

New Catalyst System for Easy-Care Cotton Finishing

A. HEBEISH,* *Textilforschung Krefeld, Frankenring 2, West Germany*

Synopsis

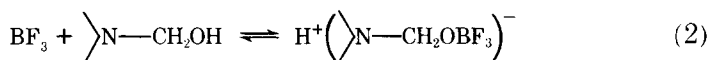
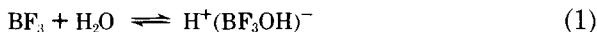
A new catalyst system, based on a mixture of boron trifluoride-acetic acid complex ($\text{BF}_3 \cdot 2\text{CH}_3\text{COOH}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), has been examined in cotton finishing treatment for producing easy-care properties. It provides strong catalysis in crosslinking cotton with a series of N-methylol finishing agents when the pad-dry-cure process is applied. Curing can be carried out at a temperature of 130–150°C for a period of 1–3 min, dependent on the temperature used. The resilience and abrasion resistance properties as well as the degree of polymerization (D.P.) of the crosslinked cotton so obtained were equivalent or slightly better than those of crosslinked cottons catalyzed by conventional catalysts. The influence of the new catalyst as well as a number of conventional catalysts, viz., ammonium chloride, ammonium dihydrogen phosphate, magnesium chloride hexahydrate, and zinc nitrate hexahydrate, on some properties of cotton fabrics was also investigated. The behavior of these catalysts in the presence of the N-methylol finishing agent was quite different from their behavior in its absence. With the exception of ammonium salts, the D.P. of crosslinked cotton was much higher than that of cotton treated with the catalyst only. The opposite holds true for the abrasion resistance.

INTRODUCTION

The use of boron trifluoride independently or as coordination compound for vinyl polymerization has been reported.¹ Cationic graft polymerization of unsaturated compounds onto cellulose could also be effected under the catalytic influence of boron trifluoride.² In addition, all epoxy resin systems can be polymerized at elevated temperatures with the aid of boron trifluoride.³⁻⁶ Boron trifluoride addition compounds with amide such dimethylformamide have found use as curing agents.⁷

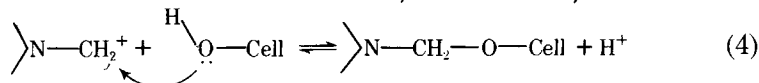
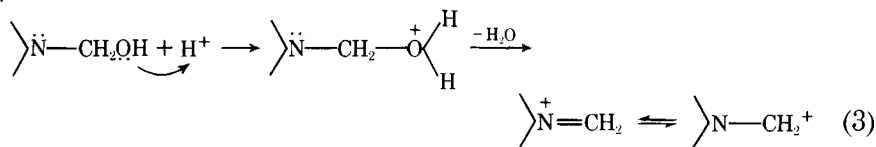
In other ring-opening-type reactions, boron trifluoride has been used to polymerize dioxane⁸ and dioxolane.⁹ A number of patents have been issued on the solution polymerization of trioxane¹⁰ and the copolymerization of trioxane with other cyclic ethers.¹¹ However, to the author's knowledge, no detailed information has yet been published on the possible use of boron trifluoride in easy-care finishing treatments of cotton.

It is believed that boron trifluoride would effect reaction of N-methylol compounds with cellulose. Boron trifluoride probably forms complexes with water or the N-methylol compound itself, as shown by the mechanism suggested by eqs. (1) and (2):



* Present address: National Research Centre, Dokki, Cairo, Egypt.
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These complexes donate protons to the N-methylol compounds to give carboonium ions, eq. (3), which are required for inducing its reaction with cellulose, eq. (4):



Attempts to use boron trifluoride-acetic acid complex as a catalyst for easy-care finishing treatments of cotton were not successful due to bath instability. However, further efforts have led to a highly active catalytic system based on a mixture of boron trifluoride-acetic acid complex and magnesium chloride hexahydrate. This communication details preparation and properties of this catalyst as well as its feasibility in easy-care cotton finishing. In addition, the potential value of the new catalyst in comparison with conventional catalysts is evaluated.

EXPERIMENTAL

Cotton Fabric. Mill-scoured and bleached cotton fabric (plain weave construction, 27 wefts per cm, 27 warps per cm) was used without further purification.

N-Methylol Compounds. With the exception of dimethylolurea, the N-methylol compounds were obtained as 50% pure aqueous solutions. The amounts of these compounds given throughout the paper are related to the solid substance. The reagents used were: dimethylolethyleneurea (DMEU), dimethyloldihydroxyethylene urea, dimethylolpropyleneurea, dimethylolethyl carbamate, dimethylol-4-methoxy-5,5-dimethylpropyleneurea, modified dimethylolurea, N-methylolacrylamide, and dimethylolurea. Application of these reagents using the pad-dry-cure method to the cotton fabric in absence of any catalyst imparts no improvement in crease recovery, indicating that no traces of the potential catalysts in the N-methylol finishing agent.

