Chemical Factors Affecting Soiling and Soil Release from Cotton-Containing Durable Press Fabric. VI. Effect of Introduction of Carboxymethyl Groups in the Cotton Component of Polyester/Cotton Blend*

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Synopsis

Partial carboxymethylation of the cotton component of polyester/cotton blend prior to durable press finishing with dimethyloldihydroxyethylene urea in presence of $MgCl_2 \cdot 6H_2O$ was carried out under different conditions to control the carboxyl content as well as alteration of the blend components accompanying the chemical modification. The susceptibility of these modified blend samples before and after crosslinking to aqueous and nonaqueous oily soiling and their ability to release the soil was examined. The general indications are that introduction of carboxymethyl groups in the molecular structure of the cotton component of the blend imparts soil release characteristics of the blend provided that (a) the condition of partial carboxymethylation is not accompanied by profound changes in neither the microstructure of the cotton component nor in the polyester content of the blend and (b) the carboxymethyl content should not be so high. It is proposed that the anionic nature of the modified cotton component of the blend during washing helps in repelling the negatively charged soil particles from the blend surface. In addition, a reduction in the interfacial tension at the soil–water interface assists in rolling up the soil and subsequent removal. This can be turned to the opposite if the electrostatic repulsion is masked through creation of soft swollen environment by significantly increasing the carboxymethyl content, decreasing the polyester content, and/or increasing the swellability of cotton component of the blend.

INTRODUCTION

The wide spread use of blends of cotton with synthetic fibers as well as finishing of cotton or its blends with a view to impart easy care and durable press properties has led to increasing complaints regarding rapid soiling and difficulty in removing soil during laundering. The subject has been extensively reviewed elsewhere.[1]

Recent studies[2–4] from this division have disclosed that chemical modification of cotton via etherification or grafting with acrylic acid exerts a considerable influence on the aqueous and nonaqueous soiling and soil release. Inclusion of low and high molecular weight CMC or conventional soil release agents or poly(acrylic acid) also affected the soiling and soil-release properties of cotton and polyester/cotton blends.

In a previous report,[2] we have disclosed that introduction of carboxymethyl groups in the molecular structure of cotton cellulose via partial carboxymethy-

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lation of 100% cotton fabric exerts a considerable influence on the susceptibility of cotton before and after crosslinking towards aqueous and nonaqueous oily soils and this susceptibility depends upon the degree of swelling of cotton accompanying the modification and, to some extent, upon the magnitude of carboxymethyl content. In this work, trials have been made to apply the partial carboxymethylation procedures to polyester/cotton blend fabric under conditions similar to those of 100% cotton fabric with a view to clarifying the effect of the physical as well as chemical modification of the cotton component of the blend on the behavior of the blend towards aqueous and nonaqueous oily soils.

EXPERIMENTAL

Polyester/Cotton Blend Fabric

Mill scoured and bleached plain weave (23 picks × 23 ends/cm) polyester/cotton blend fabric was used throughout this investigation. Chemical analysis of the blend shows that it contains polyester and cotton at a ratio of 49.7:50.3.

Reagents

Monochloroacetic acid, sodium hydroxide, sodium carbonate, and magnesium chloride hexahydrate were of reagent grade chemicals. Dimethyloldihytdroxyethylene urea (DMDEU) was used as the crosslinking agent. This was supplied by BASF, West Germany, under the commercial name Fixapret CPA and Velustrol PA supplied by Hoechst AG, West Germany, was employed as nonionic softener.

Chemical Modification of Cotton: Partial Carboxymethylation

Partial carboxymethylation of the cotton component of the blend fabric was performed using four conditions. These will be referred to as Condition A, Condition B, Condition C, and Condition D.

Condition A

Monochloroacetic acid solution was prepared and neutralized with the equivalent amount of sodium carbonate. Samples of polyester/cotton blend fabric were padded in this solution to a wet pickup of ca. 75%, and then air dried. The samples were then padded in aqueous solution of sodium hydroxide (25%) to a wet pickup of ca. 100%, and rolled and batched for 4 h in polyethylene cover. The treated samples were then unrolled, washed with water, neutralized with dilute hydrochloric acid (0.1N), washed with water again, and finally dried under ambient conditions. Samples containing different caraboxyl content were obtained by varying the monochloroacetic acid concentration from 0.5 to 3N.

Condition B

Details of the experimental techniques used above were applied in Condition B except that a 5% aqueous solution of sodium hydroxide, a batching time of 24 h, and a range of monochloroacetic acid concentration of 0.5–5N were used.

Condition C

Similar to Condition B except that the monochloroacetic acid–sodium hydroxide treated fabric was subjected to heat treatment at 100°C for 6 min, instead of 24 h batching.

