

ECO-Friendly Durable Press Finishing of Cellulose-Containing Fabrics

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ABSTRACT: To impart easy-care properties to cellulose-containing fabrics along with avoiding any harmful effects of formaldehyde on both the health and the environment, attempts have been made to use citric acid (CA) as an ester crosslinking agent along with different catalytic systems in the absence and presence of certain additives. Further, fixation conditions, type of crosslinking agent, as well as type of substrate have been studied. Results revealed that the enhancement in carboxyl content, performance properties, and the decrease in tear strength (TS) as well as in whiteness indices (WI) of the finished fabric samples were increased by increasing CA concentration up to 80 g/L and by raising thermofixation temperature from 140 up to 180°C for 90 s. Inclusion of triethanolamine hydrochloride (TEA. HCl), decreased the carboxyl content, TS, color strength K/S, as well as oily stain release rating (SRR) of the finished fabric samples along with an increase in bound nitrogen (%N), wrinkle recovery angle WRA, and an improvement in WI without affecting the durable press rating (DP). Within the range examined (0–30 g/L), increasing PEG-600 concentration improved the wet resiliency, TS, as well as WI properties of the finished samples. Increasing DMDHEU ratio in the CA/DMDHEU crosslinking system gave rise to an increase in %N, WRA (dry and wet), DP, as well as in free CH₂O of finished fabrics, along with a slight improvement in WI values. On the other hand, the TS, carboxyl content, K/S, SRR values of the finished fabric samples were lower at a higher DMDHEU ratio. Increase in carboxyl content, %N, WRA (dry and wet), DP and SRR, as well as extent of post dyeing (K/S) of the treated fabric samples upon using different ester crosslinking agents followed the descending order: citric acid > pyromellitic dianhydride. The opposite holds true for the TS, and WI values. Among the esterifying catalysts used, and for a given set of finishing conditions, NaH₂PO₂ · H₂O proved to be the most effective one, and the following order of effectiveness may be drawn: NaH₂PO₂ · H₂O > K₂HPO₄ > Na₃-citrate > Na₂-tartrate. Inclusion of silicone softener in the finishing formulation brought about an improvement in softness degree, WRA, %N, DP, TS as well as K/S values along with a decrease in carboxyl content, SRR, and WI values of the treated fabric samples, regardless of the used silicone softener. The performance properties of the finished fabric samples were determined by the type and nature of the substrate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2243–2253, 2002

Key words: crosslinking; esterification; fibers

INTRODUCTION

Crosslinking of cellulose with *N*-methylol crosslinking agents to impart wrinkle-resistance, shrink-

proofing, and smooth drying properties by virtue of chemical reaction with cellulosic hydroxyl groups to form covalent crosslinks in the interior of cellulosic fibers have previously been done.^{1–3} However, at the present time, presence of formaldehyde in the finished product, working atmosphere, as well as in wastewater streams is considered as highly objectionable due to the mutagenic activity of various

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aldehydes, including formaldehyde.^{4–7} The acceptable limits for formaldehyde, which is a probable human carcinogen, have been defined as 300 ppm for outer clothings, 75 ppm for clothes indirect contact with the skin, and 20 ppm for baby's clothings.^{8–11} On the other hand, the final textile products not only have to be eco-friendly, but also have to be produced by clean technologies.^{11,12}

Accordingly, the present work is undertaken with a view of: (1) proper applying of citric acid as a nonformaldehyde cellulose reactant, (2) searching for the best finishing formulation and condition for attaining high-performance properties of finished products, (3) understanding the mode of interactions among finishing bath components and cellulose structure, as well as (4) complying with the ecological consideration and eco-standards.

EXPERIMENTAL

Materials

Mill-scoured and bleached: cotton fabric of 110 g/m², viscose fabric of 220 g/m², polyester/cotton blend (65/35) fabric of 140 g/m², cotton/polyester blend (65/35) fabric of 180 g/m², and viscose/polyester blend (65/35) fabric of 200 g/m² were used.

Citric acid (C₆H₈O₇ · H₂O), pyromellitic dianhydride (C₁₀H₂O₆), Na-hypophosphite monohydrate (NaH₂PO₂ · H₂O), dipotassium hydrogen phosphate (K₂HPO₄), trisodium citrate (C₆H₅O₇Na₃), and disodium tartrate (C₄H₄O₆Na₂) were of reagent grade.

Arkofix[®] NG (dimethyloldihydroxyethylene urea—DMDHEU—Clariant), and Maxilon[®] Brill. Orange 2R (basic-Ciba) were of technical grade.

