# Easy-Care Properties of Simultaneously Grafted and Crosslinked Cotton Fabrics

A. HEBEISH,[1,*] R. REFAI,[1] M. K. ZAHRAN,[2] and A. A. ALI[1]

[1]National Research Centre, Textile Research Division, Dokki, Cairo, and [2]Helwan University, Faculty of Science, Chemistry Department, Helwan, Cairo, Egypt

## SYNOPSIS

The concurrent grafting of acrylic acid (AA) and crosslinking of dimethyloldihydroxyethyleneurea (DMDHEU) with cotton fabric in the presence of ammonium persulfate $[(NH_4)_2S_2O_8)]$, magnesium chloride hexahydrate $(MgCl_2 \cdot 6H_2O)$, and ammonium chloride $(NH_4Cl)$ catalysts were studied. These salts were separately used or as a binary mixture of $(NH_4)_2S_2O_8/MgCl_2 \cdot 6H_2O$ or $(NH_4)_2S_2O_8/NH_4Cl$. The pad–dry–cure method was employed for the fabric treatment under a variety of conditions. The latter include the nature and kind of the single catalyst as well as pair-mixed catalysts, the concentrations of the catalyst and AA, and temperature and duration of curing. The effects of these conditions on the values of the carboxyl content and crease recovery angle (CRA) of the treated fabrics were evaluated. The tensile strength, elongation at break, dyeability, aqueous and nonaqueous oily soiling, and soil-release properties of the treated fabrics were also examined. Results obtained indicated that all treated fabrics have superior properties, except tensile strength and elongation at break, as compared with the untreated fabric (control). However, beside the AA-grafting and DMDHEU-crosslinking reactions, there are other types of reactions catalyzed by the salts used, viz., the addition reactions between AA molecules and the cellulosic hydroxyls as well as between AA and DMDHEU hydroxyls. The tentative mechanisms for these reactions are suggested. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Many reports have dealt with the improvements of the cotton fabric properties via either acrylic grafting[1-4] or N-methylol crosslinking[5-7] reactions. However, the conjunction of acrylic monomers together with N-methylol compounds to operate simultaneous grafting and crosslinking reactions with cellulose is limited.[8-11]

While most of the acrylics grafting improve the properties of cotton fabric such as affinity for basic dyes,[12] the tensile strength and elongation at break,[13] the resistance to aqueous soil and nonaqueous soiling, and ease of soil removal,[14,15] most of the N-methylol crosslinking agents bring about the opposite of these properties to the cotton fabric.[16-18] However, the fabrics crosslinked with this type im-

part a higher crease recovery angle (CRA) and smooth-dry performance.[19-21]

With the above in mind, concurrent acrylic grafting and N-methylol crosslinking with cotton cellulose using the pad–dry–cure method were studied in this work with a view to obtain cotton with improved performance properties. To achieve the goal, concurrent grafting and crosslinking were considered. Dimethyloldihydroxyethyleneurea (DMDHEU) was selected as the crosslinking agent and acrylic acid (AA), as the grafting agent, and ammonium persulfate $[(NH_4)_2S_2O_8]$, magnesium chloride hexahydrate $(MgCl_2 \cdot 6H_2O)$, and ammonium chloride $(NH_4Cl)$ as catalysts were used. Besides its catalytic effect, $[(NH_4)_2S_2O_8]$ initiates the AA-grafting reaction onto cotton fabric. All these salts accelerate the crosslinking reaction of DMDHEU with the cellulose chains. However, the results of this work reveal amazingly that these salts favor the addition reactions, to a limited extent, between AA molecules and cellulosic hydroxyls and, to a large extent, be-

HEBEISH ET AL.

tween AA molecules and DMDHEU as crosslinks and/or free molecules. The mechanisms of addition reactions, which can probably occur during the course of the fabric treatment, are also suggested.

## EXPERIMENTAL

### Cotton Fabric

Mill-scoured and bleached plain weave (23 picks × 23 ends/cm) cotton fabric was used throughout the present work. This fabric will be regarded as the untreated fabric control.

### Chemicals

The crosslinking agent used was Arkofix NG, based on 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), kindly supplied by Hoechst. Acrylic acid (AA), ammonium persulfate [$(NH_4)_2S_2O_8$], magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and ammonium chloride ($NH_4Cl$) were reagent grade.

### Fabric Treatment

This was carried out by the pad–dry–cure method. The cotton fabric was padded through two dips and two nips in a solution containing the DMDHEU, AA, and the catalyst to a wet pickup of ca. 80% on the weight of the fabric (owf). At this end, the fabric was stretched back to its original dimensions on a pin frame for drying and curing. Details of the conditions used are given in the text. The cured fabrics were then washed at 65°C in a small washing machine (Caloor 2000, France), using a solution containing 2 g/L of a detergent at a material-to-liquor ratio 1 : 100. Finally, the fabric was dried, conditioned, and examined for different properties.

### Interaction with Methylene Blue

The treated cotton fabric was dyed with an aqueous solution containing 2% methylene blue dye (C.I. basic blue 9) and 5% sodium sulfate. The dyeing bath temperature was raised to 100°C in 10 min and left at this temperature for another 15 min. The cotton fabric was then squeezed, washed with water, and treated in an aqueous bath containing a 2% wetting agent at 60°C for 30 min. The colored fabrics were rinsed with hot followed by cold tap water and left to dry at room temperature.

