Effect of Structural Changes of Cotton by Acid Hydrolysis and Crosslinking on Soiling and Soil Release

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Synopsis

The effect of acid hydrolysis (0.5N HCl at 60°C for 5–90 min) on the soiling and soil release properties of cotton fabric before and after crosslinking was investigated. The effect of acid hydrolysis of crosslinked cotton under similar conditions on the same properties was also undertaken. Crosslinking with and without nonionic softener was carried out using dimethylol dihydroxyethlene urea and magnesium chloide hexahydrate as a catalyst. Aqueous and non-aqueous oily dispersions of carbon black were used for soiling. Results of these studies disclosed that acid hydrolysis prior to crosslinking imparted aqueous and oily soil resistance to the cotton, particularly during the very initial stages of hydrolysis treatment. Crosslinking of cotton and acid-treated cottons in the absence of softener accentuated soil resistance. The opposite holds true for crosslinking in the presence of softener. Short acid treatment of cotton before and after crosslinking decreased the ability of cotton to release the aqueous and oily soils. On the other hand, acid hydrolysis of crosslinked cotton improved aqueous and non-aqueous soil-resistance provided that the duration did not exceed 30 min. Hydrolysis accentuated also the ease of oily soil removal, but aqueous soil release was adversely affected. The results were interpreted in terms of changes in the physical and chemical structures of cotton and crosslinked cottons brought about by acid hydrolysis.

INTRODUCTION

The effect of chemical and physical characteristics of the fabric surface on soiling and soil release has been studied, but literatures dealing with this contain mostly conflicting reports.[1-7] Recently we have reported on the effects of various chemical modifications of and inclusion of different polymeric additives in cotton and polyester/cotton blend fabrics on soiling and soil release properties before and after these fabrics were given durable press (crosslinking) teatments.[8-32] Results of these studies indicated that soiling and soil release are governed by the chemical characteristics of the introduced groups, polymer, or copolymer in the molecular structure of the fibers; these characteristics determine the affinity of the soil for the modified fibers. Physical changes occuring during the chemical modification of fibers exerts also a significant influence on the degree of soiling and ease of soil removal. The nature of additive compounds as well as softener incorporated in the crosslinking formulation and their mode of interaction with the fibers during the crosslinking treatments alter soiling and soil

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release characteristics of the finished fabrics. The same holds true for media of soiling and the presence of oil therein.

This work was undertaken with a view of studying the effect of changes in the physical and chemical structure of cotton fabric brought about by acid hydrolysis on the soiling and soil release characteristics of the fabric before and after crosslinking treatments. The work was further extended to include investigation concerning the effect of acid hydrolysis of crosslinked cottons on the soiling and soil release.

EXPERIMENTAL

Material

Mill-scoured and bleached plain weave (23 picks × 23 ends/cm) cotton fabric was used throughout this investigation.

Reagents

Hydrochloric acid was of laboratory grade chemicals. Dimethylol dihydroxyethylene urea (DMDEU) was used as the crosslinking agent. This was supplied by BASF, West Germay, under the commercial mame Fixapret CPA. Velustrol PA supplied by Hoechst, West Germany, was used as the nonionic softener.

Acid Hydrolysis Treatments

Samples of cotton fabrics as well as crosslinked cotton were steeped in $0.5N$ hydrochloric acid at a temperature of 60°C for different periods of time, ranging from 5 to 90 min, keeping the material-to-liquor ratio of 1:10. Samples after acid hydrolysis were washed repeatedly with distilled water until free from acid and dried in air at room temperature.

Crosslnking Treatments

Unless otherwise stated, crossliking 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. 80%. At this end the fabric was stretched back to its original dimensions on pin frames for drying, 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.

Analysis and Testing

Copper number[33] and nitrogen content[34] were determined according to reported methods. Crease recovery was measured using crease recovery apparatus type FF- 07 (Metrimpex). Preparation of aqueous and nonaqueous oily soils and the method of soiling and laundering as well as soil and soil removal measurements were detailed in previous reports.[14,15]

RESULTS AND DISCUSSIONS

Acid Hydrolysis of Cotton Prior to Crosslinking

Copper Number

The effect of hydrochloric acid acid treatment on the reducing properties of cotton fabric, expressed as copper number, is shown in Table I. Obviously, the copper number increases significantly by prolonging the duration of acid treatment. This is in full agreement with previous work[35] which ascribed this to liberation of more reducing end groups occuring as a consequence of hydrolytic scission of the cellulose chains of cotton.