Condition D

Fabric sample was steeped in a mixture containing ethyl alcohol (63 mL) and toluene (55.4 mL). To this, a calculated amount of sodium hydroxide solution (44.8%) was added in 1 min, followed by addition of monochloroacetic acid. The reaction mixture was then kept at 65°C for 70 min with continuous mechanical stirring. At this end, the fabric sample was removed from the reaction mixture, washed well with water, neutralized with dilute acetic acid, washed with water, and air dried. Samples containing different carboxyl content were obtained by varying the monochloroacetic acid concentration from 0.05 to 0.5 mol chloroacetic acid per mole anhydroglucose unit of cotton cellulose.

Carboxyl Content

Determination of the carboxyl groups of partially carboxymethylated polyester/cotton blend was carried out according to a reported method.[5] These groups were expressed as milliequivalents (meq) COOH/100 g blend.

Crosslinking Treatment

Unless otherwise stated, the crosslinking treatment was carried out as follows. Fabric samples were padded through two dips and two nips in a solution containing DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) to a wet pickup of ca. 75%. At this point, the fabric was stretched back to its original dimensions on pin frames for drying, and then for curing. Drying was carried out for 5 min at 100°C and curing for 5 min at 160°C. The samples were then conditioned at 65% relative humidity and 25°C for 48 h before testing for soiling and soil-release properties.

Aqueous Soil

Aqueous soil was prepared as follows: To 10 g carbon black were added 90 mL distilled water and 1 g dispersing agent (Irgasol DA gran., Ciba-Geigy, Switzerland). This was placed into a stoppered bottle half-filled with glass balls and shaked mechanically using a shaking machine for 30 min. The result of this was a smooth, uniform soil mixture. This stock solution was diluted with water so as to have aqueous soil mixture consisting of aqueous stock soil mixture:water 1:99.[6]

Nonaqueous Oily Soil

Nonaqueous oily soil was prepared as follows: 10 g carbon black and 90 g motor oil were ground in a mortar with a hand pastle until the materials were uniformly mixed. Dilute soil dispersions were prepared by diluting the stock mixture with carbon tetrachloride so as to give nonaqueous oily soil consisting of oily stock soil mixture:carbon tetrachloride 1:99.[6]

Soiling

Fabric samples were padded one dip, one nip through the soil dispersions under a tight squeeze roll pressure. The samples were then dried at ambient conditions.[6]

Laundering

The soiled samples were laundered at 65°C in a small washing machine (Calor 2000, France) using a solution containing 7.5 g/L detergent (Ariel, made in France by Procter and Gamble, France) at a material-to-liquor ratio 1:100. Three washing cycles, 5 min each, were given followed by three water rinses in the same washing machine.[6]

Soiling and Soil Removal Measurements[7]

A Beckman Spectrophotometer Model 26 with an integrating sphere was adjusted normally to 1 mm opening slit at 700 nm wavelength using $MgSO_4$ plate as a reference was employed to monitor the magnitude of soiling and soil removal. Four measurements were made on each side of the sample (10 × 10 cm) to give a total of eight readings. The latter were averaged to give a single value. All samples were measured against a white background consisting of four layers of filter paper. Since all treated samples and the corresponding controls had essentially equal initial reflectance before soiling, it was decided to use reflectance values as the means of estimating the soil content after soiling and the extent of soil after laundering as follows[8,9]:

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

where R is the reflectance (measured at wavelength 700 nm) and K and S are the absorption and scattering coefficients respectively.

$$\text{Degree of soiling (DS)} = (K/S)_{su} - (K/S)_{uu}$$

$$\text{Percentage of soil removal} = \frac{(K/S)_{su} - (K/S)_{sw}}{(K/S)_{su} - (K/S)_{uu}} \times 100$$

where $(K/S)_{uu}$ = (K/S) value for unsoiled unwashed sample; $(K/S)_{su}$ = (K/S) value for soiled unwashed sample; and $(K/S)_{sw}$ = (K/S) value for soiled washed sample.

Crease Recovery

A Wrinkle Recovery Tester, T. J. Edwards Inc., U.S.A., was used for crease recovery measurements throughout the present work.[10]

Tensile Strength

The tensile strength and elongation at break (warp and weft) were measured on the Tensile Strength Testing Machine type FMGW 500 (Veb Thuringer Industriewerk Rauenstein) at 25°C and 65% relative humidity. The results quoted are the means of 10 breaks for each warp and filling with a test length of 20 cm at a constant breaking time of 20 s.

Rating

Samples were evaluated for rating by comparison with the standard samples of "Wash'n Wear Standards" of AATCC distributed by T. J. Edwards, Inc., Boston, MA.[11]

Moisture Regain

The moisture regain was determined by the vacuum desiccator method with sodium nitrite to give 65% RH at 21 ± 1°C.

Water Imbibition

The water imbibition was determined by impregnating the conditioned samples (65% RH at 21 ± 1°C) in water for 15 min, and then centrifuged (4000 RPM) for 10 min. The weights of the samples before impregnation and after centrifuging were reported. Water imbibition (WI) can be calculated from the relation

$$\mathrm{WI} = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1 and W_2 are the weights of centrifuged and conditioned samples, respectively.

