

Multifunctional Finishing with Monochlorotriazine β -cyclodextrin and Tetrol

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In this work a multifunctional textile material was realized by means of two pad-dry-cure treatments. The first treatment made use of a tetrol (Tetronic 701) in the padding stage and it resulted in excellent cotton cleaning effects, materialized in the increase of its wettability. The second treatment was performed with monochlorotriazine β -cyclodextrin (MCT- β -CD) at concentrations of 9-15%, in the presence of 2.5-3.0% Na_2CO_3 as catalyst. The presence of MCT- β -CD on the cotton fabric was confirmed by the results of the spectroscopic (FT-IR, XPS) and calorimetric/thermo-gravimetric analyses (DSG/TGA). The qualitative test with phenolphthalein indicated the formation of a compound with the inclusion of cellulose grafted with Tetronic 701 inside the MCT- β -CD taper cavity. The MCT- β -CD presence on the support already grafted with Tetronic 701 determined the preservation of textile support wettability and a significant improvement of the wrinkle-proofing capacity. The wrinkle-recovering angles (WRA) registered values between 205 and 246 degrees, i.e. much higher than those of the witness (WRA < 185). The increase of wettability was confirmed by the lower values of the angles at the contact with water and by high values of water absorption through capillarity.

Keywords: Tetrol, monochlorotriazine β -cyclodextrin, wrinkle proofing, contact angle, capillarity

Cotton is the most used material for manufacturing vestimentary articles. The wearing comfort of the cotton articles is ensured if the textile support is hydrophilic and possibly crease-resistant. The wettability of the cellulose-based textiles can be accomplished through the preparation operations (alkaline or enzymatic cleaning) [1, 2] and it can be improved by grafting (with products rich in polar groups) subsequent to the preparation operations [3]. The grafting agents resulting in the best water absorption capacities are the butane tetracarboxylic acid [4] and certain polyols [5].

Conferring a good crease-recovering capacity implies the treatment of the hydrophilized supports with certain wrinkle-proofing agents. During the time, several products were used as wrinkle-proofing agents, starting with urea-formaldehyde products [6,7] and glyoxal [8-10], to the non-formaldehyde compounds: polycarboxylic acids [11-15], chitosan [16-18]. In all the cases, grafting results in good crease-proofing effects, but is also makes worse the water absorption capacity.

Monochlorotriazine- β -cyclodextrin (MCT- β -CD) is a multifunctional product (it has at least two Cl groups and seven primary HO groups) that might be used as crease-proofing agents without diminishing the textile water absorption capacity [19-21]. In this work we present the manner to obtain a multifunctional textile material through successive hydrophilizing and crease-proofing treatments. The wettability is improved by grafting a tetrol on the cellulose material, while the crease-recovering capacity is produced in a second stage, by treating it with MCT- β -CD. The utilized tetrol is the commercial product Tetronic 701, which does not confer wrinkle-proofing

effects, but significantly improves the wettability [22-24]. This was applied through a pad-dry-cure technology, namely: impregnation of the cellulose material with concentrations of 30-50% Tetronic 701 and 2.5% MgCl_2 (as catalyst) - squeezing- drying (100°C for 3 min) - condensation (160°C for 3 min). Tetronic 701 accomplished two functions: cleaning agent (it removed part of the wax existing in the cotton by solving the fats) and grafting agent.

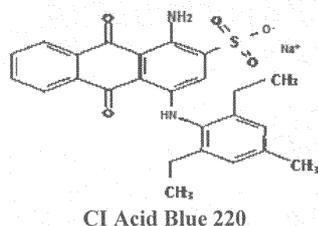
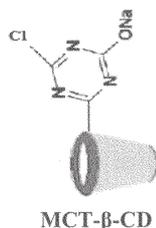
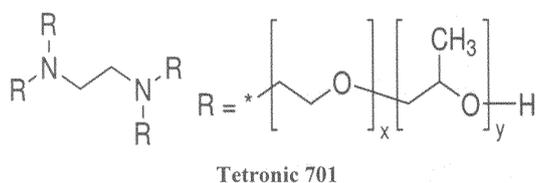
MCT- β -CD was also applied through a pad-dry-cure procedure, namely: impregnation of the grafted material with Tetronic 701 with concentrations of 9-15% Tetronic 701 and 2.5-3.0% Na_2CO_3 (as catalyst) - squeezing- drying (100°C for 3 min) - condensation (160°C for 3 min). An inclusion compound was obtained, in which MCT- β -CD is the host, and the tetrol grafted on cotton is the guest. The presence of this compound was confirmed by the spectroscopic (FT-IR, XPS), calorimetric/thermo-gravimetric and tinctorial analyses. The multi-functionality of the final product (wettability and wrinkle-proofing at the same time) was confirmed by the values of the contact angle, capillarity and wrinkle-recovering angles. The inconvenient of this procedure used to create two simultaneous effects is its short durability (the compound only resists to five cycles of domestic washing).