Additives used were triethanolamine hydrochloride, TEA · HCl, (C₆H₁₅NO₃·HCl), polyethylene glycol (PEG-600), Sandoperm[®] FES (nonionic self-crosslinking silicone microemulsion of aminofunctional silicones, Bayer), and Hostopal[®] 3634 (alkylaryl polyglycol ether-nonionic wetting agent, Hoechst).

METHODS

Fabric Treatment

A typical treatment consisted of padding the fabric to approximately 80% wet pickup with an aqueous formulation composed of a crosslinking agent, a catalyst, as well as additives. The padded fabric was mounted on pin frames, dried at 85°C for 3 min, and cured at 180°C for 90 s in a circulating air oven. The

treated fabrics were then washed at 50°C for 15 min in the presence of 2 g/L Na₂CO₃ along with 1 g/L nonionic wetting agent to remove excess and un-fixed reactants as well as byproducts, dried, and conditioned prior to fabric evaluation. Typical formulations used in the treatment as well as fixing conditions are given in the text.

Post Dyeing

Portions of the treated fabrics and an untreated control were dyed, in Launder Ometer Jars, with occasional stirring under conventional conditions. Finished fabrics were dyed for 60 min at 90°C with a 15-min cool down to 60°C, followed by a 15-min rinse in running tap water. Samples of treated fabrics were dyed in a bath containing: Maxilon[®] Brill. Orange 2R 3% (owf), nonionic wetting agent 1 g/L, as well as sodium sulphate 10% (owf) at a liquor-to-fabric ratio (LR) of 20 : 1, and pH 4.5 using Na-acetate/acetic acid buffer.¹³

Fabric Evaluation

Carboxyl content was determined according to the Cirino method.¹⁴ Nitrogen content was determined according to the Kjeldahl method. Quantitative determination of the free formaldehyde content was performed according to the Japanese Law "Harmful Substances—containing Household Products Control Law No. 112/1973."

Standard methods were used to measure dry and wet wrinkle recovery angles (AATCC Test Method 66-1984), as well as Elmendorf tearing strength (ASTMD-1424-83) in the warp direction.

Durable press (DP) appearance rating was determined by comparison with plastic replicas (AATCC Test Method 124-1984).

CIE Whiteness Index was measured on treated fabric samples by AATCC Test Method 110-1989 using a Milton Roy Color Mate Spectrophotometer as were color strength (K/S) values. K/S values of postdyed samples were automatically calculated from reflectance data by use of the Kubelka-Munk equation:¹⁵

$$K/S = (1 - R)^2/2R,$$

where *R* is the reflectance of the dyed fabric at the wavelength of maximum absorption, *K* is the absorption coefficient, and *S* is the scattering coefficient. The higher the K/S value, the greater the dye receptivity of the fabric.

The oily stain release rating (SRR) was assessed according to the AATCC Test Method 130-1974.

Table I Performance Properties of Cotton Finished with Different CA/SHP Concentrations

CA/SHP Conc. (g/L)	—COOH Content (mEq/100 g sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	WI	K/S	SRR
		Dry	Wet					
Untreated cotton	2.1	155	135	1.0	100	78.4	0.3	2.5
20/20	19.2	172	161	1.8	91.3	69.9	0.54	3.0
40/40	35.5	202	183	2.7	85.1	64.8	0.75	3.5
60/60	55.6	225	209	3.2	75.4	61.1	0.96	4.0
80/80	82.0	242	225	3.5	68.5	58.6	1.15	4.5

Cotton fabric treated to a wet pickup of 80% (owf) with citric acid (CA), sodium hypophosphite monohydrate (SHP), and [nonionic wetting agent], 2 g/L; then dried at 85°C for 3 min, cured at 180°C for 90 s, rinsed at 50°C for 15 min, and dried at 85°C for 3 min.

WRA: wrinkle recovery angle (degree); DP: durable press appearance rating after laundering cycle, TS: tear strength (warp direction); WI: whiteness index; K/S: color strength of postdyed samples; SRR: oily stain release rating of finished samples.

RESULTS AND DISCUSSION

With a view towards enhancing the performance properties of easy-care finished cellulose-containing fabrics along with avoiding any harmful effects of formaldehyde on both the health and the environment, attempts have been made to use citric acid as an ester crosslinking agent along with different catalytic systems, in the absence and presence of certain additives. Further, fixation conditions, type of crosslinking agent, as well as type of substrate have been studied. Results obtained along with appropriate discussion follow.