Aqueous Soiling

Table I shows the degree of aqueous soiling for the acid-treated and untreated cotton samples. It is evident that the acid treatment reduces the susceptibility of the cotton fabric to aqueous soiling, though there is a tendency for the degree of soiling to increase by increasing the duration of acid treatment. That is, the highest aqueous soil resistance is achieved under the influence of the very initial acid attack (during the first 5 min). Since the initial acid attack takes place almost exclusively on the surface of the fiber, current data would suggest that aqueous soiling is a surface phenomenon. It seems likely that, during the initial acid attack, the most accessible portion of cotton cellulose is removed and, as a result, the amenability of the cotton fabric to pick up the aqueous soil decreased.

Crosslinking without softener of cotton cellulose before and after acid treatment augments the ability of cotton and acid-treated cotton to pick up the aqueous soil (Table I). However, the degree of soiling of acid-treated cotton is still much lower as compared to cotton. A different situation is encountered when crosslinking was performed in the presence of a nonionic softener. The degrees of soiling of the acid-treated cotton samples are sig-

TABLE I
Effect of Acid Hydrolysis of Cotton Fabric on the Degree of Aqueous Soiling and Soil Release before and after Crosslinking[a]

Duration of acid treatment (min)	Copper no.	Before crosslinking		After crosslinking in the absence of softener		After crosslinking in the presence of softener	
		Degree of soiling	% soil removal	Degree of soiling	% soil removal	Degree of soiling	% soil removal
0	0.039	0.411	87.5	0.520	94.5	0.510	86.6
5	0.222	0.313	79.0	0.503	87.6	0.595	86.4
15	0.288	0.321	78.9	0.464	91.3	0.658	84.1
30	0.405	0.336	78.0	0.481	92.0	0.642	84.9
60	0.536	0.342	79.1	0.449	93.2	0.667	85.0
90	0.614	0.354	79.4	0.433	94.4	0.684	86.2

[a][HCl], 0.5 N; temperature, 60°C; material:liquor ratio, 1:10. Crosslinking formulation: [DMDEU], 120 g/L; [$MgCl_2 \cdot 6H_2O$], 20 g/L; [softener], 7.5 g/L.

nificantly higher than their corresponding cotton samples. Furthermore, the problem of soiling is aggravated by prolonging the duration of acid treatment. This suggests that inclusion of nonionic softener in crosslinked cotton containing aldehydic groups reduces, to a large extent, the resistance of the finished fabric to aqueous soiling. Presence of aldehydic groups together with the nonionic softener in crosslinked cotton seems to accentuate the affinity of the latter to aqueous soiling.

Aqueous Soil Removal

Table I shows the effect of acid treatment on the soil release characteristics of cotton fabric. Obviously, a 5-min treatment reduces the ability of cotton to release the aqueous soil. Further prolongation of acid treatment leaves the soil release characheristics of cotton practically unaltered. This indicates that the soil release is governed by modification of the surface of the fabric since progressive attack of the acid by increasing the duration of the treatment would be expected to proceed beyond the fiber surfaces. As a consequence, no significant change in soil release properties of cotton is observed by increasing the duration of acid treatment.

The effect of crosslinking in the absence of softener on the aqueous soil release properties of cotton and acid treated cottons is shown in Table I. It is clear that crosslinking enhances significantly the ability of cotton to release the aqueous soil. The same holds true for acid-treated cotton samples. However, the following are of interest: Acid treatment of the cotton fabric for 5 min prior to crosslinking decreases significantly the ability of crosslinked cotton to release the aqueous soil. The percent soil removal of crosslinked cotton and acid-pretreated-crosslinked cotton amounts to 94.5% and 87.6%, respectively. Increasing the time of acid pretreatment from 5 min to 90 min is accompanied by progressive increment in percent soil removal, and, indeed, fabric sample pretreated with the acid for 90 min followed by crosslinking possesses an almost equal percent soil removal to the crosslinked cotton sample.