Experimental part

Materials and methods

The experiments were performed on 100% cotton textiles that were previously subject to desizing and scouring [1]. The characteristics of the cotton fabric were the yarn count of 19 Tex on the warp direction and 17 Tex on the weft direction, and its specific weight of 150 g/m².

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Scheme 1. Chemical structures of the products Tetronic 701, MCT-β-CD and C.I. Acid Blue 220 dye

Table 1
FORMULAE FOR COTTON FABRIC PADDING

Sample code	Padding I		Padding II	
	Tetronic 701 (%)	Mg Cl ₂ (catalyst) (%)	MCT-β-CD (%)	Na ₂ CO ₃ (catalyst) (%)
S1	3	2.5	-	-
S2	9	2.5	-	-
S3	15	2.5	-	-
S4	-	-	9	2.5
S5	-	-	9	3
S6	-	-	15	2.5
S7	15	2.5	9	2.5
S8	9	2.5	15	2.5
S9	9	2.5	9	3
S10	9	2.5	9	2.5

The utilized chemicals were ethylenediamine tetrakis (ethoxylate-block-propoxylate) tetrol, known as Tetronic 701, purchased from Aldrich Company, monochlorotriazine β-cyclodextrin (MCT-β-CD) from Wacker-Chemie, Germany, MgCl₂ and Na₂CO₃ and C.I. Acid Blue 220 from Merck Company.

The product used to make the cotton sample wettable was a polyol known under the trading name of *Tetronic 701* [22, 24]. The chemical structures of the main substances used for padding are presented in scheme 1.

Tetronic 701 is in fact a surface active agent (surfactant) with poly(ethylene oxide)/poly(propylene oxide) linear diblocks anchored on the molecule of a diamine situated in the molecule central position. It has the HLB number ranging between 1 and 7, therefore has a high affinity for oil.

MCT-β-CD components are: 7 α-D(+)-glucopyranosic units bound α-1,4-glycosidic that generate the image of a truncated cone void at the inside; a triazine cycle whose reactivity is increased due to the presence of the chlorine atom and/or of ONa group. MCT-β-CD has two types of reactive groups: Cl attached to the triazine group and primary OH groups attached to each pyranose unit. From this point of view, MCT-β-CD can be considered as a polyol, having at most 7 primary OH groups [19-21].

Treatment conditions

The receipts used to test the possibilities of obtaining water absorption effects cumulated with wrinkle-recovering effects are indicated in table 1. The effects produced by individual treatment with Tetronic 701 at various working concentrations were tested. At the same time, the effects generated only by MCT-β-CD were also tested in the presence of 2.5-3.0% catalyst. The treatment with both Tetronic 701 and MCT-β-CD was carried out by repeating twice the pad-dry-cure technology, and the formulas used for each padding stage are given in table 1. The conditions used in the dry and cure operations from the both treatments were: drying at 100°C for 3 min, condensation at 160°C for 3 min.

ATR-FTIR

ATR-FTIR analysis of the treated cotton samples with polyols were carried out on Multiple Internal Reflectance Accesory (Specac, USA) with ATR KRS-5 crystal of thallium bromo-iodine, with 25 reflections and 45° angle of investigation. This accessory was attached to a spectrophotometer FTIR-ATR-IR Affinity-1 Shimadzu (Japan) recording the spectra being performed with 250 scans in the 4000-600cm⁻¹ scale. After recording, the absorption spectra were processed electronically using Panorama program from the company LabCognition.

XPS

XPS analysis of samples of cotton was carried out using the apparatus Axis Kratos Analytical Ultra DLD with monochromatic aluminum source (power 150 W).

Calorimetric/thermo-gravimetric analyses

Calorimetric/thermo-gravimetric analyses (DSC and TGA) were performed on DSC 2920 Modulated DSC device/Hi Res Modulated TGA 2950, Thermo-gravimetric Analyzer. DSC/TGA curves were recorded at the heating rate of 20°C/min in an atmosphere of nitrogen.

The thermo-gravimetric method measures the mass of a sample according to the temperature, while it is heated or cooled at a controlled rate, and is maintained at a given temperature for a period of time. The registration is the thermo-gravimetric curve. In this device, the sample is placed in an inert crucible, which is attached to a microbalance and a furnace positioned around the sample. It continuously measures the weight of a sample according to the temperature.