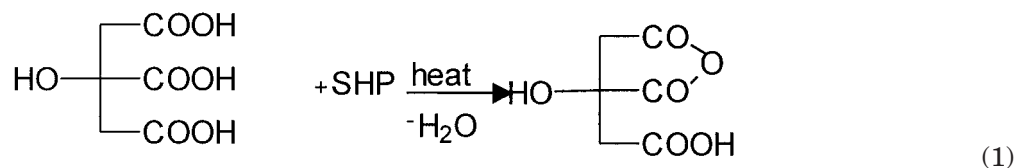
Citric Acid Concentration

Table I shows the effect of citric acid (CA) concentration on the performance properties of the ester-crosslinked cotton fabric. It is clear that, for a given treatment conditions, increasing the finishing agent concentration up to 80 g/L in the finish-

ing formulations brings about: (1) a significant increase in the carboxyl content of the CA-treated fabric along with an improvement in both the SRR as well as the dyeability, expressed as K/S, with the used basic dye that can be attributed to the increase in the amount and accessibility of the free-COOH groups grafted onto the finish/fabric matrix;^{16,17} (2) a noticeable improvement in the resiliency as well as the DP ratings along with a progressive decrease in the tear strength retention of the treated cotton as a direct consequence of increasing the extent of ester crosslinking and restricting the movability of the cellulose chains;^{18,19} and (3) a reduction in the whiteness indices of the CA-finished fabrics, which is a direct consequence of partial dehydration of CA and formation of aconitic acid.²⁰

This suggests that ester crosslinking of cotton cellulose (Cell.OH) by CA in the presence of Na-hypophosphite (SHP) as a catalyst can be explained according to the following tentative mechanism:

Formation of a Cyclic Anhydride Intermediate^{17,21}



Esterification of Cellulose-Hydroxyl Groups

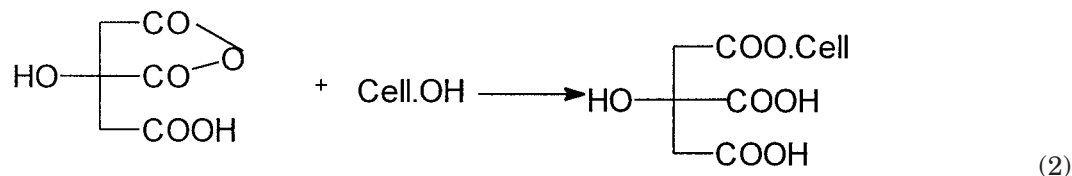
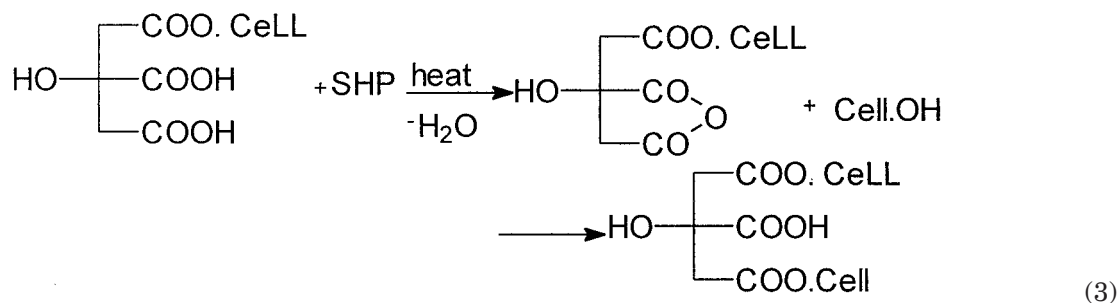


Table II Performance Properties of the CA-Treated Cotton in Presence of Different Amounts of TEA · HCl

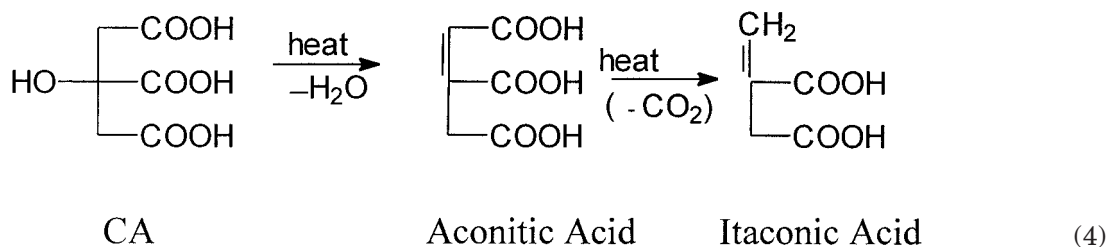
TEA · HCl (g/L)	N, (%)	—COOH Content (mEq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	WI	K/S	SRR
			Dry	Wet					
Untreated cotton	—	2.1	155	135	1.0	100	78.4	0.3	2.5
0	—	82.0	242	225	3.5	68.5	58.6	1.15	4.5
5	0.017	80.0	246	230	3.5	68.0	61.0	1.04	4.3
10	0.05	77.4	252	236	3.5	67.3	62.4	1.00	4.2
15	0.074	72.0	260	244	3.6	65.8	65.0	0.92	4.0

Treating bath: [CA], 80 g/L; [SHP], 80 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s. N: nitrogen content. For explanation of abbreviations, see footnote to Table I.