### Soils, Soiling, and Laundering Procedures

Preparation of the aqueous and nonaqueous oily soil as well as the procedures for soiling and laundering of the soiled samples were described in an earlier publication.[22]

### Testing and Analysis

The treated fabrics were evaluated using the following: The carboxyl content was determined by the alkalimetry method.[23] The dry crease recovery angles were measured using the iron recovery apparatus, type FF-07 (Metrimpex). The warp tensile strength and elongation at break were determined by the strip method according to ASTM procedures D-2256–66T. The color strength of the fabric samples dyed with methylene blue, expressed as $K/S$ (where $K$ and $S$ are the absorption and scattering coefficients, respectively), was measured and calculated according to a method described elsewhere.[24] The measurements of the degree of soiling and ease of soil removal were carried out using a Beckmann spectrophotometer Model 26 as described in detail in a previous publication.[22]

## RESULTS AND DISCUSSION

### Tentative Mechanisms

When AA is incorporated in the treating mix containing DMDHEU and a suitable catalyst, various reactions can occur simultaneously. These reactions are largely governed by the catalyst used. The ammonium persulfate, $(NH_4)_2S_2O_8$, used in this work whether alone or in adjunction with either $MgCl_2 \cdot 6H_2O$ or $NH_4Cl$ serves as an initiator for the AA-grafting reaction[25,26] and as an acidic catalyst for the DMDHEU-crosslinking reaction with the cotton cellulose.[27]

Surprisingly, it was observed that, in absence of the persulfate initiator, the use of either $MgCl_2 \cdot 6H_2O$ or, in particular, $NH_4Cl$ considerably increases the carboxyl content value of the AA–DMDHEU-treated cotton fabric. This suggests that these salts, viz., $MgCl_2 \cdot 6H_2O$ and $NH_4Cl$, may activate the carbon–carbon double bond of AA to undergo addition reactions with the cellulose and DMDHEU hydroxyl groups. A similar observation for the acid-initiated addition of a cellulosic hydroxyl group to the activated double bond of acrylic esters and amide has been reported earlier.[28]

Typical of the addition reaction that may occur between AA and the hydroxyl groups of DMDHEU

**Table I   Effect of Nature and Kind of Catalyst and Increased AA Concentration on the Carboxyl Content and CRA of AA–DMDHEU-treated Fabric**

| Concn of Acrylic Acid (g/L) | Without Catalyst | | $MgCl_2 \cdot 6H_2O$ (10 g/L) | | $(NH_4)_2S_2O_8$ (10 g/L) | | $NH_4Cl$ (8 g/L) | |
|---|---|---|---|---|---|---|---|---|
| | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) |
| 0 | 129 | 1.62 | 140 | 5.3 | 156 | 6.33 | 154 | 9.51 |
| 50 | 225 | 8.77 | 251 | 12.73 | 278 | 22.22 | 281 | 19.98 |
| 100 | 252 | 16.77 | 271 | 14.34 | 296 | 34.22 | 287 | 43.17 |
| 200 | 263 | 19.96 | 280 | 22.22 | 300 | 61.38 | 272 | 50.25 |

Untreated fabric (control): Carboxyl content (M.E./100 g cellulose) = 5.58. Dry crease recovery angles (w + f) = 122°. [DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min; curing, 160°C for 3 min.

and/or cellulose may be represented by the reaction mechanism suggested by eqs. (1)–(3):
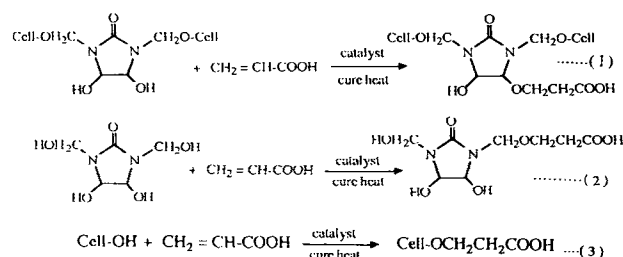


It was also observed that treatment of the cotton fabric with AA (100 g/L) in the absence of the catalyst brings about a fabric with a 7.93 meq —COOH group/100 g cellulose. This is against a 9.9, 11.99, and 18 meq —COOH group/100 g cellulose for fabrics similarly treated but in the presence of $NH_4Cl$ (8 g/L), $MgCl_2 \cdot 6H_2O$ (10 g/L), and $(NH_4)_2S_2O_8$ (10 g/L), respectively.

On the other hand, incorporation of DMDHEU in the pad solution would considerably increase the carboxyl content of the fabric treated under the same conditions by virtue of reactions (1) and (2). The product of reaction (3), i.e., carboxyethyl cellulose, would also act as a built-in catalyst for the cross-linking reaction of DMDHEU.[29] Besides, the ability of the reactant containing carboxylic and hydroxyl groups to undergo esterification reactions at the elevated temperatures of curing is also possible.

With the above in mind, experiments were designed to study the major factors affecting the properties of cotton fabric treated with the AA–DMDHEU system in the presence of $(NH_4)_2S_2O_8$ along with either $MgCl_2 \cdot 6H_2O$ or $NH_4Cl$.

## Reaction Conditions Affecting the Carboxyl Content and CRA of the Treated Fabrics

Table I shows the carboxyl content and CRA of AA–DMDHEU-treated fabrics when different concentrations of AA were used in the absence and in the presence of $(NH_4)_2S_2O_8$, $NH_4Cl$, or $MgCl_2 \cdot 6H_2O$. It was found, under the conditions cited in this table and in absence of the catalyst, that there is an increment in the values of CRA of the AA–DMDHEU-treated fabrics as the concentration of AA increases from 50 to 200 g/L. Incorporation of the catalyst $(NH_4)_2S_2O_8$, $NH_4Cl$, or $MgCl_2 \cdot 6H_2O$ in the treating mix causes further significant increment in both the carboxyl content and CRA values of the treated fabrics. These increments are greatly enlarged as the concentration of AA increases up to 200 g/L concentration; the increment follows the order

$$(NH_4)_2S_2O_8 > NH_4Cl > MgCl_2 \cdot 6H_2O$$

Table II shows the effect of $(NH_4)_2S_2O_8$ concentration on the carboxyl content and CRA of the fabric when treated with DMDHEU (100 g/L) and AA (50 and 100 g/L), dried at 80°C for 3 min, and cured at 160°C for 3 min. It is evident that as the concentration of $(NH_4)_2S_2O_8$ increases (within the studied range) both the carboxyl content and CRA values of the so-treated fabrics increase, regardless of the AA concentration used, but with the certainty that higher carboxyl and CRA values are obtained at a higher concentration of AA (i.e., 100 g/L).