The take-up degree

The taking over of polyols from the solution treatment, at the end of pad-dry-cure technology can be assessed using the take-up degree. The take-up degree, Y_p was determined using equation (1):

$$Y_p = 100 \cdot (W_a - W_b) / W_b \quad [\%] \quad (1)$$

Y = take-up degree;

W_b⁰ = mass of cotton fabric before of wrinkle - proofing;

W_b^a = mass of cotton after wrinkle -proofing

Durability of wrinkle-proofing treatment

Durability testing was performed by the method of dyeing. We used an acid dye, nonspecific to cellulosic substrates, which normally does not dye the cotton. Obtaining good colour strength after dyeing of the samples

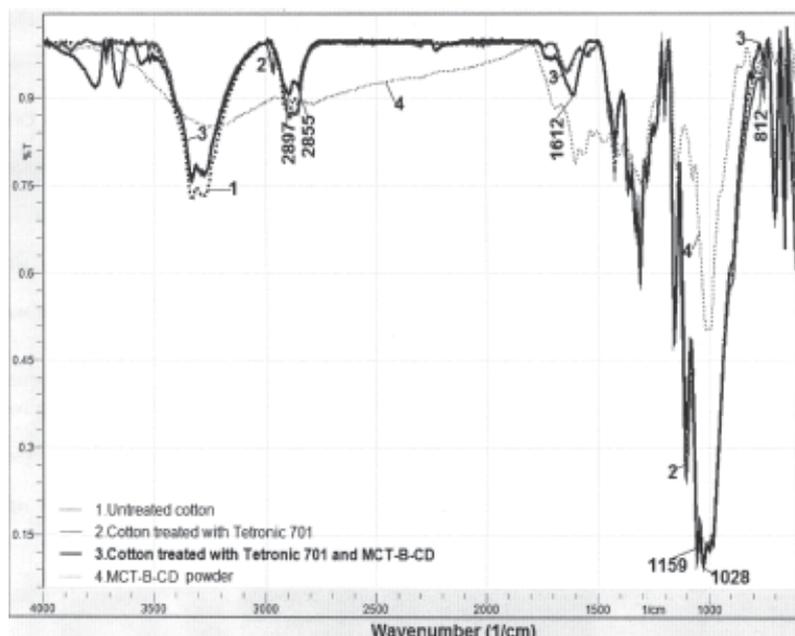


Fig. 1. IR spectra of the samples after the treatment with MCT-β-CD

treated with the two polyols confirm their presence on that support textile. Color differences between treated samples and the standard sample indicate that previously treatments are durable under severe conditions of dyeing (temperature and long duration).

Colour differences were examined using a spectrophotometer Spectroflash type Datacolor SF 300. Dyeing was conducted as follows: within the first 15 min, the samples were kept in an acid medium ($pH = 4.5$) and were then dyed at $100^{\circ}C$ for 90 min in the Mathis Polycolor 2002 machine. After dyeing the samples were treated with soap (in a solution de 1g/L DS Lavoton at $100^{\circ}C$ for 10 min), rinsed and dried at room temperature.

Wrinkle recovering angles (WRA)

Wrinkle-proofing effects produced by the two polyols were appreciated by the wrinkle recovery angle values (WRA). The wrinkle-recovering angle was determined according to the German standard DIN 53890. The Metrimplex FF-01 apparatus was used to determine the wrinkle recovering angles as the average of 10 measurements along both the warp and the weft directions.

Contact angles and capillarity

Contact angles and capillarity were determined in agreement with literature data [25] on balance GBX 3S Tensiometer. Each value was calculated as average of five determinations identical.

Results and discussions

Spectroscopic analyses

The presence of MCT-β-CD on the samples pre-treated with Tetronic 701 was revealed by means of two spectroscopic methods: FT-IR and XPS.

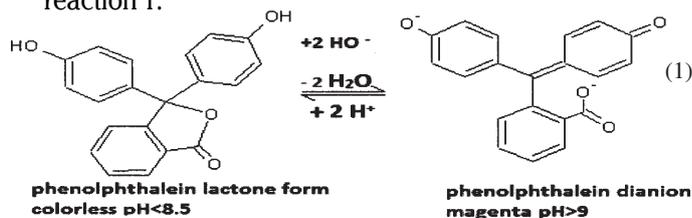
FT-IR Analysis

The spectrum of the sample S10 indicates the presence of MCT-β-CD (fig. 1).

From figure 1 one can notice that the final samples only preserve part of the characteristics of the samples pre-treated with Tetronic 701, the appeared modifications indicating that part of the chemical structure of Tetronic 701 is included in the MCT-β-CD cavity, as follows: the disappearance of the peak at 2970cm^{-1} (CH stretching

(methoxy groups from Tetronic 701(w)), aspect/height of the peaks $2897\text{-}2855\text{cm}^{-1}$, lack of any indices to confirm the formation of ether bond between Tetronic 701 and MCT-β-CD ($1028\text{ - }1159\text{cm}^{-1}$). The presence of MCT-β-CD is confirmed by the appearance of the peaks at 1612cm^{-1} (corresponding to C=N stretch) and at 812 cm^{-1} afferent to C-Cl stretch) [26].

Additionally, in order to verify the hypothesis of Tetronic 701 inclusion in the MCT-β-CD cavity, we resorted to the test with phenolphthalein. At first, a solution of 1% phenolphthalein solution was made by means of ethanol. From this solution, 5 drops were added to a solution of 10 mL NaOH with the concentration of 0.1 mol/L. the appearance of the magenta colour was noticed, specific to phenolphthalein in basic medium ($pH > 9$), as the literature also indicates [27-30]. At $pH < 8.5$, colorless lactone-type phenolphthalein is found in solution. When pH exceeds 9.0, the di-anionic form of phenolphthalein appears (colored in magenta), according to the chemical reaction 1.