The above can be explained if one considers the onset of acid treatment on cotton cellulose. Acid treatment causes degradation of the cotton via creation of aldehydic groups along the cellulose chain molecules, as evidenced by the increase in copper number previously discussed as well as removal of accessible regions, as reported elsewhere.[36] Aldehydic groups help establish a sort of interaction between the soil and the fiber, thereby making soil removal difficult.[37] Against this is the removal of accessible regions since they can provide resting places for the soil and accommodate a large aggregation of soil particles which are difficult to remove. Current data suggest that progressive removal of the accessible regions by increasing the time of acid treatment prevails over the influence of aldehydic groups, thus leading to improvement in ease of soil removal.

Incorporation of monionic softener in the crosslinking formulation impairs the aqueous soil release properties of the crosslinked cotton (Table I). A similar situation is encountered with the acid-treated cotton samples when crosslinked under similar conditions. However, the effects of changes in the physical and chemical properties of cotton brought about by increasing the duration of acid treatment are not significant as in case of crosslinking without softener. The latter seems to mask the effects of these changes.

Nonaqueous Oily Soiling

Table II shows the effect of acid treatment of cotton for different periods of time on the succeptibility of cotton to nonaqueous oily soiling. It is apparent that acid-treated samples are more resistant to the nonaqueous oily soiling as compared to the untreated cotton sample. Moreover, the improvement in oily soil resistance of cotton brought about by acid treatment is dependent upon the extent of hydrolysis. Samples treated with hydrochloric acid for up to 15 min acquire higher oily soil resistance than the untreated cotton sample. No further significant improvement in the oily soil resistance of cotton could be achieved by allowing the acid treatment to proceed for more than 15 min. Since the extent of hydrolysis, as measured by the copper number, increases by increasing the time of acid treatment, the insignificant differences in oily soil resistance properties between samples treated with the acid for shorter and longer periods of time indicate that oily soiling is a surface phenomenon. This is rather in accordance with previous studies[37] dealing with oxidation of cotton with sodium hypochlorite.

Treatment of cotton and acid-treated cotton samples with DMDEU in presence of $MgCl_2 \cdot 6HO_2$ brought about crosslinked cottons which acquire lower degree of oily soiling (Table II). That is, crosslinking imparts a certain degree of oily soil resistance to both cotton and acid-treated cotton samples. However, the imparted resistance of the latter is more significant than the former. There is even a tendency for the resistance to oily soiling to increase by increasing the duration of acid treatment.

Incorporation of nonionic softener in the crosslinking formulation enhances the susceptibility of the cotton and acid-treated cotton samples to nonaqueous oily soiling. However, the situation is more aggravated with the acid-treated cotton samples to nonaqueous oily soiling. However, the situation is more aggravated with the acid-treated cotton samples (Table II). An indication of this is that the combined effect of aldehydic groups

TABLE II
Effect of Acid Treatment of Cotton Fabric on the Degree of Nonaqueous Oily Soiling and Soil-Release Properties before and after Crosslinking[a]

Duration of acid treatment (min)	Copper no.	Before crosslinking		After crosslinking in the absence of softener		After crosslinking in the presence of softener	
		Degree of soiling	% soil removal	Degree of soiling	% soil removal	Degree of soiling	% soil removal
0	0.039	0.885	97.9	0.760	97.5	0.970	64.5
5	0.222	0.764	94.2	0.620	97.4	1.014	63.9
15	0.288	0.750	95.1	0.602	97.5	1.096	63.8
30	0.401	0.755	96.8	0.583	97.5	1.075	63.7
60	0.536	0.755	96.8	0.570	97.7	1.119	63.7
90	0.614	0.745	97.0	0.562	97.7	1.170	64.0

[a] [HC1], 0.5 N; temperature, 60°C; material:liquor ratio, 1:10. Crosslinking formulation: [DMDEU], 120 g/L; [$MgCl_2 \cdot 6H_2$], 20 g/L; [softener], 7.5 g/L.

and the nonionic softener is to accentuate the affinity of cotton to nonaqueous oily soiling.

Nonaqueous Oily Soil Removal

Table II shows the effect of acid treatment on the nonaqueous oily soil release characteristics of cotton. It is clear that acid treatment of cotton reduces substantially the ease of nonaqueous oily soil removal, particularly during the initial stages of acid treatment. In other words, the percent soil removal is considerably lower with samples treated with the acid for shorter than for longer periods of time. If one considers the adverse effect of aldehydic groups created along the cellulose chain molecules on one hand and the effect of partial removal of the accessible regions of cotton cellulose on the other hand on the ease of soil removal, it is obvious that the relatively higher removal of the accessible regions of cotton cellulous is responsible for the relatively high percent oily soil removal observed with samples treated for longer time with the acid. Removal of the most accessible regions of cotton cellulose results in cotton being less accessible and, therefore, less penetrable by the oily soil. In short, cotton samples treated with the acid for longer periods of time are not able to accomodate large aggregates of soil particles by virtue of their lower accessibility as compared to cotton samples treated with acid for short periods of time.