Ester Crosslinking of Cotton Cellulose^{20,22}



Partial Dehydration of CA^{23,24}



Nitrogenous Additive Concentration

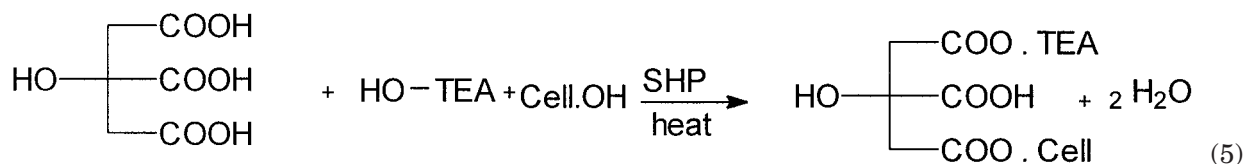
Table II shows the performance properties of CA-treated cotton fabrics in the presence of different amounts of triethanolamine hydrochloride (TEA · HCl) as a nitrogenous additive. It is clear that inclusion of TEA · HCl in the finishing formulation is accompanied by: (1) a decrease in the carboxyl content, tear strength retention, basic dye receptivity, as well as in the soil release rating of the ester-crosslinked cotton fabrics that can be discussed in terms of: reaction of CA-carboxyls with TEA · HCl-hydroxyl groups to form a three-dimensional net-

work of TEA–CA–cellulose, thereby minimizing the concentration of free carboxyl groups as well as fixing a cationic active sites onto the finish fabric matrix;^{25–28} (2) an increase in the bound nitrogen, a slight improvement in fabric resiliency without affecting smoothness appearance, along with an improvement in whiteness indices of the finished cotton fabrics that is a direct consequence of: fixing the TEA · HCl into the CA/cellulose matrix [eqs. (5)–(7)], along with minimizing the extent of CA-dehydration to form unsaturated acids, for example, aconitic acid , respectively.^{24,25,29}

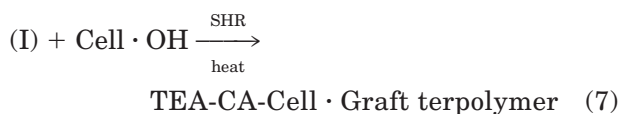
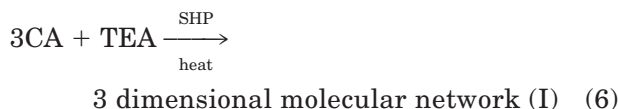
Table III Performance Properties of the CA-Treated Cotton in Presence of Different Amounts of PEG-600.

PEG-600 (g/L)	N, (%)	—COOH Content (mEq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	WI	K/S	SRR
			Dry	Wet					
Untreated cotton	—	2.1	155	135	1.0	100	78.4	0.3	2.5
0	0.074	72.0	260	244	3.6	65.8	65.0	0.92	4.0
10	0.07	70.3	256	250	3.5	67.2	68.7	0.90	4.0
20	0.06	67.5	250	257	3.5	69.8	70.9	0.84	3.8
30	0.04	65.0	245	262	3.4	72.4	73.8	0.75	3.5

Treating bath: [CA], 80 g/L; [SHP], 80 g/L; [TEA.HCl], 15 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s. For explanation of abbreviations, see footnote to Table 1.



and/or

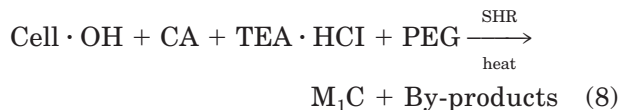


Glycol Additive Concentration

The effect of adding PEG-600 to the CA/SHP/TEA finishing formulation on the performance properties of treated cotton fabrics is shown in Table III. It is clear that, within the range examined (0–30 g/L), the inclusion of PEG-600 resulted in: (1) a negative effect on the carboxyl content, bound nitrogen, dry resiliency, DP rating, SRR, and K/S values of the finished postdyed samples, probably due to the decrease in both the extent of ester crosslinking of the cellulosic hydroxyl groups as well as fixation of the TEA onto the finish/fabric matrix resulting from PEG-hydroxyl end groups competition for esterification of CA-carboxyls to give higher polymer grafts on and/or into the finished cotton, thereby minimizing the values of the aforementioned properties,^{24,26} and (2) a positive impact on wet resiliency, tear

strength retention as well as fabric whiteness properties reflecting the role of PEG-600 on: enhancing the swellability of the cellulose structure thereby enabling better penetration and esterification within the fabric structure, introducing hydrophilic hydroxyl groups thereby imparting a more hydrophilic crosslinked structure with higher moisture absorption, and retarding and/or minimizing, to some extent, the removal of alpha-hydroxyl group of CA during heat curing, i.e., reversing the dehydration reaction causing formation of unsaturated acids, for example, aconitic acid as a source of yellowing.²⁴