Two drops of this colored solution were put on each sample from a series of three. The history of this treatment applied to this series of samples subject to tests was as follows:

- witness sample (S0), namely the previously untreated sample;
- sample S4, treated only with 9% MCT-β-CD;
- sample S10, pre-treated with 9% Tetronic 701, then treated with 9% MCT-β-CD (according to the indications from the table 1).

In figure 2 one can notice that the application of two drops of basic solution of phenolphthalein on each of the three samples, results in the appearance of magenta color (specific to phenolphthalein in a basic medium) on both the untreated sample (a), and on the sample pre-treated with Tetronic 701, and then treated with MCT-β-CD (c).

On the sample only treated with MCT-β-CD (b), no color stain was noticed because a host-guest type compound is

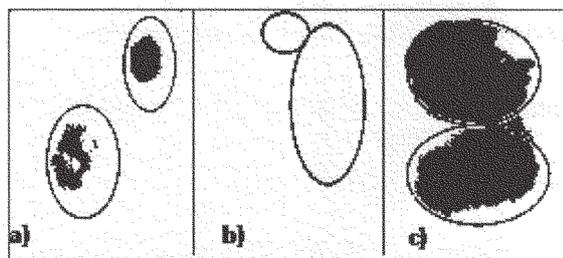


Fig. 2. Results of the tests with basic phenolphthalein: a) witness; b) cotton treated only with MCT-β-CD (S4); c) cotton pre-treated with Tetronic 701 and then treated with MCT-β-CD (S10)

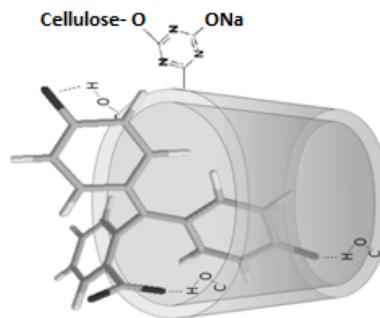
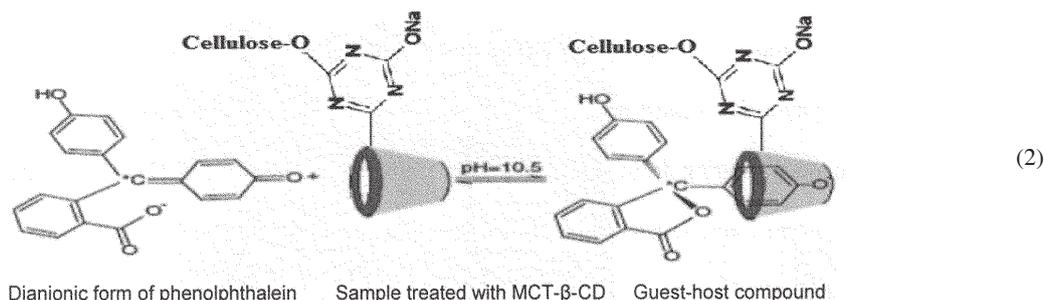


Fig. 3. Diagram of the generation of hydrogen bonds between monochlorotriazine-β-cyclodextrin from the treated textile, and the di-anion phenolphthalein

formed between the di-anionic phenolphthalein and monochlorotriazine beta cyclodextrin [31], according to the chemical reaction 2.



During the formation of the guest-host compound the phenolphthalein di-anion is complexed due to the formation of three hydrogen bonds (fig. 3) with the cyclodextrin molecule. Therefore, the Van-der Waals bounds between the guest molecule (phenolphthalein) and the cyclodextrin non-polar cavity are not very significant in this compound. These intermolecular interactions determine the phenolphthalein molecule to twist tighter around the central carbon atom. The de-localization of the conjugated π electrons is affected accordingly, such that the colour disappears [29].

The penetration of the basic phenolphthalein into the cavity of monochlorotriazine-β-cyclodextrin is possible, as this is empty. This is not the case for the sample pretreated with Tetronic 701 and then treated with MCT-β-CD. This already has its cavity occupied by a large part of the non-polar chain of Tetronic 701 (several methoxy groups), and therefore the phenolphthalein will be visible on the surface of this sample as a magenta-coloured stain.

XPS analysis

The untreated cotton sample has in its constitution only C1s and O1s atoms. The elemental analysis of the sample S10 treated with MCT-β-CD (also pre-treated with Tetronic 701) indicates beside C 1s, O 1s, N 1s, Na 1s, the presence of Cl 2p atom. The atoms N 1s, Na 1s and Cl 2p come from MCT-β-CD and confirm in this way the existence of MCT-β-CD on the treated samples. Figure 4 indicates the percentages of 5.19% for N 1s, 15.66% for Cl 2p and 8.94% for Na 1s.

Thermal, calorimetric (DSC) and thermo-gravimetric (TGA) analyses

The calorimetric behaviour of the cotton samples pre-treated with tetrol and then with MCT-β-CD within the temperature range 25-300°C has been studied, in order to determine the area of the endothermic peak (by computational of normalized integral) (fig.5).