Drop Disappearance

The drop disappearance was measured by allowing a drop of water to fall on the sample and measuring the time needed for this drop to disappear.[12]

Water Transport

Evaluation of water transport, as a measure of wettability properties of samples under investigation, was carried out as per a reported method.[13]

RESULTS AND DISCUSSION

Aqueous Soiling

Samples before and after being modified according to the above-mentioned conditions were soiled with aqueous dispersions of carbon black, and the degree of soiling was calculated. The results obtained are set out in Tables I–IV. It is seen that, regardless of the conditions of partial carboxymethylation used, the

TABLE I
Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Conditions[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Aqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.50
13.2	0.313	86.84	0.525	88.98	0.495	84.27
18.92	0.322	87.34	0.521	90.57	0.462	84.94
33.88	0.311	88.30	0.477	93.31	0.461	86.67
43.12	0.312	80.50	0.495	93.41	0.469	85.15
60.72	0.305	78.94	0.404	92.41	0.472	87.00

[a] Condition A: the blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 25% NaOH solution and batching for 4 h.

latter imparts soil-resistant properties to the blend since the degree of soiling of the modified samples is subsequently lower than that of the control. However, the conditions of modification, and to some extent the carboxymethyl content, exert a considerable influence on the degree of soiling. By way of example, mention is made of the following: At nearly the same carboxymethyl content, samples prepared according to Condition D are much more resistant to aqueous soiling than samples prepared as per Condition A. Meanwhile, both samples A and D picked up less aqueous soil as compared with samples modified by applying Conditions B and C.

The effect of increasing the carboxymethyl content of the modified cotton of the blend on the degree of aqueous soiling depends upon the partial carboxymethylation conditions used (Tables I–IV). Under Condition A, when the carboxymethyl content in the blend (expressed as meq COOH/100 g blend) amounts to 13.2, a substantial reduction in the degree of soiling is observed. Further increment in the carboxymethyl content up to 60.72 meqs COOH/100 g blend had no significant effect on the degree of soiling, whereas with Conditions B and C there is a tendency that the degree of soiling increased slightly as the carboxy-

TABLE II
Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition B[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Aqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.5
2.04	0.321	86.61	0.648	87.87	0.548	81.19
9.07	0.340	89.99	0.642	87.87	0.521	81.29
13.09	0.356	90.13	0.582	88.03	0.535	83.83

[a] Condition B: The blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 5% NaOH solution and batching for 24 h.

TABLE III
Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition C[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Aqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.5
1.01	0.328	86.11	0.755	87.84	0.583	81.27
4.54	0.358	88.51	0.767	89.15	0.609	84.30
9.76	0.387	90.81	0.775	91.07	0.701	85.78

[a] Condition C: The blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 5% NaOH and heating at 100°C for 6 min.

methyl increased from 2.04 to 13.09 and from 1.01 to 9.7 meq COOH/100 g blend, respectively. A different situation is encountered with nonaqueous partial carboxymethylation, i.e., Condition D. With the latter, optimal soil resistance was obtained with sample having 19.26 meq COOH/100 g blend. Below or above this value, the resistance to aqueous soiling decreased (Table IV).

Based on the above, it is obvious that: (a) introduction of ionizable carboxymethyl groups in the cotton component of polyester/cotton blend reduces the ability of the blend to pick up aqueous soil regardless of the conditions of partial carboxymethylation; (b) the degree of soiling depends upon the physical changes, which are reflected on swellability and hydrophilicity of the blend, as will be shown later, accompanying the chemical modification; (c) loss in polyester content of the blend is determined by the conditions of the said modification as it will be shown later (Table X), but this loss seems to play no significant role in the susceptibility of the blend to aqueous soiling; (d) the onset of carboxymethyl content on the degree of soiling is governed by the conditions of partial carboxymethylation; and (e) soiling essentially depends upon changes occuring on the surface of the fibers of the blend fabric.

Table I–IV show the effeect of treating the polyester/cotton blend, before and after partial carboxymethylation under different conditions, with DMDEU in

TABLE IV
Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition D[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Aqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	0.531	88.5	0.660	85.4	0.712	80.5
5.15	0.446	91.64	0.726	88.14	0.646	89.24
19.26	0.185	95.36	0.426	94.12	0.285	98.84
63.61	0.223	89.35	0.577	92.12	0.504	89.58

[a] Condition D: The blend fabric was treated with different concentrations of monochloroacetic acid and NaOH in ethyl alcohol/toluene mixture at 65°C for 70 min.