Based on previous findings, a simplified reaction scheme of the ester crosslinking of cotton cellulose with CA as a finish and SHP as a catalyst in the presence of both the TEA and PEG-600 as reactive additives follows:



where M₁C is a modified ester-crosslinked cotton cellulose containing free carboxyl groups along with grafted cationic active sites and polyol moieties.

Curing Temperature

Performance properties of cotton fabrics finished with CA (80 g/L), SHP (80 g/L) along with TEA

Table IV Performance Properties of the CA-Treated Cotton at Different Curing Temperatures and Fixation Methods

Fixation Method	Condition °C/90 s	N, (%)	—COOH Content (mEq/100 g) Sample	WRA (w + f) ^o		DP Rating	TS (w) Retained, %			
				Dry	Wet		WI	K/S	SRR	
Pad-Dry-Cure	140	0.025	42.5	195	202	2.5	83.2	76.2	0.45	3.0
	160	0.030	53.9	222	235	3.0	76.5	75.1	0.58	3.2
	180	0.040	65.0	240	262	3.4	72.4	73.8	0.75	3.5
	200	0.045	68.3	246	265	3.5	65.9	67.7	0.80	3.5
Pad-Cure	180	0.036	60.0	232	250	3.2	74.0	75.6	0.65	3.5

Treating bath: [CA], 80 g/L; [SHP], 80 g/L; [TEA.HCl], 15 g/L; [PEG-600], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

For explanation of abbreviations, see footnote to Table 1.

· HCl (15 g/L) and PEG-600 (30 g/L) additives as functions of curing temperature are given in Table IV. It is clear that, raising the thermofixation temperature from 140 up to 180°C for 90 s brings about (1) a significant improvement in the carboxyl and nitrogen contents, dry and wet resiliency, smoothness appearance, as well as extent of postdyeing, expressed as K/S values; (2) a slight decrease in the fabric whiteness along with a slight improvement in soil release rating, and (3) a noticeable reduction in tear strength of the finished cotton fabrics. This is a direct consequence of (1) increasing the extent of dehydration from neighbouring carboxyl groups resulting in formation of cyclic anhydride intermediates, (2) enhancing the extent of cellulose esterification as well as modification via fixing of TEA · HCl and PEG in and/or onto the CA/Cell.OH matrix, and (3) helping dehydration from the alpha-hydroxyl group of CA to generate unsaturated acids that cause discoloration of the finished fabrics.^{22,24}

Further increase in thermofixation temperature, i.e., beyond 180°C, brings about a remarkable decrease in both the whiteness and the tear strength retention properties along with a slight or non-improvement on the other performance properties. This could be due to a further increase in formation of unsaturated acids as a result of excessive dehydration from the alpha-hydroxyl groups of CA, as well as a greater extent of ester crosslinking in addition to thermal degradation and discoloration of cotton cellulose at the highest curing temperature, at 200°C, respectively.

Table IV also shows the effect of fixation method, i.e. pad-dry cure or pad-flash cure on the performance properties of the treated fabrics. It reveals that the extent of ester crosslinking as well as fabric modification, expressed as carboxyl

and nitrogen contents, dry and wet resiliency, DP rating, the decrease in tear strength, the extent of discoloration, as well as the K/S value of the treated postdyed samples, follow the descending order: Pad-dry cure (at 180°C/90 s) > pad-flash cure (180°C/90 s).