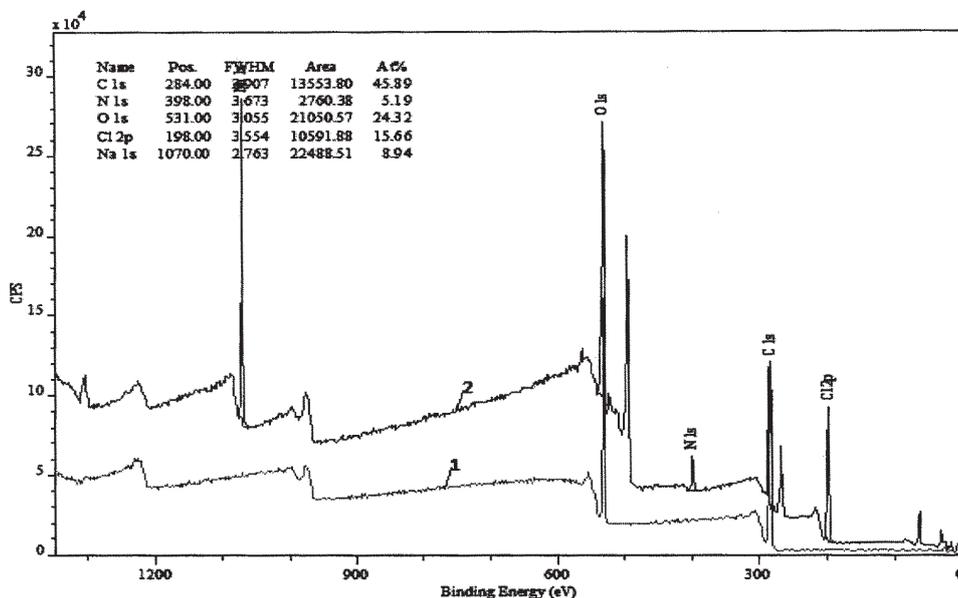


Fig. 4. XPS spectra for the witness sample (1) and the sample treated with Tetronic 701 and MCT β-CD (2)

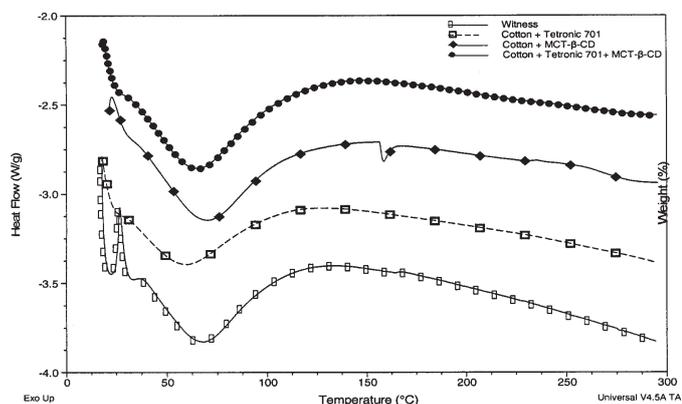


Fig. 5. Comparison of DCS curves

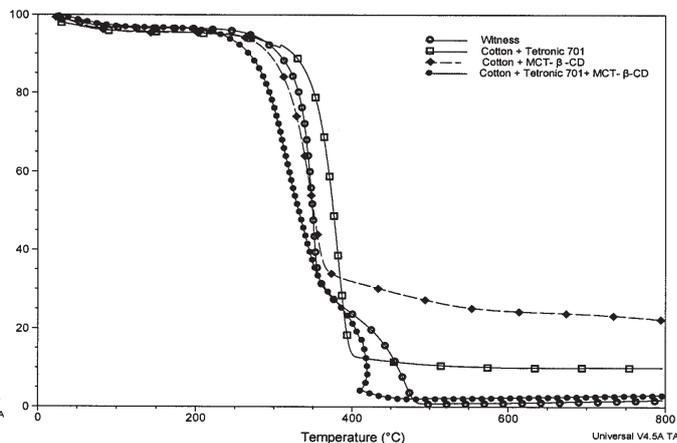


Fig. 6. Thermo - gravimetric curves

Sample	ETAPA	T_{onset}^a	T_{peak}^b	T_{endset}^c	W^d (%)	Residue ^e (%)
Witness	I	38.72	68.24	105.1	3.51	1.79
	II	321.25	341.32	356.93	66.46	
	III	369.01	450.72	473.02	28.24	
Cotton+Tetronic 701	I	30.67	68.34	105.02	4.6	10.03
	II	356.38	375.40	396.34	85.37	
Cotton+MCT-β-CD	I	38.44	70.47	141.16	3.79	22.33
	II	319.18	343.26	367.35	73.88	
Cotton+Tetronic 701 + MCT-β-CD	I	38.21	68.70	125.06	4.711	3.049
	II	280.91	308.05	335.19	65.11	
	III	360.48	386.76	413.05	27.13	

^a T_{onset} - temperature at which each stage starts;

^b T_{peak} - temperature at which the reaction rate reaches its maximum in each stage;

^c T_{endset} - temperature at which each stage ends;

^d W (%) - percentage mass loss from each stage;

^e Residue (%) amount of degraded sample that remains at temperatures exceeding 800°C.