Table III shows the effect of the $(NH_4)_2S_2O_8$ (5 g/L)/$NH_4Cl$ (4–8 g/L) and $(NH_4)_2S_2O_8$ (5 g/L)/ $MgCl_2 \cdot 6H_2O$ (4–10 g/L) mixtures on the carboxyl content and the CRA of fabrics treated with DMDHEU (100 g/L) and AA (50 and 100 g/L) using

**Table II   Effect of Ammonium Persulfate on the Carboxyl Content and Dry Crease Recovery Angle of AA–DMDHEU-treated Fabric**

| Concentration of Ammonium Persulfate (g/L) | Acrylic Acid (50 g/L) | | Acrylic Acid (100 g/L) | |
|---|---|---|---|---|
| | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) |
| 0 | 225 | 8.77 | 264 | 16.77 |
| 2.5 | 255 | 12.70 | 274 | 21.54 |
| 5.0 | 266 | 16.76 | 279 | 24.65 |
| 7.5 | 273 | 21.45 | 290 | 31.83 |
| 10.0 | 278 | 22.22 | 296 | 34.22 |

[DMDHEU], 100 g/L; pad–dry–cure method; drying, 80°C for 3 min; curing, 160°C for 3 min.

the pad–dry–cure method. Apparently, in such pair-mixed catalysis, increasing the concentration of $NH_4Cl$ (from 4 to 8 g/L) and $MgCl_2 \cdot 6H_2O$ (from 4 to 10 g/L) causes an increment in the values of the carboxyl content and CRA of the treated fabrics, irrespective of the AA concentration used. Furthermore, the catalytic efficiencies of the $(NH_4)_2S_2O_8/MgCl_2 \cdot 6H_2O$ and $(NH_4)_2S_2O_8/NH_4Cl$ mixtures are strongly amended at a higher AA concentration (i.e., 100 g/L). It is also observed (Table III) that the AA–DMDHEU-treated fabrics have lower values of carboxyl content and CRA in the absence than in the presence of the catalyst. The untreated fabric, of course, has the lowest values.

Table IV shows the influence of AA concentration and curing temperature on the carboxyl content and CRA of the fabric treated with DMDHEU and AA in the absence and in the presence of $(NH_4)_2S_2O_8$ alone or admixed with either $NH_4Cl$ or $MgCl_2 \cdot 6H_2O$. As compared to other conditions cited

in this table, the AA–DMDHEU-treated fabrics showed a higher carboxyl content and CRA values when the AA concentration was 100 g/L and the curing temperature was adjusted at 160°C. With the catalysts used under these conditions, the increments in the values of carboxyl content and CRA follow the sequence

$(NH_4)_2S_2O_8/NH_4Cl$

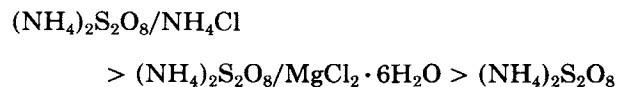$$> (NH_4)_2S_2O_8/MgCl_2 \cdot 6H_2O > (NH_4)_2S_2O_8$$

Table V shows the effect of curing temperature on the carboxyl content and CRAs of the fabrics treated with DMDHEU (100 g/L) and AA (50 and 100 g/L) in the presence of either the $(NH_4)_2S_2O_8$ (5 g/L)/$NH_4Cl$ (6 g/L) or $(NH_4)_2S_2O_8$ (5 g/L)/$MgCl_2 \cdot 6H_2O$ (6 g/L) catalyst mixture. The data of this table reveal that as the curing duration increases (within the studied range) the values of the carboxyl

**Table III   Influence of Pair-mixed Catalysts on the Carboxyl Content and CRA of AA–DMDHEU-treated Fabric**

| Concentration of $NH_4Cl$ or $MgCl_2 \cdot 6H_2O$ | Ammonium Persulfate (5 g/L) + $NH_4Cl$ | | | | Ammonium Persulfate (5 g/L) + $MgCl_2 \cdot 6H_2O$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Acrylic Acid (50 g/L) | | Acrylic Acid (100 g/L) | | Acrylic Acid (50 g/L) | | Acrylic Acid (100 g/L) | |
| | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) | CRA (Degree) | Carboxyl Content (M.E./100 g Cell) |
| 0 | 254 | 12.68 | 266 | 19.18 | 254 | 12.68 | 266 | 19.18 |
| 4 | 279 | 19.66 | 278 | 27.30 | 267 | 21.06 | 291 | 31.70 |
| 6 | 281 | 20.86 | 286 | 32.99 | 269 | 21.61 | 296 | 33.18 |
| 8 | 287 | 25.95 | 289 | 36.09 | 274 | 24.20 | 301 | 37.35 |
| 10 | — | — | — | — | 299 | 25.95 | 308 | 39.26 |

[DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min; curing, 140°C for 3 min.

