88	190	184
2	96	93	100	98	196	191
3	104	102	109	106	213	208
4	99	89	92	90	191	179
5	92	87	100	95	192	182
6	86	82	97	96	183	178
7	87	86	96	93	183	179
8	92	90	98	95	190	185
9	88	86	92	93	180	179
10	89	86	94	94	183	180

** samples have the same codes as in table 2.*
*** W - warp and F - weft*

Table 9
WRA VALUES FOR SAMPLES TREATED WITH TETROL

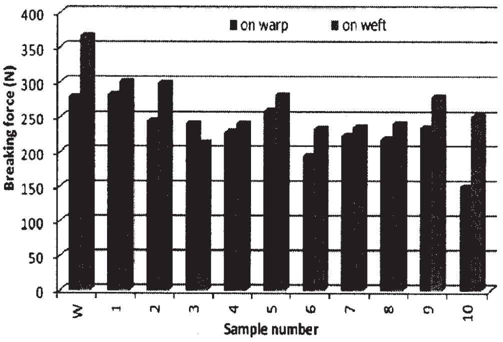


Fig. 6. Values of physical strength (the treatment conditions of samples are presented in table 2)

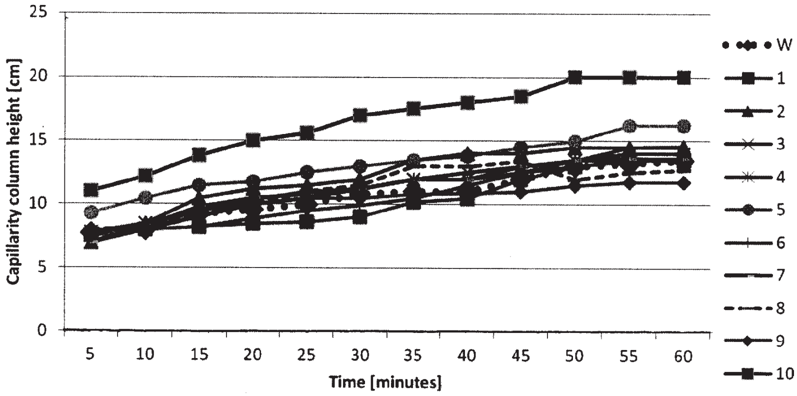


Fig.7. Capillary rise curve

advanced cleaning degree. It is known that the removal of pectic substances is performed by the hydrolyzation and gradual de-polymerization of the polygalacturonic acids, the resulted acids passing in soluble sodium salts (the final hydrolysis products are the sodium salts of the galacturonic acids, and the sodium methylate).

The samples 1 - 4 were dyed the worse, therefore they have more Tetronic 701 covalently bond to cellulose than the samples 5 -10.

In table 8 one can see that all the samples from 1 to 10 are lighter than the witness, as they have a positive lightness difference. This means that the witness lightness is smaller than that of the examined samples, therefore the examined samples dyed more intensely, which is correlated with the negative value of ΔC^*. The values $\Delta a^* < 0$ and $\Delta b^* > 0$ indicate that the samples dyed with Methylene Blue are less blue and less red. There can be two hypotheses: either the dye is not unitary, or it has two chromofore groups, one for blue with an intensified light absorption capacity, and another one for red, with a more reduced capacity. The negative value of the ΔC^* difference indicates either a more advanced cleaning of the textile support, or a hypsochromic tetrol effect. The negative value of ΔH^* difference shows that one of the parameters **a** and **b** is negative, and another is positive, i.e. "**b**" is negative (Methylene Blue) and "**a**" is positive, as being the red component.

Data from Table 8 show that all the samples are less coloured than the witness, namely they are lighter, their aspect resulting from a lower content of red and blue.

Wrinkle recovering angles, WRA

The highest values of the wrinkle-recovering angles are obtained for the samples encoded 1 - 5, i.e. under the condition of the utilization of 10 - 50% Tetronic 701 concentrations, at 3 min impregnation time and condensation at 160°C, condensation time of 3 minutes in the presence of $MgCl_2$ (table 9). The sample no. 5 tested under identical conditions with the sample 4, but using NaH_2PO_2 as catalyst, results in slightly higher WRA, but with a taking-up degree Y_P slightly smaller (fig. 2). Even if the NaH_2PO_2 catalyst does not result in marked sample yellowness, it has the disadvantage of high cost.