Table 2
THERMO-GRAVIMETRIC CURVES
CHARACTERISTICS

Table 3
VALUES OF TAKING-UP DEGREE

Sample code	Treatment receipts				Y_p (%)
	Padding I		Padding II		
	Tetronic 701 (%)	Mg Cl ₂ (catalyst) (%)	MCT-β-CD (%)	Na ₂ CO ₃ (catalyst) (%)	
S1	3	2.5	-	-	2.91
S2	9	2.5	-	-	1.96
S3	15	2.5	-	-	2.30
S4	-	-	9	2.5	8.10
S5	-	-	9	3	8.70
S6	-	-	15	2.5	14.23
S7	15	2.5	9	2.5	15.35
S8	9	2.5	15	2.5	15.66
S9	9	2.5	9	3	15.17
S10	9	2.5	9	2.5	15.32

The advantage of the DSC method consists in the fact that the endothermic peak area is proportional with the dehydration enthalpy [32, 33]. Under these circumstances, if the enthalpy of a treated sample is bigger than that of the witness, this means that the samples are more hydrophilic.

In figure 5 the witness has an enthalpy of 74.9 J/g, while the sample treated with Tetronic 701 has 75.1 J/g, and the sample treated only with MCT-β-CD has 118.9 J/g. The sample pre-treated with Tetronic 701 and also treated with MCT-β-CD has an enthalpy of 112.3 J/g. In conclusion, all tested samples are more hydrophilic than witness.

The thermo-gravimetric curves (fig. 6) were recorded in nitrogen atmosphere at 20°C/min and their characteristics are presented in table 2.

Taking-up degree

Table 3 presents the values of the taking-up degree Y_p . These depend on the treatment conditions (concentrations of Tetronic 701 and/or MCT-β-CD, catalyst concentration). The sample S8 has the highest taking-up degree.

Durability of treatments effects revealed by tinctorial methods

In an acid medium created by the presence of the acetic acid becomes possible to dye the samples treated with the acid dye C.I. Acid Blue 220. The acid medium (pH = 4 - 4.5) results both in the protonation of the NH₂ groups from the dye, and the appearance of the positive charges at the level of the N atom from Tetronic 701.

Dyeing is possible because the NH₃⁺ groups from the dye exert an electrostatic attraction on the negative groups (OH⁻) from the treated samples, and N⁺ from Tetronic 701 interact at the ion level with the OH⁻ groups from MCT-β-CD or from cellulose.

The values of the colour strength obtained as the result of dyeing with C.I. Acid Blue 220 are illustrated in figure 7. The used dye being of acid type, it has in its structure both anionic SO₃²⁻ groups, and amine groups. The anionic groups will present affinity for the positivated groups of Tetronic 701 (N⁺) acquired during the protonation stage. The utilization of Tetronic 701 in excess (15%) will not result in the most intense dyeing because in this case, besides the action of grafting on cotton, tetrol will also improve the textile cleaning effect by solving significant wax quantities, which will result in a more intense degree of white, therefore in a poorer colour strength after dyeing.

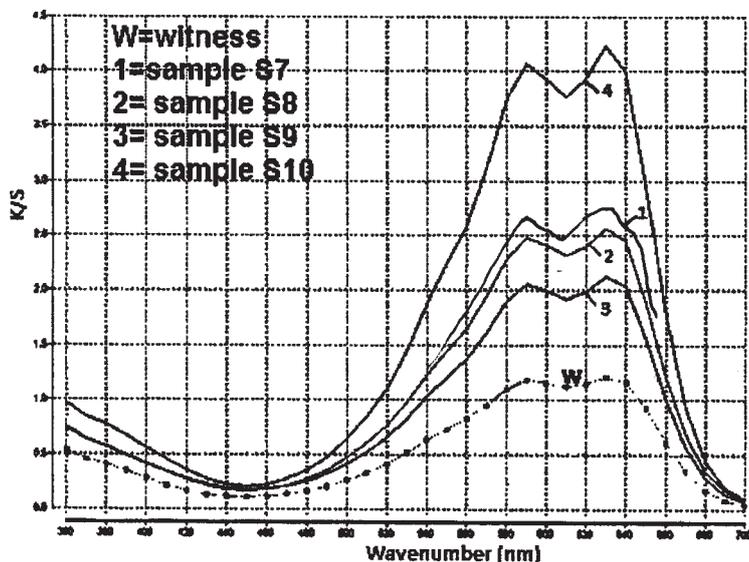


Fig. 7. Variation of color intensity and hues of the treated samples (significances of S7-S10 samples are the same as in table 1)