The variation in the performance properties of the cured samples, as a function of curing technique, after treating with the same finishing formulation, could be associated with the differences in (1) extent of formation of cyclic anhydride intermediates, (2) extent of ester crosslinking of cotton cellulose, (3) extent of modification of the crosslinked structure, (4) number, length, and location of ester crosslinks, (5) hydrophilicity as well as electronegativity of the finished fabric, and (6) extent of finishing ingredients migration.^{31–33}

CA/DMDHEU Finishing System

Table V shows the effect of partial replacement of CA with DMDHEU in the finishing formulations on the performance properties of the finished cotton fabrics. It is clear that, within the range examined, increasing DMDHEU in CA/DMDHEU crosslinking system brings about: (1) a significant increase in the bound nitrogen, dry and wet resiliency, smoothness appearance along with a significant decrease in tear strength retention of the CA/DMDHEU-crosslinked cotton fabrics, which is a direct consequence of increasing both the extent of ether and ester crosslinking; (2) a slight improvement in the whiteness indices of the finished fabrics reflecting the positive effect of DMDHEU on reducing, to some extent, the dehydration of CA to form unsaturated acids by capping of the alpha-hydroxyl group in CA via reaction with the —NCH₂OH groups of

Table V Performance Properties of the CA-Treated Cotton Using CA/DMDHEU Finishing System

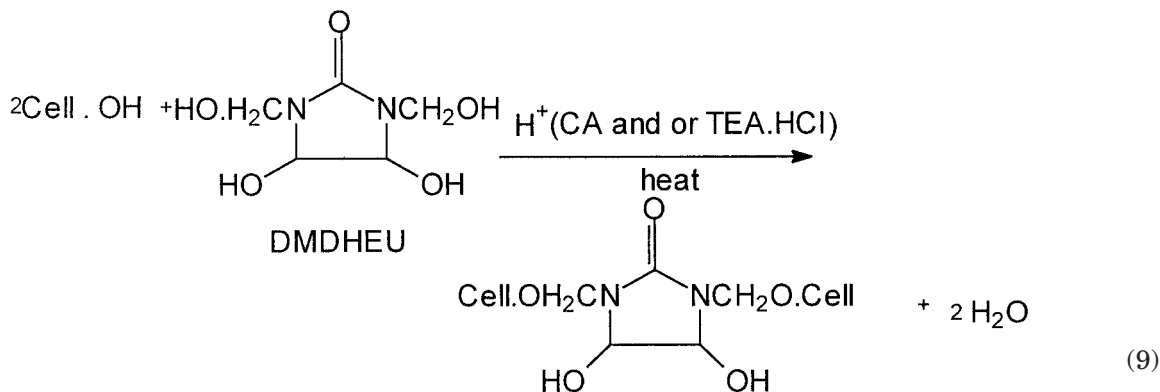
Finishing System		N, (%)	—COOH Content mEq/100 g Sample	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	Free-CHO (ppm)	WI	K/S	SRR
CA	DMDHEU			Dry	Wet						
80	0	0.040	65.0	240	262	3.4	72.4	0	73.8	0.75	3.5
60	20	0.299	60.3	256	273	3.6	69.4	15	74.9	0.66	3.3
40	40	0.478	56.8	269	285	4.0	65.9	36	75.6	0.58	3.0

Treating bath: [CA], 80 g/L; [SHP]; 80 g/L; [TEA · HCl], 15 g/L, [PEG-600], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

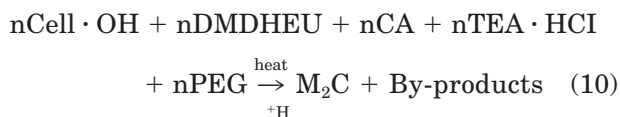
For explanation of abbreviations, see footnote to Table 1.

DMDHEU under the given finishing conditions; (3) a decrease in the carboxyl content, postdyeing with the used basic dye as well as in soil release ratings of the finished fabrics as a direct consequence of reducing the amount of free carboxyl groups on the finish/fabric matrix as well as swellability and hydrophilicity of the crosslinked cellulose structure; and (4) an increase in the free-CH₂O of the finished fabrics from 0 to 35

ppm. This suggests that, presence of the cellulosic substrate (CelloH), along with CA, DMDHEU, SHP, TEA · HCl, as well as PEG-600 at high temperature, would be expected to promote the following reactions and/or interactions: (a) ester crosslinking of cellulose [eqs. (1)–(3)]; (b) fixation of TEAHCl and PEG onto the finish/fabric matrix [eqs. (5)–(8)]; (c) ether crosslinking of the cotton cellulose:^{19,25}



(d) fixation of citric acid, TEA · HCl, as well as PEG onto the ether-crosslinked structure:³⁴



where M₂C is a modified ether-crosslinked cotton cellulose containing free carboxyl groups, tertiary amino groups, as well as polyol residues; (e) capping of the alpha-hydroxyl group in CA:

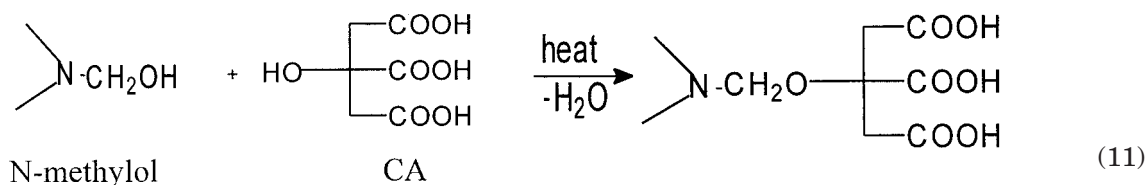


Table VI Performance Properties of Cotton Finished with Different Esterifying Agents

Esterifying Agent	N, (%)	—COOH Content (mEq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) retained: %	WI	K/S	SRR
			Dry	Wet					
CA	0.040	65.0	240	262	3.4	72.4	73.8	0.75	3.5
PDA	0.025	50.9	195	178	2.5	86.8	78.9	0.52	3.0

Treating bath: [Esterifying Agent], 80 g/L; [SHP], 80 g/L; [TEA.HCl], 15 g/L; [PEG-600], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

PDA: Pyromellitic Dianhydride. For explanation of abbreviations, see footnote to Table 1.

Esterifying Polyacids

Table VI shows the effect of using CA or pyromellitic dianhydride (PDA), as a finishing agent, on the extent of ester crosslinking as well as the performance properties of the treated cotton fabrics. It is clear that, for given finishing conditions, the improve in: carboxyl and nitrogen contents, resiliency, DP, and SRR ratings as well as in K/S values of the treated postdyed samples follows the descending order: CA > PDA.

The opposite holds true for the tear strength retention and whiteness values of the treated fabrics, reflecting the differences between the aforementioned crosslinkers in: (1) polycarboxylic acid reactivity, (2) activation energy, (3) functionality, (4) structure as well as thermal stability, (5) level and extent of esterification, (6) location, number, and length of crosslinks, as well as (7) tendency to side interactions with other ingredients in the finishing formulation.⁷

Esterifying Catalysts

Table VII demonstrates the variation in the performance properties of CA-treated fabric

samples using phosphorous-containing catalysts, i.e., NaH₂PO₂ and K₂HPO₄, as well as Na-salts of hydroxy acids, i.e., Na₃-citrate and Na₂-tartrate, catalysts. Among those studied, for a given set of finishing conditions, SHP proved to be the most active one, and the following order of the effectiveness may be drawn: NaH₂PO₂ · H₂O > K₂HPO₄ > Na₃-citrate > Na₂-tartrate, reflecting the differences among these esterifying catalysts in:^{1,16,21,35} (1) extent of dissociation; (2) pH of finishing formulation; (3) mode and mechanism of catalyysis, for example, SHP serves as a catalyst only, while Na₃ citrate serves as a CA donor as well as a catalyst; and (4) extent of modification of treated cotton-cellulose structure.

Softener Additives

The effect of incorporation of some silicone softeners in CA-finishing formulations on the performance properties of finished cotton fabrics are shown in Table VIII. It is evident that inclusion of the silicone softener in the finishing formulation brings about: (1) a remarkable improve in softener

Table VII Performance Properties of the CA-Treated Cotton Using Different Esterifying Catalysts

Esterifying catalyst	N, (%)	—COOH Content (mEq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	WI	K/S	SRR
			Dry	Wet					
NaH ₂ PO ₂ · H ₂ O	0.040	65.0	240	262	3.4	72.4	73.8	0.75	3.5
K ₂ HPO ₄	0.035	59.8	220	235	3.2	75.2	71.4	0.70	3.5
Na ₃ -Citrate	0.029	40.8	185	208	2.9	80.9	74.8	0.60	3.0
Na ₂ -Tartrate	0.025	45.3	198	215	3.0	78.6	73.4	0.66	3.0

Treating bath: [CA], 80 g/L; [Catalyst], 80 g/L; [TEA.HCl], 15 g/L; [PEG-600], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

For explanation of abbreviations, see footnote to Table 1.

Table VIII Performance Properties of the CA-Treated Cotton in Presence of Silicone Softeners

Softening Agent	N, (%)	—COOH Content (Meq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	Handling	WI	K/S	SRR
			Dry	Wet						
None	0.040	65.0	240	262	3.4	72.4	Harsh	73.8	0.75	3.5
Sandoperm®										
FES	0.073	45.8	259	272	3.6	78.9	very-soft	68.7	1.30	3.0
Persoftal®										
SAN	0.140	55.6	252	268	3.7	82.5	very-soft	71.3	1.45	3.0

Treating bath: [CA], 80 g/L; [SHP], 80 g/L; [TEA.HCl], 15 g/L; [PEG-600], 30 g/L; [silicone softener], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