presence of $MgCl_2 \cdot 6H_2O$. Evidently, the degree of soiling increased significantly after the treatment, i.e., after crosslinking. This is observed irrespective of the nature of the substrate used. However, still persisting with A (samples) and D (samples) of higher carboxymethyl content is the finding that the modified blend samples acquired a lower degree of soiling as compared with the crosslinked control sample. With samples prepared according to Conditions B and C, on the other hand, the resistance to aqueous soiling was comparable to, if not even lower than, that of the crosslinked control sample. This reflects the effect of the nature of the substrate on the affinity of the latter to aqueous soil. It is reasonable to assume that, though all modified cotton component in polyester/cotton blend samples bear carboxymethyl groups, yet the location, distribution, and frequency of these groups differ much, depending upon the conditions used. The polyester component in the blend is also variably affected by variation in the modification treatments. Current data (Tables I–IV) suggest that Conditions A and D bring about modified polyester/cotton blend samples with high resistance to soiling before and after crosslinking whereas the high resistance of the B and C samples was offset after crosslinking.

Incorporation of nonionic softener in the DMDEU finishing bath of the crosslinking treatment enhanced substantially the degree of soiling of the crosslinked control sample. With modified polyester/cotton blend samples, crosslinking in presence of nonionic softener had practically no effect on the degrees of soiling of these blends irrespective of partial carboxymethylation conditions used prior to crosslinking treatments (Tables I–IV). This implies that the adverse effect of softener by virtue of its high affinity to pick up the aqueous soil is prevailed over by repulsion occuring between the soil and the negatively charged modified blend surfaces. It is also likely that the softener reduces surface irregularities and lowers the surface area of the modified blend, thereby outweighing its own adverse effect.

Aqueous Soil Release

Table I shows that partial carboxymethylation of the cotton component in the polyester/cotton blend using Condition A exerts an adverse effect on the ease of aqueous soil removal provided that the carboxyl content is higher than ca. 40 meq COOH/100 g blend. Introduction of lower amounts of carboxymethyl groups in the cotton component of the blend has no significant effect on the aqueous soil-release properties of the blend.

Table II shows that less aqueous carbon black was retained on modified polyester/cotton blend having ca. 13 meq COOH/100 g blend as compared with the control (untreated blend) when the modification was carried out according to Condition B. Lower carboxyl content than the said value does not affect significantly the magnitude of soil removal. A similar situation is encountered with blend samples modified using either Condition C (Table III) or Condition D (Table IV).

A comparison between the soil-release characteristics of the modified blend samples prepared under different conditions would generally lead to the following order:

D (samples) > B (samples) > C (samples) > control (sample) > A (samples)

The order seems to be valid even at roughly the same carboxyl content of the modified blend. This reflects the changes in the physical structure of the blend occurring simultaneously with the partial carboxymethylation and the effect of such changes on ease of soil removal. Among these changes are (a) opening up the cotton structure, (b) increasing the swellability of the cotton fiber, (c) decreasing the polyester content in the blend, and (d) changing the surface of both cotton and polyester in the blend. Needless to say, these changes are governed by the conditions of modification. While Condition A is expected to have the most tremendous effect on (a), (b), and (d) due to the high alkali concentration used, Conditions B and C would have the least effect on these changes. Condition D, on the other hand, proved to be the most drastic as far as the loss in polyester content is concerned. The magnitude of entrapment of the soil particles between the fibers of the blend fabric would depend upon the ability of the fibers to swell. Hence, the inferiority of A (samples) suggests that softening and swelling of these samples during laundering may be a complicating factor that masks the effect of electrostatic repulsion.

Treatment of the control (untreated polyester/cotton blend) with DMDEU and $MgCl_2 \cdot 6H_2O$ as a crosslinking formulation reduces the ability of the blend to release the soil. The opposite holds true for the modified samples (Tables I–IV). The decreased soil removal found with the control could be attributed to the fact that crosslinking increases the hydrophobic nature of the cotton component in the blend while decreasing that of polyester. However, a balance between hydrophobicity and hydrophilicity does not seem to be achieved in this way. The imparted hydrophilicity to polyester may not be enough to counterbalance the hydrophobicity conferred on cotton or vice versa. Crosslinking of the control is likely to increase the energy of the fabric–water interface and reduce the energy of the fabric–soil interface, thereby adversely affecting the soil-release characteristics of the blend.

The enhancement of ease of soil removal by crosslinking (in absence of softener) of the partially carboxymethylated blend samples suggests that crosslinking brings about a good balance between hydrophobicity and hydrophilicity in the blend. Hence, during laundering, hydrophilicity and hydrophobicity would be expected to affect fiber–water interfacial energy and soil–fiber interfacial energy. It has been reported[14] that any modification or treatment which increases the energy of the fabric–water interface and reduces the energy of the fabric–soil interface would have an adverse effect on the soil release properties of the fiber. Partial carboxymethylation of the cottom component in the polyester/cotton blend prior to crosslinking apparently decreases the affinity of the blend to the soil while increasing the affinity to water. As a result, besides assessing the modified blend to swell in the aqueous wash medium and to mechanically force away the soil from fiber surface and interstices, the pendent carboxymethyl groups facilitates the diffusion of water into the blend interior and consequently assists in soil removal from the hydrated interface between the soil and the crosslinked fabric.