**Table IV   Effect of Increased AA Concentration and Curing Temperature on the Carboxyl Content and CRA of AA–DMDHEU-treated Fabric**

| Acrylic Acid Concentration (g/L) | 140°C | | | | | | 160°C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ammonium Persulfate (5 g/L) | | Ammonium Persulfate (5 g/L) + MgCl₂·6H₂O (6 g/L) | | Ammonium Persulfate (5 g/L) + NH₄Cl (6 g/L) | | Ammonium Persulfate (5 g/L) | | Ammonium Persulfate (5 g/L) + MgCl₂·6H₂O (6 g/L) | | Ammonium Persulfate (5 g/L) + NH₄Cl (6 g/L) | |
| | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) | CRA (Deg) | Carboxyl Content (M.E./100 g Cell) |
| 0 | 239 | 6.35 | 201 | 7.41 | 255 | 9.5 | 263 | 7.40 | 272 | 9.43 | 281 | 15.73 |
| 50 | 254 | 12.68 | 268 | 21.45 | 281 | 20.83 | 269 | 16.65 | 284 | 25.69 | 300 | 32.07 |
| 100 | 266 | 19.18 | 296 | 34.18 | 286 | 29.80 | 280 | 24.13 | 295 | 38.94 | 308 | 45.45 |

[DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min; curing time, 3 min.

content and CRA of the so-treated fabrics are sequentially increased, irrespective of AA concentration and type of catalyst used. However, at any given curing condition, a higher concentration of AA brings about more increments in the values of the carboxyl content and CRA of the treated fabrics than does the lower concentration. Furthermore, comparing the efficiencies of $(NH_4)_2S_2O_8/NH_4Cl$ and $(NH_4)_2S_2O_8/MgCl_2 \cdot 6H_2O$ mixtures under the conditions cited in this table, it is seen that the former has a higher catalytic efficiency toward AA grafting and DMDHEU crosslinking as well as toward AA/DMDHEU and AA/cellulose addition reactions than does the latter.

## The Discussion

The increments in both the carboxyl content and CRA values of the fabrics treated with the AA/DMDHEU mixture in the absence of the catalyst reflects the ability of DMDHEU to crosslink cellulose chains in the presence of AA. Increasing the concentration of the latter increases the acidity of the pad solution and this, in turn, heightens the efficiency of the DMDHEU crosslinking reaction. Besides, under the influence of the elevated curing temperature applied, some of the AA molecules may penetrate and then polymerize within the fiber and some may react with the DMDHEU hydroxyls. Increasing the acidity of the treating solution by increasing the AA concentration may favor the AA/DMDHEU addition reaction. This may occur via the self-catalyzing effect of AA.

The presence of the catalyst, viz., $(NH_4)_2S_2O_8$, $NH_4Cl$, or $MgCl_2 \cdot 6H_2O$, in the AA–DMDHEU treating formulation would greatly accelerate the crosslinking addition as well as the grafting reactions with the cellulose. While $(NH_4)_2S_2O_8$ would be expected to enhance all these reactions via generation of more acidic moieties and free-radical species, $NH_4Cl$ or $MgCl_2 \cdot 6H_2O$ would enhance the addition and grafting reactions.

Each of these salts is an acidic or acid-liberating compound and this feature principally favors the crosslinking and addition; both are acid-catalyzed reactions. Accordingly, these reactions are progressively enhanced as the concentration of the catalyst increases whether alone (Table II) or in an admixture (Table III).

Moreover, the efficiencies of these catalysts in question are strongly related to the amount of AA as well as to the curing temperature, i.e., as the AA concentration and curing temperature increase, the catalyst efficiencies and, in turn, the extent of graft-

**Table V  Influence of Curing Duration on the Carboxyl Content and CRA of AA–DMDHEU-treated Fabric**

| Acrylic Acid Concn (g/L) | 120°C | | | | 140°C | | | | 160°C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3 min | | 5 min | | 3 min | | 5 min | | 1.5 min | | 3 min | | 5 min | |
| | CRA (Degree) | a | CRA (Degree) | a | CRA (Degree) | a | CRA (Degree) | a | CRA (Degree) | a | CRA (Degree) | a | CRA (Degree) | a |
| MgCl$_2$·6H$_2$O (6 g/L) + (NH$_4$)$_2$S$_2$O$_8$ (5 g/L)[b] | | | | | | | | | | | | | | |
| 50 | 255 | 6.09 | 265 | 10.16 | 269 | 21.61 | 281 | 19.12 | 287 | 18.18 | 284 | 25.14 | 298 | 30.42 |
| 100 | 261 | 15.23 | 279 | 17.23 | 296 | 33.18 | 297 | 29.45 | 290 | 37.63 | 295 | 38.94 | 302 | 42.47 |
| NH$_4$Cl (6 g/L) + (NH$_4$)$_2$S$_2$O$_8$ (5 g/L)[b] | | | | | | | | | | | | | | |
| 50 | 238 | 6.1 | 257 | 19.19 | 281 | 20.86 | 296 | 23.29 | 292 | 30.52 | 300 | 32.55 | 305 | 39.50 |
| 100 | 241 | 17.29 | 268 | 22.37 | 286 | 32.99 | 299 | 30.41 | 296 | 39.68 | 308 | 45.65 | 311 | 46.39 |

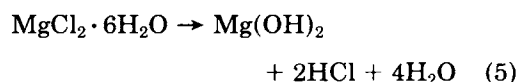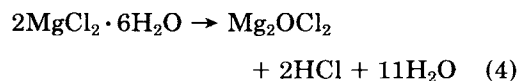[DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min.
a Carboxyl content, M.E./100 g cell.
b Pair-mixed catalysts.

ing, crosslinking, and addition reactions increases. The net result of these effects is the increments in the values of carboxyl content and the CRA of the AA–DMDHEU-treated fabrics.