For explanation of abbreviations, see footnote to Table 1.

ness degree of the finished fabrics along with a noticeable increase in tear strength retention; (2) an improvement in the bound nitrogen, resiliency, DP rating, as well as dye receptivity; and (3) a decrease in the carboxyl content, soil release rating, as well as whiteness indices, regardless of the used softener. This could be discussed in terms of (1) coating and/or encapsulating the cellulosic fibers with a softener film thereby enhancing the softness degree; (2) reduction of interyarn friction along with formation of interfiber and interyarn bonds thereby improving fabric resiliency and its smooth drying properties; (3) facilitating the fiber slippage as well as improving the fiber/yarn mobility within the fabric structure thereby increasing tear strength retention; (4) interaction with active ingredients in the finishing formulation, fixation onto, as well as modification of the crosslinked cellulose structure thereby increasing the bound nitrogen, decreasing the number of carboxyl groups, enhancing dye receptivity, as well as hindering and/or minimizing the soil release; and (5) thermal oxidation of the used softeners during the curing step thereby causing fabric discoloration and whiteness minimization.³⁶⁻⁴⁰ Changes in the values of the aforementioned performance properties upon using different softeners would be expected to rely on:^{33,41-44} (1) chemical nature and molecular structure of the softener; (2) softener form, for example, elastomer, microemulsion, etc; (3) reactivity and affinity for the used substrate; (4) mode and extent of reaction and/or interaction among other ingredients as well as cellulose structure; (5) location and extent of distribution; and (6) tendency to entrap the dye molecules and retard the release of the soil particles.

Cellulose-Containing Substrates

As far as the change in the performance properties of the finished fabrics as a function of the type of the substrate is concerned, and for a given set of finishing conditions, the data in Table IX reveal that: (1) ester crosslinking of cellulose-containing fabrics under investigation seems to enhance nitrogen and carboxyl contents, resiliency, smooth drying properties, dye receptivity, and soil release rating along with a reduction in fabric tear strength as well as whiteness indices regardless of the used substrate; (2) the magnitude of the aforementioned properties of the finished samples are determined by the nature and type of substrate, i.e., physical and chemical structure, amorphous-to-crystalline ratio, hydrophilicity-to-hydrophobicity ratio, fabric construction, functionality, as well as ability to interact with the finishing bath ingredients along with extent of modification;^{36,37,45}) and (3) the higher the cellulose component, the greater the extent of ester crosslinking.

CONCLUSIONS

Citric acid can be used as an esterifying agent for cellulose-containing fabrics to impart them formaldehyde free easy-care properties using sodium hypophosphite as a catalyst. Under the conditions employed, incorporation of (a) TEA · HCl in the finishing formulation results in enhancing the WRA and W.I. along with a little reduction in TS, K/S, and SRR; and (b) PEG-600 in the finishing formulation results in improving TS and WI along with a reduction in WRA, K/S, and SRR. The extent of crosslinking upon

Table IX Performance Properties of the CA-Treated Cellulosic-Containing Fabrics

Substrate	N, (%)	—COOH Content (mEq/100 g Sample)	WRA (w + f) ^o		DP Rating	TS (w) Retained, %	WI	K/S	SRR
			Dry	Wet					
Cotton	0.040	65.0	240	262	3.4	72.4	73.8	0.75	3.5
Cotton/Polyester (65/35)	0.030	50	250	220	4.0	76.8	90.0	0.55	3.2
Cotton/Polyester (35/65)	0.022	41.9	270	250	4.5	80.9	95.2	0.25	3.0
Viscose	0.075	59.9	280	180	4.5	65.3	83.7	0.64	4.0
Viscose/Polyester (65/35)	0.046	44.1	285	200	4.5	73.4	87.0	0.47	3.5

Treating bath: [CA], 80 g/L; [SHP], 80 g/L; [TEA.HCl], 15 g/L; [PEG-600], 30 g/L; [silicone softener], 30 g/L; [nonionic wetting agent], 2 g/L; dry 85°C/3 min, cure 180°C/90 s.

For explanation of abbreviations, see footnote to Table I.

using citric acid is higher than that upon using pyromellitic dianhydride. Among the esterifying catalysts used for a given set of finishing conditions, sodium hypophosphite is the best, and the following order of effectiveness can be drawn: $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} > \text{K}_2\text{HPO}_4 > \text{Na}_3\text{-citrate} > \text{Na}_2\text{-tartrate}$. The presence of silicone softener in the finishing formulation results in enhancing softness degree, WRA, TS, and K/S values with a decrease in SRR and WI values. Finished fabric properties depend on the type and nature of cellulosic substrate.

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