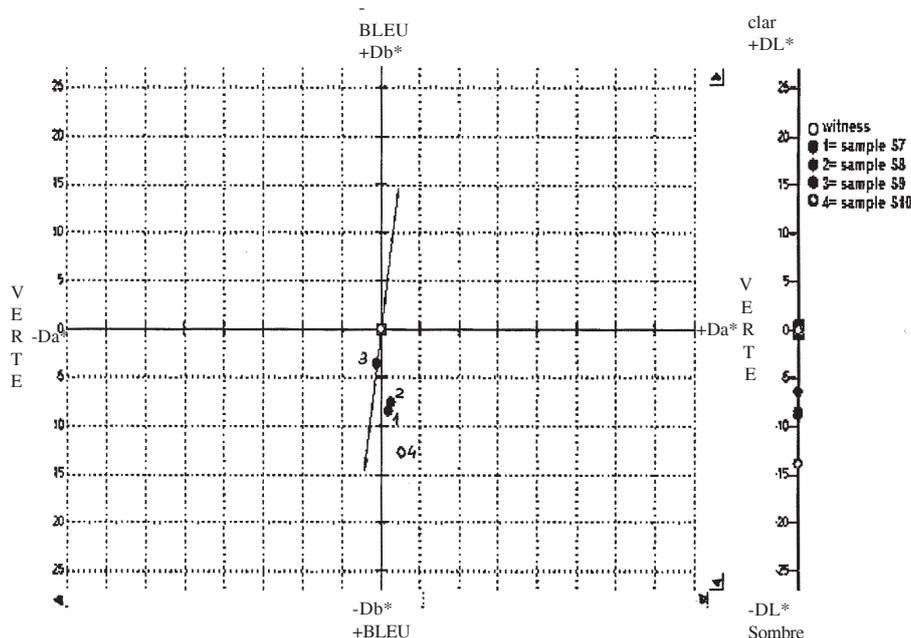


Fig. 8. CIE LAB graph

The amine groups of C.I. Acid Blue 220 get protonated in the acid medium utilized during dyeing and will preferably attract the anions (HO^- or Cl^-) from MCT- β -CD. The dual behaviour of affinity is proved by the very straight contiguity of the curves 1 and 2 for K/S (affertent to the samples S7 and S8) produced with maximum concentrations of Tetronic 701 (15%) and MCT- β -CD (15%) respectively.

The aspect of the curves 3 and 4 affertent to the samples S9 and S10 proves that the maximum catalyst (Na_2CO_3) efficacy occurs at 2.5%.

The CIE Lab graph indicates the following aspects: the treated and dyed samples have K/S values higher than the witness one; they are bluer, with red or green hues. The chromatic characteristics of the samples treated with Tetronic 701 and MCT- β -CD and dyed with C.I. Acid Blue 220 are highlighted in figure 8 and table 4.

The colour differences ΔE^* have been estimated by means of the values ΔL^* , ΔC^* , Δb^* , Δa^* and ΔH^* (table 4); the significance of these variables are: ΔE^* is the color difference between the examined sample and the witness,

i.e. the distance between the corresponding positions in the CIE LAB space; ΔL^* is the brightness difference; ΔC^* is the saturation difference; Δa^* and Δb^* are the chromatic parameters; ΔH^* is the hue difference [34-45].

One can notice that all the samples have the brightness difference $\Delta L^* < 0$, which means that they were dyed more intensely than the witness. The treated samples are less bright $\Delta L^* = L_{\text{sample}} - L_{\text{witness}}$. The values $\Delta C^* > 0$ indicate the unitary character of the used dye.

The chromatic parameters Δa^* and Δb^* indicate the colour shift to red (through the positive values of Δa^*), and to blue respectively (through the negative values of Δb^*). Negative values for ΔH^* indicate that by dyeing with C.I. Acid Blue 220, the sample S9 becomes greener than the witness, and the samples S7, S8 and S10 ($\Delta H^* > 0$) are redder than the witness [34-38]. The values of ΔE^* indicate very big colour differences as compared to the witness. Even if the sample S9, produced with all the treatment reactants added in equal concentrations (9%), has K/S > 2.5 , it has the smallest ΔE^* and therefore it presents the

Sample code	ΔL^*	Δa^*	Δb^*	ΔC^*	ΔH^*	ΔE^*
S7	-8.91	0.93	-8.51	8.35	1.91	12.36
S8	-8.54	1.23	-7.63	7.44	2.07	11.51
S9	-6.43	-0.54	-3.57	3.61	-0.01	7.38
S10	-13.95	2.65	-12.78	12.51	3.75	19.10