Nevertheless, at a curing temperature of 160°C, the binary mixture of (NH$_4$)$_2$S$_2$O$_8$/NH$_4$Cl has superior efficiency to promote the above reactions than does (NH$_4$)$_2$S$_2$O$_8$/MgCl$_2$·6H$_2$O. This is because, at this temperature, the NH$_4$Cl decomposes at a faster rate than does MgCl$_2$·6H$_2$O and/or the tendency of the latter to react with the hydroxyl and carboxyl groups which are responsible for the various reactions (Table IV).

The significant enhancement in the carboxyl content and CRA of the AA–DMDHEU-treated fabric by increasing the curing time and/or temperature (Table IV) may be associated with the following:

(a) Enhancement of decomposition rate of (NH$_4$)$_2$S$_2$O$_8$ to generate more free radicals and acidic moieties[26,27] capable of increasing the extent of grafting, crosslinking, and addition reactions. The decomposition rate of (NH$_4$)$_2$S$_2$O$_8$ seems to be more enhanced in the presence of NH$_4$Cl than in the presence of MgCl$_2$·6H$_2$O.

(b) Enhancement of the decomposition rate of the MgCl$_2$·6H$_2$O catalyst and, accordingly, the liberated amount of HCl should increase. Liberation of HCl from MgCl$_2$·6H$_2$O under the influence of curing temperature is represented by eq. (4)[30] or (5) or both:

$$2MgCl_2·6H_2O \rightarrow Mg_2OCl_2$$
$$+ 2HCl + 11H_2O \quad (4)$$

$$MgCl_2·6H_2O \rightarrow Mg(OH)_2$$
$$+ 2HCl + 4H_2O \quad (5)$$

The liberated HCl would accelerate the formation of DMDHEU crosslinkages along with the cellulose chains[31] as well as the addition reactions of AA/DMDHEU and AA/ cellulose. As the amount of liberated HCl increases, the extent of these reactions enlarge. It is understandable that the restriction of the relative movement or slippage of structural elements of the cotton fiber, via crosslinking of DMDHEU (and its derivatives) with the cellulose chains, is most probably responsible for imparting the CRAs of the treated fabrics.

**Table VI    Tensile Strength and Dyeing Properties of the Treated Fabrics**

| Acrylic Acid Concn (g/L) | Ammonium Persulfate (5 g/L) | | | | Ammonium Persulfate (5 g/L) + MgCl$_2 \cdot$6H$_2$O (6 g/L) | | | | Ammonium Persulfate (5 g/L) + NH$_4$Cl (6 g/L) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | d | a | b | c | d | a | b | c | d |
| **140°C** | | | | | | | | | | | | |
| 0 | 6.35 | 42.67 | 6.67 | 0.749 | 7.41 | 42 | 5.5 | 0.749 | 9.5 | 40.17 | 6.5 | 0.908 |
| 50 | 12.68 | 42.50 | 7.5 | 0.875 | 21.45 | 40.25 | 7.5 | 0.926 | 20.83 | 39.0 | 6.33 | 1.913 |
| 100 | 19.18 | 41.33 | 7.17 | 1.118 | 33.18 | 39 | 6.0 | 1.508 | 32.99 | 34.67 | 5.33 | 2.22 |
| **160°C** | | | | | | | | | | | | |
| 0 | 7.40 | 34.33 | 4.33 | 1.868 | 9.43 | 40.83 | 5.67 | 2.48 | 15.73 | 28.33 | 7.33 | 2.26 |
| 50 | 16.65 | 31.0 | 6.0 | 3.37 | 25.69 | 32.0 | 4.0 | 3.44 | 32.07 | 28.5 | 5.17 | 2.85 |
| 100 | 24.13 | 26.33 | 5.33 | 3.56 | 38.94 | 28.67 | 5.17 | 4.73 | 45.45 | 25.0 | 5.17 | 3.09 |

Untreated fabric: Warp tensile strength = 58 (lb). % Elongation-at break = 10.67. $K/S$ value = 0.903. [DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min.; curing time, 3 min; [C.I. basic blue 9] methylene blue, 2%.
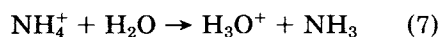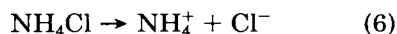[a] Carboxyl content (M.E./100 g cell).
[b] T.S. (lb).
[c] % Elongation.
[d] $K/S$.

(c) Enhancement of the decomposition rate of aqueous NH$_4$Cl catalyst with the resultant formation of more hydrogen protons, according to

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \qquad (6)$$

$$NH_4^+ + H_2O \rightarrow H_3O^+ + NH_3 \qquad (7)$$

$$Cl^- + H_2O \rightarrow HCl + {}^-OH \qquad (8)$$

Since the conjugate acid cation NH$_4^+$ is strong, reaction (7) proceeds to a considerable extent. On the other hand, the conjugate base Cl$^-$ is weak, which implies that it has very little tendency to accept the proton and form HCl. Reaction (8), consequently, does not proceed to any considerable extent. Considering the decomposition reaction of NH$_4$Cl at the curing temperature, increasing the latter may cause this reaction to go to completion. Moreover, the rapid evaporation of NH$_3$ molecules (out of the fabric surface) during the curing may shift reaction (7) to the right and the result is the increase of hydronium H$_3$O$^+$ (or, more simply, H$^+$) ion formation (Le Chatelier's principle). Increasing the concentration of H$^+$ ions as the duration of curing increases would accelerate the crosslinking and addition reactions mentioned before.

(d) Favoring the kinetic energies of the reactants DMDHEU and AA to a speedy reaction independently with the cellulose hydroxyls and to react with each other to form AA/DMDHEU addition derivatives capable to crosslink cellulose chains.

The effects (a)–(d) are much enhanced when the fabric was treated with higher AA concentration (i.e., 100 g/L) than with lower AA concentration (i.e., 50 g/L).