The data (Tables I–IV) further indicate that the ease of soil removal of the modified blend samples after crosslinking does not follow the order given above. Crosslinking indeed masks the differences in soil removal by imparting a good balance of hydrophilicity and hydrophobicity. Thus the small differences in percent soil removal observed with A (samples), B (samples), C (samples), and D (samples) could be traced back to differences in hydrophilicity and hydrophobicity, the magnitude of which depends upon the nature of the substrate.

Addition of nonionic softener in the crosslinking formulation adversely affect the soil release characteristics, regardless of the substrate used (Tables I–IV). However, the modified blend samples still acquire high capability to release the soil as compared with the control, in full contrast with 100% cotton[2] and reflects the role of polyester.

The adverse effect of the nonionic softener on soil release properties may be explained, as previously reported,[2] as follows: Apart from its own soiling action another important function of the softener seems to be its tendency to pick up and retain the soil particles. The softener provides a soft fabric surface in which the soil particles get deeply embedded and are held tenaciously.

Nonaqueous Oily Soiling

Table V shows the soiling characteristics of partially carboxymethylated cotton prepared according to Condition A. It is seen that the ability of this modified blend to pick up nonaqueous oily soil is lower as compared with the control (untreated polyester/cotton blend). In addition, there is a tendency that the degree of soiling decreases as the carboxyl content of the blend increases up to ca. 34 meq COOH/100 g blend and then remains almost constant upon further increase in carboxyl content. This is rather in contrast with the soiling behavior of 100% cotton which was partially carboxymethylated under similar conditions.[2] The lower resistance of 100% cotton modified via partial carboxymethylation using Condition A was associated with opening the cellulose structure by the presence of carboxymethyl groups together with the increased accessibility accompanying the modification under this particular condition (Condition A). If this explanation is accepted, current data would suggest that association of polyester and cotton fibers in the blend fabric does restrict swelling of cotton fibers brought about by the opening up of the cotton structure and/or does increase its accessibility. They further suggest that the blend components become so intimately associated that accommodation of the oily soil in the blend becomes difficult.

Table VI shows that the degree of nonaqueous oily soiling of partially car-

TABLE V

Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition A[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Nonaqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.2	1.306	88.9	1.473	60.88
13.2	1.226	87.6	1.333	91.37	1.483	52.51
18.92	1.225	84.97	1.120	88.64	1.399	50.81
33.88	0.954	77.75	1.060	87.61	1.369	39.45
43.12	0.943	77.39	1.072	85.66	1.339	32.86
60.72	0.962	71.07	1.062	82.10	1.221	13.85

[a] Condition A: The blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 25% NaOH solution and batching for 4 h.

TABLE VI

Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition B[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Nonaqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.2	1.306	88.9	1.473	60.88
2.04	0.953	94.05	1.003	83.10	1.312	58.37
9.07	1.073	93.81	1.036	85.78	1.321	58.61
13.09	1.079	93.98	1.042	81.97	1.276	43.89

[a] Condition B: The blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 5% NaOH solution and batching for 24 h.

boxymethylated polyester/cotton blend prepared as per condition B is lower than that of the control. The same holds true for blend samples prepared using Condition C (Table VII) and Condition D (Table VIII). With all these samples (B, C, and D samples) there is also a general tendency that the improvement in

TABLE VII

Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition C[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Nonaqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in presence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.20	1.306	88.90	1.473	60.88
1.01	0.868	92.12	1.040	83.65	1.267	55.32
4.54	0.951	92.35	0.982	83.39	1.199	55.00
9.76	0.982	93.11	1.062	85.00	1.267	56.91

[a] Condition C: The blend fabric was padded with different concentrations of sodium monochloroacetate followed by padding with aqueous 5% NaOH and heating at 100°C for 6 min.

TABLE VIII

Effect of Partial Carboxymethylation of Cotton Component of Polyester/Cotton Blend Using Condition D[a] before and after Crosslinking with DMDEU (120 g/L) and $MgCl_2 \cdot 6H_2O$ (20 g/L) on Nonaqueous Soiling and Soil-Release Properties of Blend

Carboxyl content (meq COOH/100 g blend)	Before crosslinking		After crosslinking in absence of softener		After crosslinking in absence of softener	
	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal	Degree of soiling	% Soil removal
Untreated	1.306	87.20	1.306	88.90	1.473	60.88
5.15	0.979	93.00	0.963	89.41	1.159	67.42
19.26	1.262	90.53	0.890	90.86	1.080	89.54
63.61	1.267	83.49	1.084	77.37	1.043	69.01

[a] Condition D: The blend fabric was treated with different concentrations of monochloroacetic acid and NaOH in ethyl alcohol/toluene mixture at 65°C for 70 min.

oily soil resistance decreased by increasing carboxymethyl content of the blend. Indication of this is that it is not the magnitude of carboxymethyl content that decides the degree of soiling but rather the alteration in the blend component inevitably occurs during the partial carboxymethylation.