When cotton and acid-treated cotton samples were given crosslinking treatments with and without softener, the ease of nonaqueous oily soil release characteristics variable changed. However, the effect of extent of acid hydrolysis (duration of acid treatment) is offset by crosslinking. As is evident from Table II, no significant differences in percent oily soil removal are observed with respect to cotton and acid-treated cottons after crosslinking. Neverthless, the adverse effect of the nonionic softener on ease of oily soil removal is seen in cotton and acid-treated cotton samples. Apart from its soiling action, the softener provides an environment in which the oily soil can by favorably embedded.

Acid Hydrolysis of Crosslinked Cotton

Crease Recovery

Table III shows the effect of acid treatment on the crease recovery angle of crosslinked cotton. It is seen that the crease recovery decreases sharply after acid treatment for 5 min. Thereafter, no change in crease recovery could be observed by prolonging the time of hydrolysis up to 90 min. It seems likely that the effective crosslinks are hydrolyzed during the initial stages of acid treatment, and, as a result, cotton acquires the original crease recovery, i.e., the crease recovery of cotton before crosslinking. A similar situation is encountered when cotton crosslinked in the presence of nonionic softener was subjected to the same acid treatments.

TABLE III
Effect of Acid Treatment on Aqueous Soiling and Soil-Release Properties of Crosslinked Cotton[a]

Duration of acid treatment (min)	Crease recovery angle		N content (%)		Samples crosslinked in the absence of softener		Samples crosslinked in the presence of softener	
	Without softener	With softener	Without softener	With softener	Degree of soiling	% soil removal	Degree of soiling	% soil removal
Zero	280	285	1.668	1.591	0.520	94.8	0.51–	86.6
5	153	148	0.127	0.141	0.443	73.4	0.368	67.7
15	150	147	0.117	0.135	0.418	72.2	0.374	65.2
30	150	146	0.109	0.122	0.404	72.3	0.374	57.1
60	150	146	0.107	0.114	0.404	71.9	0.364	45.5
90	150	146	0.090	0.089	0.390	72.1	0.371	43.7

[a][HC1], 0.5 N; temperature, 60°C; material:liquor ratio, 1:10. Crosslinking formulation: [DMDEU], 120 g/L: [$MgC1_2 \cdot 6H_2$], 20 g/L; [softener], 7.5 g/L.

Nitrogen Content

Table III shows the effect of acid treatment on the nitrogen content of cotton crosslinked in the presence and absence of softener. Here, too, the nitrogen content decreases sharply after 5-min acid treatment. Residual nitrogen decreases marginally by increasing the duration of acid treatment within the range studied. This implies that acid treatment causes not only breakage of the crosslinks but also splitting off of the DMDEU reaction products.[38]

Aqueous Soiling

Table III shows the degree of aqueous soiling of cotton and acid-treated cotton samples. It is obvious that acid treatment of crosslinked cotton fabric imparts a certain degree of aqueous soil resistance to the fabric. Samples treated with hydrochloric acid for up to 15 min acquire higher soil resistance than crosslinked sample. No further improvement in the soil resistance of cotton could be achieved by allowing acid treatment of crosslinked cotton to proceed for more than 15 min. The same holds true when cotton crosslinked in the presence of nonionic softener was subjected to similar acid treatments but higher resistance to aqueous soiling could be achieved.

As already pointed out, acid treatment causes scission of effective crosslinks as well as almost complete removal of DMDEU reaction products. Besides this, acid treatment has been reported to bring about molecular degradation of cotton cellulose together with changes in its physical structure.[36] Since crosslinking of cotton cellulose, as shown in the foregoing section, has no adverse effect on aqueous soiling, it is logical to conclude that the imparted soil resistance to crosslinked by acid treatment is associated with changes in its physical structure. Apparently, partial removal of the most accessible regions of cotton cellulose as well as recrystallization during acid treatment are the essential features of such changes.