While the Mg$^{2+}$ ions tend to react with the compounds containing hydroxyl and/or carboxyl groups, the NH$_4^+$ ions tend, particularly at higher AA concentration and higher curing temperature, to decompose rapidly and to form protons which, in turn, accelerate the different reactions of these compounds. This would explain the higher catalytic efficiency of NH$_4$Cl as compared with MgCl$_2 \cdot$6H$_2$O when both are separately mixed with (NH$_4$)$_2$S$_2$O$_8$ in the pad solution.

## Tensile Properties

Table VI shows the dependence of tensile properties (i.e., tensile strength and elongation at break) of the cotton fabrics treated under various conditions. Parallel experiments were made using different pad solutions consisting of DMDHEU (100 g/L) only or mixed with AA concentrations of either 50 or 100 g/L in the presence of (NH$_4$)$_2$S$_2$O$_8$ (5 g/L),

$(NH_4)_2S_2O_8$ (5 g/L)/$NH_4Cl$ (6 g/L), or $(NH_4)_2S_2O_8$ (5 g/L)/$MgCl_2 \cdot 6H_2O$ (6 g/L). The so-treated fabrics were then independently cured at 140 and 160°C. It is apparent that all the treated fabrics exhibit losses in the tensile strength and elongation at break after the treatment. The extent of these losses are strongly affected by the conditions of the fabric treatment, i.e., at a specified cure temperature, fabrics treated with DMDHEU in the presence of either $(NH_4)_2S_2O_8$ or the binary mixture of $(NH_4)_2S_2O_8$/$NH_4Cl$ or $(NH_4)_2S_2O_8$/$MgCl_2 \cdot 6H_2O$ show lower losses in tensile strength and elongation at break than do those of fabrics treated with the AA/DMDHEU mixture under the same conditions of treatment. Higher AA concentration (i.e., 100 g/L) as well as higher curing temperature (i.e., 160°C) causes successive losses in tensile strength. On the other hand, the lower concentration of AA (i.e., 50 g/L) would, with few exceptions, slightly improve the elongation at break of the treated fabrics, as compared to fabrics treated in the absence of AA or that treated with higher AA concentration.

It is also observed (Table VI), with the catalysts used at any given conditions of treatment, that the extents of losses in tensile strength of the fabric follow the order

$(NH_4)_2S_2O_8$/$NH_4Cl$

$> (NH_4)_2S_2O_8$/$MgCl_2 \cdot 6H_2O > (NH_4)_2S_2O_8$
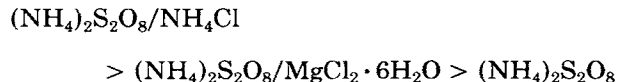
The aforementioned results may be explained in terms of the following reasons:

1. Degradation of cellulose chains via the acidic and/or acid-liberating catalysts used. The more acidic the catalyst is, the more capable it is to depolymerize the cellulose chains.[19] The $(NH_4)_2S_2O_8$ has, of course, a lower efficiency to degrade the cellulose chains than that of the mixed catalysts. Considering the latter, the binary mixture catalysts of $(NH_4)_2S_2O_8$/$NH_4Cl$ have the highest dual acidic and, in turn, the highest dual degradative effect upon the cellulose chains than that of the other binary mixture catalysts, viz., $(NH_4)_2S_2O_8$/$MgCl_2 \cdot 6H_2O$. Furthermore, the degradation of cellulose chains via $(NH_4)_2S_2O_8$ oxidation should also be considered.

2. Slippage restriction of the fiber structural elements by means of the taut crosslinkages formed within the fiber.

3. Rigidity of the fiber structure using DMDHEU crosslinkages comprising rigid rings.

In view of the above reasons, there is no doubt that the higher AA concentration as well as the higher curing temperature should enlarge the extent of the above effects and, in turn, enlarge the extent of strength losses of the treated fabrics. It must be emphasized that the poly(AA) deposited within the fabric is a soft polymer and, therefore, causes a slight improvement in the elongation at break of the fabrics treated, beside other the pad components, with 50 g/L of AA.[13] The adverse holds true when the fabric was treated with 100 g/L of AA. This is because with the latter concentration the aforesaid effects (a), (b), and (c) were then predominant.

## Dyeability

Table VI shows the dyeability of the fabrics treated under the aforementioned conditions when these fabrics were dyed with methylene blue (C.I. basic blue9) dye. It is seen that all the treated fabrics, with few exceptions, exhibit much more dye receptivity than does the untreated fabric (control). However, the extent of dye receptivity of the treated fabrics is governed by the treatment conditions applied, i.e., the extent of dye receptivity of the fabric cured at 160°C is more than that of those cured at 140°C under the same conditions. This is evidenced by the higher $K/S$ values of the former compared with the latter. In addition, fabrics treated with DMDHEU in the presence of either $(NH_4)_2S_2O_8$ or the binary mixture of $(NH_4)_2S_2O_8$/$NH_4Cl$ or $(NH_4)_2S_2O_8$/$MgCl_2 \cdot 6H_2O$ show less dye receptivity than do those treated with the AA/DMDHEU mixture in the presence of either of these catalysts. The higher AA concentration (i.e., 100 g/L) brings about the greatest improvement in the color strength of the treated fabrics than does the lower concentration (i.e., 50 g/L).