With the above in mind, it is probably correct to say that partial carboxymethylation of the cotton component of polyester/cotton blend fabric imparts soil resistance properties to the blend irrespective of the conditions of partial carboxymethylation used within the range examined. However, the conditions of partial carboxymethylation determine the degree of oily soiling rather than the carboxymethyl content of the blend. For example, the degree of soiling of ca. 0.95 would be achieved at carboxymethyl content of 33.88, 2.04, 4.54, and 5.15 meq COOH/100 g blend brought about by using Conditions A, B, C, and D, respectively. At any event, besides introducing ionizable carboxyl groups, partial carboxymethylation of the cotton component in the polyester/cotton blend seems to reduce (a) the interfiber and interyarn spaces, (b) the irregularities of the fiber surface, and (c) the crevices and pores. As a result, decreased oily soiling could be achieved.

Treatment of the control with DMDEU and $MgCl_2{\cdot}6H_2O$ in absence of the nonionic softener leaves the susceptibility of the blend to nonaqueous oily soiling intact. Different situation is encountered with the modified blend samples (Tables V–VIII). Partial carboxymethylation of the cotton component in the blend using Conditions A, B, and C followed by crosslinking in absence of softener enhances the ability of the modified blend to pick up nonaqueous oily soil. However, the degree of soiling of these modified substrates after crosslinking is still lower as compared with the crosslinked control. On the other hand, crosslinking in absence of softener of blend samples modified according to Condition D decreases the susceptibility of these particular samples to nonaqueous oily soiling.

Crosslinking of the control and the modified blend samples in presence of the softener increased the ability of these samples to pick up nonaqueous carbon black dispersion (Tables V–VIII). This indicates that presence of softener in the crosslinking formulation favors soiling with nonaqueous carbon black dispersion. However, the degree of soiling of the blend samples which have been partially carboxymethylated prior to crosslinking in presence of softener differs substantially from that of the control. In this regard, the resistance to nonaqueous oily soil follows the order

D (samples) > C (samples) > B (samples) > A (samples) > control (samples)

The above order is valid even at roughly the same level of carboxymethyl content a point which again substantiates the argument that alteration of the blend structure occurring during partial carboxymethylation of the blend fabric affects the susceptibility of the fabric to soiling. This is the case with respect to aqueous soil and nonaqueous oily soil. Nevertheless, the onset of this effect varies considerably since, as previously indicated, a completely different situation was observed when aqueous soil was used. Furthermore, for a given substrate, the magnitude of soiling is higher in case of nonaqueous oily soil than the aqueous soil, reflecting the effect of medium of soiling on the degree of soiling. In short, partial carboxymethylation of cotton component of polyester/cotton blend fabric variably affects the amount of soil picked up from dispersion of carbon black, depending upon the changes in the physical structure of the blend occurring concurrently with introduction of carboxymethyl groups in the cotton component as well as upon the medium of soiling (whether aqueous soil or nonaqueous oily soil). Moreover, the effect of the modification by partial carboxymethylation on soiling characteristics of the blend still persists even after crosslinking in presence and absence of nonionic softener.

Nonaqueous Oily Soil Release

Table V shows that samples modified using Condition A retain more or less equal soil as the control at a carboxy methyl content, expressed as carboxyl groups, of 13.2 meq COOH/100 g blend. Further increase in the carboxyl content decreases the soil release properties of the blend; the percent soil removal falls substantially as the carboxyl content increases. Taking into consideration the effect of the highly concentrated sodium hydroxide used (25%) in Condition A on (a) the fine structure of cotton which entails increased accessibility, (b) the polyester context in the blend which is reduced as will be shown (Table X), and (c) the carboxymethyl content which is relatively high, it is possible to say that during laundering the softening and swelling of the modified cotton component and the thinned-down polyester component of the blend may be a complicating factor that masks the effect of electrostatic repulsion. Furthermore, the state of aggregation of the carbon black in the modified blend samples, particularly those acquiring high carboxyl content, may differ considerably from the control. It is reasonable that the particles of carbon black associate to form large aggregate lattices in these modified samples by virtue of their greater accessibility and swellability. The large aggregates so formed will be entrapped between the swollen fibers of the blend fabric and become difficult to remove. Indeed, the results obtained with similarly modified blend samples but under Conditions B, C, and D substantiate this (Tables VI, VII, and VIII).

Table VII shows that the blend samples modified according to Condition B acquire better soil release properties than the control sample, irrespective of their carboxyl content. The latter has practically no effect on the percent soil removal. A similar situation is encountered with blend samples modified using Condition C (Table VII) and Condition D (Table VIII) except that with the latter condition the ease of soil removal tends to decrease at higher carboxyl content (63.61 meq COOH/100 g blend). Since Conditions B and C are not expected to cause profound changes in either the fine physical structure of the cotton component or in the polyester content of the blend due to low sodium hydroxide concentration (5%) used, it is logical that samples modified under these two conditions do not provide an ideal resting place (gel-swollen environment) for the soil as in case of samples modified using Condition A.