Aqueous Soil Removal

Table III shows the effect of acid treatment on the ease of aqueous soil removal of crosslinked cotton. It is apparent that the acid-treated samples have lower soil removal than the crosslinked cotton. Samples treated with hydrochloric acid for up to 15 in acquire lower soil removal than the crosslinked sample. No further change in the aqueous soil-release properties of acid-treated crosslinked cotton is observed by allowing the hydrolysis of crosslinked cotton to proceed for more than 15 min. A similar situation is encountered when cotton crosslinked in the presence of nonionic softener was subjected to identical acid treatment, but the reduction in ease of equeous soil removal continues to increase by incrasing duration of acid treatment.

The reduction in ease of aqueous soil removal of crosslinked cotton by acid treatment is indicative of surface modification of the cotton fibers occuring concurrently with removal of the DMDEU reaction products. It is likely that the acid-treated samples acquire higher affinity to the aqueous soil than the crosslinked cotton by virtue of the creation of aldehydic groups which strengthen the forces holding the soil within the fiber–fabric structure. In the case of samples crossliniked in the presence of nonionic softener the continuous reduction in ease of aqueous soil removal by increasing the duration of acid treatment implies that the acid succeeds in removing, almost, completely, the DMDEU reaction products without necessarily removing completely the nonionic softener.

Nonaqueous Oily Soiling

Table IV shows the effect of acid treatment on the degree of nonaqueous oily soiling of crosslinked cotton. Obviously, the acid-treated samples are more resistant to the nonaqueous oily soiling provided that the time of acid treatment did not exceed 30 min. Acid treatment of crosslinked cotton for 90 min produces a substrate with lower resistance to nonaqueous oily soiling than the crosslinked cotton. The same is the case when cotton crosslinked in presence of nonionic softener was given acid treatment but with the certainty that the resistance of acid-treated samples to the nonaqueous oily soiling is higher than the softener-containing crosslinked cotton (Tables II and IV).

Variation of the degree of nonaqueous oily soiling of the crosslinked cotton with duration of acid hydrolysis calls for the complexity of oily soiling and its dependence on the nature of the substrate. Almost complete removal of the DMDEU reaction products from cotton does not seem to account for this variation. It is rather the duel action of the acid on the DMDEU reaction products as well as on the physical and chemical structure of cotton cellulose. The affinity of the acid-modified samples to the nonaqueous oily soil determines the degree of soiling.

Nonaqueous Oily Soil Removal

Table IV shows the effect of acid treatment of crosslinked cotton on oily soil release characteristics. It is seen that appreciable enhancement in nonaqueous oily soil removal could be achieved by acid treatment of crosslinked cotton for 5 min. No further significant improvement in oily soil release properties could be ovserved by prolonging the time of acid treatment up to 90 min. Since acid treatment for 5 min causes scission of the crosslinks and removes almost completely the DMDEU reaction products as shown above, current data would suggest that these parameters are the essential cause for the enhancement in ease of nonaqueous oily soil release. This is also observed when cotton is crosslinked in the presence of a nonionic softener. However, with the latter crosslinked cotton, the acid treatment for up to 30 min favorably affects the ease of nonaqueous oily soil removal. This would suggest that removal of nonionic softener with the DMDEU reaction products is not necessarily occurring simultaneously. Increasing the duration of acid treatment helps in gradual removal of the nonionic softener, though most probably not completely.

TABLE IV

Effect of Acid Hydrolysis Treatment on Nonaqueous Oily Soiling and Oily Soil-Release Properties of Crosslinked Cotton[a]

Duration of acid treatment (min)	Crease recovery angle		N content (%)		Samples crosslinked in the absence of softener		Samples crosslinked in the presence of softener	
	Without softener	With softener	Without softener	With softener	Degree of soiling	% soil removal	Degree of soiling	% soil removal
0	280	285	1.668	1.591	0.760	97.5	0.970	64.5
5	153	148	1.270	0.141	0.650	98.6	0.678	69.5
15	150	147	1.117	0.135	0.710	98.1	0.705	70.3
30	150	146	1.109	0.122	0.740	98.8	0.742	77.3
60	150	146	0.107	0.114	0.755	98.1	0.753	77.9
90	150	146	0.090	0.083	0.770	98.6	0.768	77.8

[a][HC1], 0.5 N; temperature, 60°C; material:liquor ratio, 1:10. Crosslinking formulation: [DMDEU], 120 g/L; [$MgCl_2 \cdot 6H_2O$], 20 g/L; [softener], 7.5 g/L.

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