Also observed is that, with the catalyst used under the optimal conditions of AA concentration and curing temperature, the improvements in color strength of the treated fabrics follow the sequence

$(NH_4)_2S_2O_8$/$MgCl_2 \cdot 6H_2O > (NH_4)_2S_2O_8$

$> (NH_4)_2S_2O_8$/$NH_4Cl$
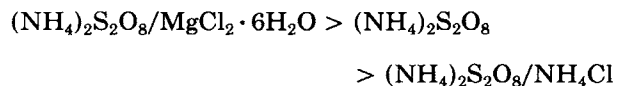
The differences in dye receptivities between the treated fabrics may be interpreted in terms of (1)

**Table VII   Aqueous Soiling and Soil-release Properties of the Treated Fabrics**

| Acrylic Acid Concn (g/L) | Ammonium Persulfate (5 g/L) | | | Ammonium Persulfate (5 g/L) + MgCl$_2$·6H$_2$O (6 g/L) | | | Ammonium Persulfate (5 g/L) + NH$_4$Cl (6 g/L) | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | b | c | a | b | c |
| 140°C | | | | | | | | | |
| 0 | 6.35 | 0.1222 | 100 | 7.41 | 0.1132 | 100 | 9.5 | 0.1452 | 100 |
| 50 | 12.68 | 0.1212 | 100 | 21.45 | 0.1102 | 100 | 20.83 | 0.1322 | 100 |
| 100 | 19.18 | 0.0982 | 100 | 34.18 | 0.1062 | 100 | 29.80 | 0.1335 | 100 |
| 160°C | | | | | | | | | |
| 0 | 7.40 | 0.1242 | 100 | 9.43 | 0.1572 | 100 | 15.73 | 0.1192 | 100 |
| 50 | 16.65 | 0.1159 | 100 | 25.69 | 0.1342 | 100 | 32.07 | 0.1122 | 100 |
| 100 | 24.13 | 0.1102 | 100 | 38.94 | 0.1302 | 100 | 45.45 | 0.1102 | 100 |

Untreated fabric: Degree of aqueous soiling (DS) = 0.1692. Percent aqueous soil removal (% SR) = 86.87. [DMDHEU], 100 g/L; pad–dry–cure method: drying, 80°C for 3 min; curing time, 3 min.

a Carboxyl content, M.E./100 g cell.
b DS (lb).
c % SR.

the extent of DMDHEU crosslinking, as well as the number, length, location, and distribution of cross-links,[32] (2) the extent of AA grafting onto the cotton fabrics, (3) the extent of AA/DMDHEU and AA/cellulose addition reactions, and (4) the nature and type of the catalytic systems.

Because the basic methylene blue dye reacts easily with the free carboxylic acid groups, the color strength is, therefore, improved with increasing incorporation of carboxylic acid groups into the fabric via grafting and addition reactions of AA. Adversely to the effect of carboxylic groups, the DMDHEU crosslinking agent gives cotton excellent dye-resist characteristics.[33,34] As a consequence, the color strength of the treated fabric is strongly dependent upon which of the two effects prevailed.

Besides the catalytic systems, (NH$_4$)$_2$S$_2$O$_8$, (NH$_4$)$_2$S$_2$O$_8$/NH$_4$Cl, and (NH$_4$)$_2$S$_2$O$_8$/MgCl$_2$·6H$_2$O would largely determine the color strength of the treated fabrics. Each of these catalysts differs from the others in the rate of dissociation and/or decomposition, the catalytic efficiency, and the mode of interaction with the carboxylic groups attached along the cellulose backbone and/or with the positively charged nitrogen of the dye molecule. Of course, increasing AA concentration and curing temperature would greatly enlarge the different roles of these catalytic systems, as discussed earlier.

The exceptions were for the fabrics treated with DMDHEU (100 g/L) in the presence of either (NH$_4$)$_2$S$_2$O$_8$ or the binary mixture of (NH$_4$)$_2$S$_2$O$_8$/

MgCl$_2$·6H$_2$O and cured at 140°C and for the fabric treated with AA (50 g/L)/DMDHEU (100 g/L) in the presence of the (NH$_4$)$_2$S$_2$O$_8$ catalyst and cured at the same temperature. These fabrics show less dye receptivity than does the control. The higher extent of crosslinking and blocking of the dye sites by the crosslinks formed may be looked upon to explain the less dye receptivity (i.e., lower $K/S$ values) of these fabrics.

## Soiling and Soil-release Properties of the Treated Fabrics

### From Aqueous Soil Dispersions

The cotton fabrics, treated under the same conditions as given in Table VI, were soiled in an aqueous dispersion of carbon black. The degrees of soiling as well as soil removal were calculated as indicated in the Experimental section and the results obtained are set out in Table VII.

It is seen (Table VII) that all the treated fabrics display better resistance to the aqueous soiling than does the untreated fabric (control). This is observed regardless of the conditions of the treatment applied. Moreover, a close examination of data in this table reveals that the susceptibility of the treated fabrics to soiling decreases as the carboxyl contents of these fabrics increase.

Results of Table VII show also that the treated fabrics exhibit an outstanding ability to release

aqueous soil when laundered, i.e., the percent soil removal reached the maximum (100%) for all the treated fabrics, unlike that of the untreated fabric. The % soil removal for the latter fabric amounts to about 87%.

The differences in degrees of aqueous soiling and aqueous soil removal characteristics found between the treated and untreated fabrics can be demonstrated in the following:

1. For the untreated fabric (control), the soil particles (i.e., carbon black) can penetrate within the fiber pores and crevices having different dimensions. Upon laundering of such a soiled fabric, a portion of the soil particles can be removed from the fiber pores and crevices having larger dimensions, whereas the remaining portion of these particles are still confined in, or trapped by, the pores and crevices of smaller dimensions. The trapped particles of the soil cannot migrate from the fiber pores and crevices into the bulk solution under the influence of the laundering conditions applied. On the other hand, for treated fabrics, the fiber pores and crevices of smaller dimensions are perhaps filled with the reaction products of reactant molecules and/or ions, whereas the larger dimension pores and crevices are most probably filled with AA grafts as well as with DMDHEU crosslinks. Logically, the deposition of the latter two within interfiber and interyarn voids may cover the fiber pores and crevices of smaller sizes. Therefore, when the treated fabrics were soiled with aqueous carbon black dispersion, the carbon particles may penetrate only the open and larger voids, particularly the voids between the fabric yarns (i.e., interyarn voids). Owing to the vast volumes of these voids, the carbon-particles can migrate from the fiber to the bulk solution of washing. This explains why the soil particles can be easily removed from the treated fabrics when laundered.