Samples modified according to Condition D show improved soil release properties provided that their carboxyl content is low. Increasing the carboxyl content to a considerable extent decreases the soil release characteristics of the blend and, indeed, samples having 63.61 meq COOH/100 g blend shows lower percent soil removal than the control sample (Table VIII). Although Condition D involves partial carboxymethylation in nonaqueous medium to allow surface modification; yet, as will be shown (Table X), this condition reduces the polyester content of the blend substantially. The introduction of considerable amounts of carboxymethyl groups in the cotton component together with decreasing the polyester content of the blend seem to provide a good resting place for the soil on the blend fabric.

Based on the above, it is obvious that introduction of carboxymethyl groups in the cotton component in polyester/cotton blend imparts soil release characteristics to the blend provided that (a) the condition of partial carboxymethylation is not accompanied by profound changes in either the fine physical structure of the cotton component or in the polyester content of the blend and (b) the carboxymethyl content should not be so high; increasing the carboxymethyl content is meaningless and may lead to an adverse effect. It is also understandable that the anionic nature of the partially carboxymethylated cotton component in the blend during washing helps in repelling the negatively charged soil particles from the blend surface. Furthermore, a reduction in the interfacial tension at the oil–water interface assists in rolling up of the oily soil and its subsequent removal. This state of affairs can be turned to the opposite if the electrostatic repulsion is masked through creation of soft and swollen environment by significantly increasing the carboxymethyl content, decreasing the polyester content, and/or increasing the accessibility of the cotton component of the blend.

When the blend samples modified using Condition A was treated with the crosslinking formulation containing DMDEU and $MgCl_2 \cdot 6H_2O$, their soil release characteristics improved substantially. This is observed regardless of the carboxyl content of the sample. Similar treatment slightly improves the soil release properties of the control (Table V). However, modified samples having carboxyl content of ca. 34 meq COOH/100 g blend or more are still the most difficult samples to release the soil.

Incorporation of nonionic softener in the crosslinking formulation reduces the ease of soil release properties of the modified and the control samples (Table V). Nevertheless, the decrements in soil release properties are much higher with the modified samples than with the control. Furthermore, the decrease in percent soil removal is dependent upon the carboxyl content of the modified sample; the higher the carboxyl content, the greater the decrease in percent soil removal, opposite to hundred percent cotton.[2] The softener seems to accentuate the soft and swollen environment inside the blend produced by the presence of carboxymethyl groups, leading not only to ceasing electrostatic repulsion but also to provision of a good host to which the soil aggregates are intimately associated and are difficult to wash.

Table VI shows that the effect of crosslinking in the absence of softener of samples modified using Condition B is to decrease considerably the soil release properties of the blend. The addition of softener to the crosslinking formulation causes further significant reduction in the ease of soil removal. The same holds true for samples modified using Condition C (Table VII).

With samples modified using Condition D (Table VIII), on the other hand, crosslinking in the absence of softener decreases the soil-release properties of samples having 5.15 meq COOH/100 g blend and leaves those of sample having 19.26 meq COOH/100 g blend practically unaltered. The soil-release properties of sample having 63.61 meq COOH/100 g blend decreases significantly after crosslinking. Carrying the latter in presence of nonionic softener reduces the ease of soil removal of all samples except that having 19.26 meq COOH/100 g

TABLE IX

Effect of Partial Carboxymethylation on Some Properties of Polyester/Cotton Blend before and after Crosslinking[a]

Condition of partial carboxy methylation	Carboxyl content	Rating	Drop dis-appearance (s)	Water transport (s)	Water imbibition (%)	Moisture regain (%)	Crease recovery (°)	Tensile strength (kg)		Elongation at break (%)	
							W + F	W	F	W	F
None	—	(3)	(5)	(15)	(11)	(3)	(257)	(59	47)	(11.9	26)
		4.5	7	10	9.8	2.17	310	56	43	8.5	19.5
A	48.1	(2)	(22)	(114)	(20.1)	(4.5)	(230)	(57.5	43)	(11.9	20)
		5	30	300	14.6	4.4	291	48	36.6	21	34
A	23.9	(2)	(20)	(118)	(18.5)	(4.06)	(234)	(61	44)	(18	26.5)
		5	20	295	13.1	4	281	50	35	20.5	30
A	10.3	(1.7)	(>120)	(130)	(17.5)	(3.52)	(237)	(60.5	42)	(15.5	27)
		5	15	161	9.6	3.37	282	54	38	42	32.5
B	9.9	(1.7)	(>120)	(73)	(15.8)	(3.5)	(239)	(65	42)	(15	27)
		5	16	175	8.7	3.8	284	54	36.7	22	35
C	15.9	(2)	(>120)	(65)	(16.2)	(3.67)	(232)	(63.5	41)	(15.5	30)
		5	16	175	8.8	3.19	280	53	39	21.5	37.5
C	8.05	(2)	(>120)	(66)	(15.5)	(3.41)	(238)	63	43)	(16.5	28)
		5	16	177	8.7	2.9	283	54	37	22.5	36.5
D	5.0	(2.7)	(>120)	(10)	(13)	(3.2)	—	—		—	
		5	17	—	9.0	2.88					
D	19.26	(2)	(>120)	(16)	(12)	(3.0)	—	—		—	
		5	20	—	10	3.0					
D	63.61	(1.5)	(120)	(191)	(17)	(5.5)	—	—		—	
		5	30	—	11.5	4.5					