Table 4
CHROMATIC CHARACTERISTICS

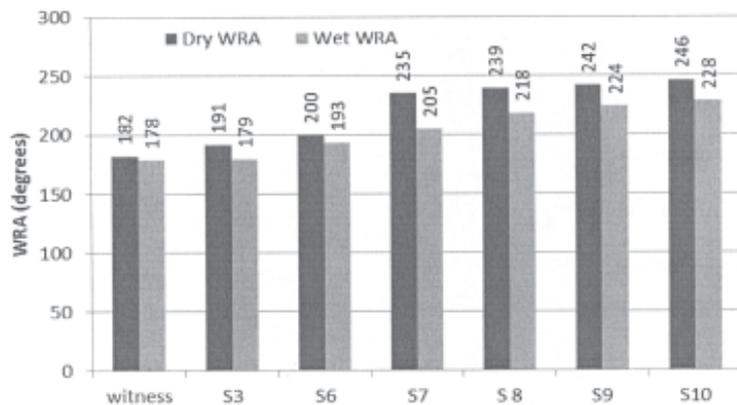


Fig. 9. Values of wrinkle-recovering angles

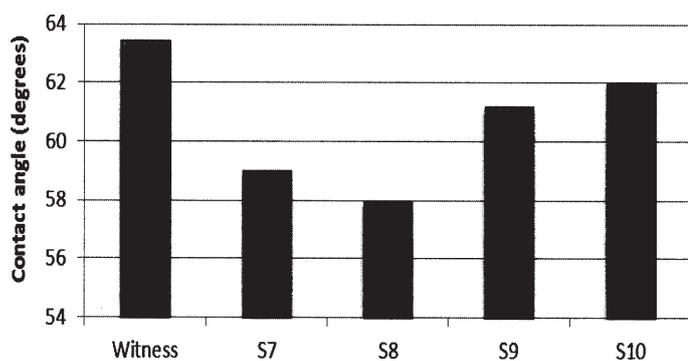


Fig.10. Values of the contact angles

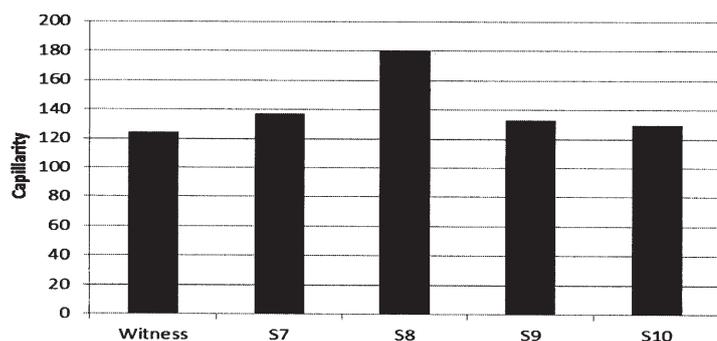


Fig. 11. Values of capillarity

smallest deviation from the witness hue, followed by the samples S8, S7 and then S10.

Taking into account the treatment conditions used before dyeing, one can say that each of the three parameters (the concentrations of Tetronic 701, of MCT- β -CD and of the catalyst Na_2CO_3) have an influence on ΔE^* and on the other parameters that reveals the color differences as compared to the witness. Therefore, S9 is brighter than the other samples, yet less bright than the witness; it will be dyed more intensely than this in blue with green hues.

The time durability of the inclusion compound is reduced, which can be explained by the lack of chemical bond between guest – host. Repeated domestic washings result in the diminution of K/S values and significant alterations of chromatic characteristics. The inclusion compound resists up to 5 repeated washing cycles.

Simultaneous wrinkle-proofing- wettability effects

The wrinkle-recovering angles increase (fig. 9) due to the existence of MCT- β -CD in the treated samples. MCT- β -CD confers certain flexibility to the assembly Tetronic 701-cellulose (partially included in the taper cavity). This flexibility permits a good motion and wrinkle-recovering [46-48]. The wrinkle-recovering angles of the dry/wet samples are much higher than those of the witness.

The contact angles corresponding to the samples treated at high concentrations of Tetronic 701 and MCT- β -CD respectively (15% in the case of samples S7 and S8) are the smallest, therefore the samples S7 and S8 get easily wet in contact with water (fig.10), which is also confirmed by the large values of capillarity (fig. 11).

Conclusions

The simultaneous wrinkle-resistant and wettability effects could only be obtained after successively applying two pad-dry-cure processes: the first one with tetrol (Tetronic 701) that confers wettability to the samples by removing the wax and at high concentrations, is grafted on the cellulose support; the second process consisted in treating with MCT- β -CD the support already treated with Tetronic 701. As the result of this last process, an inclusion compound was formed; the non-polar part of Tetronic 701 (lent by the numerous methoxy groups) penetrated inside the MCT- β -CD cavity. The presence of this inclusion compound was confirmed by the spectroscopic (FT-IR and XPS) analyses and mainly by the qualitative test carried out with phenolphthalein. The calorimetric and thermogravimetric analyses, as well as the tinctorial method confirm the presence of Tetronic 701 and MCT- β -CD on the treated samples. The wrinkle-resistant effects of the treated samples are confirmed by the increased wet and dry WRA values. The wettability of the treated samples is

confirmed by smaller contact angles and higher capillarity as compared to the untreated sample.

The shortcoming of these treatments consists in their reduced durability, as the formed inclusion compound can release the guest after several repeated washings.

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