2. The presence of the carboxylic acid groups on the interior and exterior surfaces of the treated fabrics has a negative effect on the aqueous soiling and a positive effect on the aqueous soil-release properties of these fabrics.[15,35] Both these effects increase as the carboxyl content of the treated fabric increases.

3. The nature of the fabric surface determines, to a great extent, the susceptibility of the

fabric to be soiled and to repel the soil upon laundering it. Concerning this, the untreated fabric is characterized by a rough surface and, therefore, it has a higher tendency to be soiled and a lower ability to repel the soil when laundered. The adverse holds true for the treated fabrics which are characterized by smooth surfaces.

### From Nonaqueous Oily Dispersions

Table VIII shows the soiling and soil-release characteristics of the treated cotton fabrics under investigation when soiled by oily carbon black soiling. It is obvious that all the treated fabrics acquire a higher resistance to the nonaqueous oily soiling than does the untreated fabric (control). Diminishing the total porosity as well as reducing the surface irregularities via AA grafts and DMDHEU crosslinks of all the treated fabrics as compared to those of the control would explain the lower degrees of oily soiling of the former than that of the latter. Moreover, differences in (1) the number, length, location, and distribution of the AA graft and DMDHEU crosslinks, (2) the extent of DMDHEU crosslinking and AA grafting as well as the ratio of the DMDHEU crosslinks/AA grafts, and (3) the extent of AA-addition reactions with hydroxyls of DMDHEU and cellulose may contribute to differences in resistance to the nonaqueous oily soiling found among the treated fabrics.[14,36,37]

The nonaqueous oily soil-release characteristics of the treated fabrics together with those of the control (untreated fabric) are also shown in Table VIII. As is evident, all the treated fabrics, with a lone exception, have higher abilities to release the oily soil than does the control. Furthermore, the highest percentages of the oily soil were removed from the fabrics treated with DMDHEU (100 g/L) in the presence than in the absence of AA, irrespective of the treating conditions used. In this respect, the percent oily soil removal reached the maximum (i.e., 100%) for the fabrics treated with 100 g/L DMDHEU and 100 g/L AA.

The lone exception was for the fabric treated with the formulation composed of DMDHEU (100 g/L) and $(NH_4)_2S_2O_8$ (5 g/L). When this particular fabric was oily soiled followed by laundering it to remove the soil, it was found that the percent oily soil removal is lower than that of the control.

The superiority of the treated fabrics to release the oily soil when compared with the untreated fabric (control) is in accordance with previous reports[36,38] which ascribed this superiority to

**Table VIII    Nonaqueous Oily Soiling and Soil-release Properties of the Treated Fabrics**

| Acrylic Acid Concn (g/L) | Ammonium Persulfate (5 g/L) | | | Ammonium Persulfate (5 g/L) + MgCl$_2$·6H$_2$O (6 g/L) | | | Ammonium Persulfate (5 g/L) + NH$_4$Cl (6 g/L) | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | b | c | a | b | c |
| **140°C** | | | | | | | | | |
| 0 | 6.35 | 0.5472 | 82.54 | 7.41 | 0.6802 | 88.50 | 9.5 | 0.3802 | 92.85 |
| 50 | 12.68 | 0.6482 | 90.1 | 21.45 | 0.5162 | 100 | 20.83 | 0.4992 | 100 |
| 100 | 19.18 | 0.7552 | 100 | 34.18 | 0.5702 | 100 | 29.80 | 0.4752 | 100 |
| **160°C** | | | | | | | | | |
| 0 | 7.40 | 0.6382 | 71.14 | 9.43 | 0.7312 | 94.78 | 15.73 | 0.5512 | 93.98 |
| 50 | 16.65 | 0.6802 | 88.21 | 25.69 | 0.5982 | 94.78 | 32.07 | 0.4072 | 99.44 |
| 100 | 24.13 | 0.6752 | 98.05 | 38.94 | 0.4872 | 98.79 | 45.45 | 0.5882 | 100 |

Untreated fabric: Degree of nonaqueous soiling (DS) = 0.8572. Percent nonaqueous soil removal (% SR) = 84.11. The same conditions as in Table VIII.

a Carboxyl content, M.E./100 g cell.
b DS (lb).
c % SR.

(a) better balance between hydrophilicity and oleophobicity;

(b) higher energy of the fabric–oil interface; and

(c) good wettability of the high-energy surface (high critical surface energy), due to the presence of highly hydrophilic carboxylic groups attached along the fabric surfaces.

The properties (a)–(c) of the treated fabrics greatly facilitate the removal of oily soil during washing.

The lone exception observed for the fabric treated with DMDHEU in the presence of (NH$_4$)$_2$S$_2$O$_8$ suggests that such a catalyst causes the opening up of the cellulose structure via its oxidative action during the drying and/or curing processes. This action is favored when the fabric was cured at 160°C rather than at 140°C. The opening up of the cellulose structure will suppress the tendency of the treated fabric to repel the oily soil when laundered.[15] The presence of MgCl$_2$·6H$_2$O, NH$_4$Cl, or AA together with (NH$_4$)$_2$S$_2$O$_8$ may probably subdue the oxidative effect of the latter upon the cellulose chains.

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