The WRA values corresponding to the samples 7 and 8 (realized at padding times exceeding 3 minutes), and for the samples 9 and 10 (that have both the padding and curing times higher than for the samples 1 - 4) are not considerably higher than when working under softer conditions. Moreover, the samples 6 - 10 have higher yellowness indices; therefore their recipes are not recommendable for wrinkle-proofing.

Tensile strength

After the treatment with Tetronic 701, all the samples have smaller tensile strength than the witness (fig. 6). The biggest decreases of tensile strength were found at the samples 6 - 10 that were treated under severe conditions of padding/curing: durations of 6 - 10 min and curing temperatures between 160 - 180°C. For these reasons, the versions 6 - 10 are not applicable, due to the diminution of the textile support integrity and of their mechanical resistance, as the result of the increased durations and temperatures.

Water absorption by capillarity

Capillarity is the capacity of a substance (product) to absorb a liquid: water or dyeing solution. It appears in the situation when the forces of intermolecular adhesion between liquid and solid are stronger than the forces of cohesion inside the liquid. Several liquids, among which the water, rise up by themselves if they are situated in a thin (capillary) glass tube. This phenomenon is known as capillarity effect. The height reached by the liquid is inversely proportional with the glass tube diameter. This phenomenon occurs due to high surface tension registered in the case of numerous liquids. In this work, the phenomenon of capillary rise is possible because the cotton yarns have enough voids such as pores, channels in the amorphous zones that permit the liquid (water) to rise at the height of the yarn. This capillary rise was pursued for an established time interval, and the samples were characterized by means of the curve of capillary rise (fig. 7).

The increase of the height of liquid column through the capillaries of the treated samples during one hour (in steps of 5 minutes) is indicated in figure 10. It was thus shown that the capillary absorption is ascendant for all the samples. The capillary absorption occurs with different rates during the studied time interval, but it tends to become stationary at the end of the 60 min of testing.

The treatment with Tetronic 701 improved the samples' wettability; one can notice that the witness sample has one of the smallest values of water absorption.

Tetronic 701 contributes to hydrophilicity of the samples treated as follows:

- it solves part of the residual wax existing in the cotton samples;
- it diminishes the quantity of pectic substances remained in the cotton interstices after the alkaline scouring stage;
- it binds to cellulose through covalent bonds;
- it can play the role of linking bridge for the substances that can be additionally applied. Moreover, Tetronic 701 has polar functional OH groups uninvolved in the reaction with cellulose, therefore available and also capable to form hydrogen bonds with water.

Conclusions

The treatments carried out with concentrations of 10 - 50% Tetronic 701, through padding for 3 min, drying at 100°C for 3 min, curing at 160°C for 3 min, in the presence of $MgCl_2$ as catalyst, led to favourable results from the standpoint of the wrinkle recovery angle and wettability through capillarity. The increase of any of the working parameters does not result in significant improvement of WRA or durability of the effects; but it results in a bigger degradation, materialized through sample yellowness. Even if Tetronic 701 determines sample wettability, the wrinkle proofing (evaluated by means of the wrinkle recovering angles) effects are poor. In order to preserve the sample wettability and, at the same time, to confer the best wrinkle proofing effects (higher WRA), we propose to test in the future researches a new pad-dry-cure wrinkle proofing technology based on two subsequent impregnations: padding I with Tetronic 701 – squeezing/drying/curing; padding II with other polyol- squeezing/drying/curing.

This work creates new research directions concerning the possibility to realize wrinkle-proofing hydrophilic textiles, destined to manufacture articles of clothing.