[a] Data in parentheses represent samples before crosslinking.

TABLE X
Effect of Conditions of Partial Carboxymethylation on Polyester Content and Carboxymethyl Content of Polyester/Cotton Blend Fabric[a]

Condition A		Condition B		Condition C		Condition D	
Carboxyl content	Polyester content (%)	Carboxyl content	Polyester content (%)	Carboxyl content	Polyester content (%)	Carboxyl content	Polyester content (%)
Untreated	49.7	Untreated	49.7	Untreated	49.7	Untreated	49.7
13.2	47.3	2.04	49.2	1.01	49.2	15.15	45.1
18.9	44.3	9.07	49.1	4.54	49.6	19.26	39.6
33.88	43.7	13.09	49.0	9.76	48.7	63.61	37.74
43.12	43.6						
60.72	43.4						

[a] Carboxymethyl groups are expressed in meq COOH/100 g blend.

blend. This particular sample seems to acquire a good balance between hydrophilicity and oleophobicity under the laundering condition. That is, the energy of the blend–oil interface is high while that of blend–water interface is low with respect to this sample after crosslinking. If this is accepted, easier soil removal would be expected because the particulate soil has been reported[15] to be embedded in a sheath of oil spread over the fiber surface.

Effect of Partial Carboxymethylation on Some Properties of Polyester/ Cotton Blend before and after Crosslinking

Table IX shows that partial carboxymethylation of the cotton component of polyester/cotton blend prior to crosslinking causes: (a) a striking decrease in water transport as well as in the ability of a drop of water to disappear irrespective of the conditions of partial carboxymethylation, (b) substantial enhancement in water imbibibition and moisture regain, both being dependent upon the conditions of carboxymethylation as well as carboxyl content, (c) a decrease in crease recovery, and (d) marginal improvement in tensile strength and significant enhancement in elongation at break.

The enhancement in water imbibition and moisture regain could be ascribed to the presence of carboxymethyl groups and factors associated with the modification such as the loss in polyester content and increase in cotton cellulose accessibility. The decrease in ability of the modified blend to transport water or for a drop of water to disappear on it suggests that thinning down of the polyester component under the influence of NaOH during the modificatioin process results in hydrolyzed products which are intimately associated particularly with the cotton component. As a consequence of this, the capillary rise involved in water transport as well as the sorption process involved in drop disappearance decrease. It may be argued that this is in contradiction with the reasons given for the increased moisture regain and water imbibition. However, the sufficient time allowed for water to diffuse in the case of water imbibition and moisture regain invalidate such a contradiction.

The decrease in crease recovery brought about by partial carboxymethylation of polyester/cotton blend fabric could be traced back to the decrease in polyester content of the blend. As sown below (Table X), this modification causes a considerable loss in polyester content. That no decrease in tensile strength despite the loss in polyester content is observed is rather interesting. It seems that this loss is outweighed by the significant enhancement in elongation at break of the cotton component caused by the modification treatment in which no tension was applied. That is, the elongation at break of the cotton component becomes close to that of the polyester component, and, as a result, the contributioin of the modified cotton in the tensile strength of the blend is larger as compared with the corresponding unmodified cotton component of the blend.

Table IX shows also that changes in the aforementioned properties by partial carboxymethylation of the blend still persist after the crosslinking treatment. Furthermore, the high level of wash–wear rating and crease recovery found with the modified blend are not accompanied by severe losses in strength properties. Hence, by proper selection of partial carboxymethylation conditions, it is possible to produce durable press polyester/cotton blend with high level of soil resistance and soil release characteristics besides other properties required for comfort without sacrificing much of the strength properties.

Table X shows the dependence of the polyester content of the blend on the conditions of partial carboxymethylation. It is seen that Condition D brings about the highest loss in polyester content while Condition B, the least. The polyester content follows the order:

$$\text{Condition B} > \text{Condition C} > \text{Condition A} > \text{Condition D}$$

This order is even valid at equal carboxymethyl content, reflecting the conditions of partial carboxymethylation on thinning down the polyester component via alkaline hydrolysis.

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