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References

1.RJIBA, N., NARDIN, M., DRÉAN, J.-Y, FRYDRYCH, R,. J. of Colloid and Interf. Sci., **314**, 2007, p.373.
2.WANG, Q., FAN , X. R, HUA, Z.-Z., CHEN, J., Biochem. Eng. Journal, **34**, 2007, p.107.
3.POPESCU, V.,Technology for preparation, bleaching and apreture of materials textile, Vol I Cellulosic materials, Ed. Tehnopress, Iasi, 2007.
4.ILIESCU, E., POPESCU, V., COSMIN, V., Preparation, bleaching and starch of textiles, vol. 1, Ed. TehnoPress Iasi, 2002
5.ATHUKORALA, Y., MAZZA, G., Industrial Crops and Products, **31**, 2010, p.550.
6.MURESAN, E. I., BALAN, G., POPESCU, V., Ind. Eng. Chem. Res., **52**, 18, 2013, p 6270.
7.PAPAY, A. G., MATTHEWS, B. W., THOMAS, A. S., Lubricating Oil Compositions of Improved Rust Inhibition, Patent US3,928,219/Dec. 23, 1975
8.POPESCU, V., MURESAN, E., I., GRIGORIU, A.-M., Carbohydrate Polymers, **86**, no 2 , 2011, p. 600.
9.POPESCU, V., VASLUIANU ,E., FORNA, N.-C., SANDU, I., BERCU, E., Rev. Chim. (Bucharest), **64**, no. 11, 2013, p.1284.
10.POPESCU, V., MANEA, L.R., AMARIEI, N., Materiale Plastice (Bucharest), **46**, no.1, 2009, p. 95.
11.POPESCU, V, RADU, C.D., MANEA, L.R., Industria textila, **61**, no. 1, 2010, p. 23.
12.POPESCU, V., MANEA, L. R., SANDU, I. G., CHIRCULESCU, A. I., SANDU, I., Rev. Chim. (Bucharest), **64**, no. 3, 2013, p 281.
13.VASLUIANU, E., POPESCU, V., GRIGORIU, A., FORNA, N.C., SANDU, I., Rev. Chim. (Bucharest), **64**, no. 10, 2013, p. 1104.
14.SANDU I.C.A., LUCA C., SANDU I., POHONTU, M., Rev. Chim., (Bucharest), **52**, no. 7-8, 2001, p. 409.
15.POPESCU, V., MURESAN, E.I., Ind. Eng. Chem. Res., **52** , no.37, 2013, p.13252.
16.ILIESCU, E., NAGY, GH., POPESCU, V., Superior finishing of the textile materials Vol 1, Crease-resisting, Ed. TehnoPress, Iasi, 2004.
17.PUSCAS, E.L., RADU, D.C, Introducere in cunoasterea si masurarea culorii, Ed. Dosoftei, Iasi, 1997, p.154.
18.PUSCAS, E.L., Colour theory and measurement, Ed. Rotaprint, Iaşi, 1983, p.167.
19.WARDMAN, R.H., An update on numerical problems in colour physics, Rev. Prog. Coloration, **24**, 1994, p. 55.
20.RADU, C. D., Colour measurement, Ed. Rotaprint, Iaşi, 2004, p.61.
21.SANDU, I., SANDU, I.C.A., SANDU, I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.
22.SCHANDA, J., Colorimetry, Wiley-Interscience John Wiley & Sons Inc., 2007, p. 56.
23.SANDU, I.C.A., LUCA, C., SANDU, I., Rev. Chim. (Bucharest), **51**, 2000, p. 532.
24.SANDU I., LUCA C., SANDU I.C.A., CIOCAN, A., SULITANU, N., Rev. Chim. (Bucharest), **52**, 2001, p. 485.
25.BERCU, E., DIACONESCU, R.M., RADU, C.D., POPESCU, V., European J. of Sci. and Theology, **8**, 2012, p.235.
26.SCARLET, R., MANEA, L.R., SANDU, I., MARTINOVA, L., CRAMARIUC, O., SANDU, I.G., Rev. Chim. (Bucharest), **63**, no. 7, 2012, p. 688.
27.SCARLET, R., MANEA, L.R., SANDU, I., CRAMARIUC, B., SANDU, A.V., Rev. Chim. (Bucharest), **63**, no. 8, 2012, p. 777.
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., Mat. Plast., **50**, no. 3, 2013, p.215.
30.BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., ALDEA, H.A., Mat. Plast., **49**, no. 4, 2012, p.270.
31.RADU, C.-D., BERCU, E., SANDU, I., FOIA, L.G., Mat. Plast., **51**, no. 1, 2014, p.104

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