Catalysts. Besides the new catalyst, the following catalysts were used: ammonium chloride (NH_4Cl), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). These catalysts were of reagent grade.

Preparation and Properties of the New Catalyst. Boron trifluoride-acetic acid complex (80 ml) was mixed with N,N'-dimethylformamide (200 ml). This was partially neutralized with anhydrous sodium bicarbonate (40 g) previously dissolved in deionized water. Magnesium chloride hexahydrate (150 g) was also dissolved in deionized water and added to the partially neutralized boron trifluoride-acetic acid complex. The solution so obtained was completed to 1000 ml with water and vigorously stirred. The solution was then filtered and was ready for use.

The catalyst solution is stable for more than six months. It has a pH 1.75 and a specific gravity 1.05. The aqueous solution containing the N-methylol

compound and the catalyst (30 ml/l.) exhibits a pH of 3.0 to 3.5, depending on the type of the N-methylol compound employed. With the exception of dimethylolurea, the finishing bath is very stable; no change in pH of the bath occurred during a period of 48 hr. In case of dimethylolurea, however, bath stability could be achieved by using a mixture of dimethylolurea and DMEU at a ratio of 1:1 or 2:1.

Finishing Treatment. Fabric samples were padded through two dips and two nips at room temperature to an average wet pickup of 65%. Time of impregnation never exceeded 1 min. At this point, the fabric was stretched back to its original dimensions on pin frames for drying, then for curing. An oven with circulating air was used for both drying and curing. Different pad baths were used. These and the conditions of drying and curing are detailed in the text. Unless otherwise noted, the cured samples were washed at 70°C in a slightly alkaline aqueous solution (pH 10) for 45 min. The samples were dried at ambient temperature and conditioned at 65% R.H. and 25°C for 48 hr before testing.

Acid Hydrolysis. Hydrolysis was carried out in an aqueous solution containing 5% urea and 1.5% phosphoric acid at 80°C for 30 min using a fabric-to-liquor ratio of 1:50. After hydrolysis, samples were rinsed immediately in running tap water, washed thoroughly with hot and cold distilled water, and dried as after the curing step.

Methods of Testing and Analysis. Crease recovery of fabrics was determined according to DIN 5389 (January 1972); abrasion resistance, by the accelerator method described by AATCC Test Method 93-1970; nitrogen content, by the Kjeldahl method; and formaldehyde, by a method described by Schliefer et al.¹² Viscosimetric determination of the degree of polymerization (D.P.) was carried out on samples previously nitrated according to a method described elsewhere.¹³ Moisture content was determined by weighing the sample after it had been removed from the curing chamber, drying it, and then weighing it again.

RESULTS AND DISCUSSION

Concentration of Catalyst

Figure 1 shows changes in crease recovery and per cent loss in abrasion resistance versus concentration of the new catalyst. Within the range studied, loss in abrasion resistance was proportional to the level of crease recovery, both being significantly increased by increasing the catalyst concentration.

In the absence of DMEU, the loss in abrasion resistance became significant only when catalyst concentrations higher than 15 ml/l. were used. At any event, however, the losses in abrasion resistance were much higher in the presence of DMEU than in its absence. This reflects the effect of crosslinking which causes embrittlement of the cotton fibers via restriction of the movement of the fiber microstructural units. The latter are not able to redistribute stresses during the fabric testing.

The loss in abrasion resistance in the absence of DMEU is unequivocally due to molecular degradation of cellulose through hydrolysis under the influence of the acid catalyst. Should this aspect operate also during crosslinking,

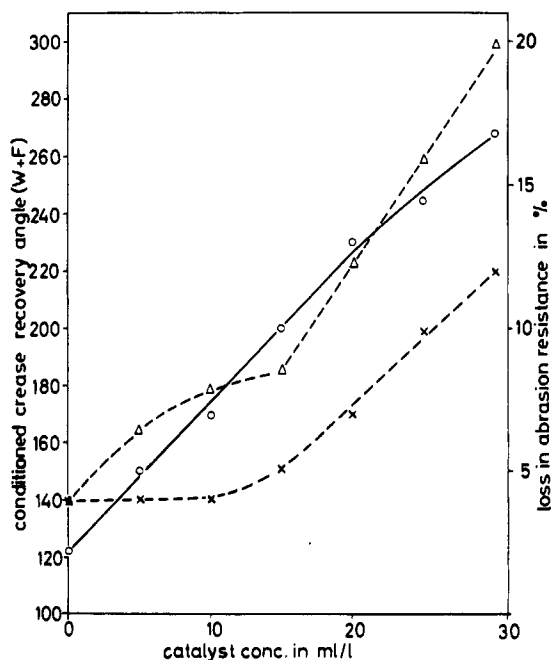


Fig. 1. Effect of concentration of the new catalyst on conditioned crease recovery and abrasion resistance of cotton fabric: (—) crease recovery; (---) per cent loss in abrasion resistance; (○) variation in crease recovery with catalyst concentration; (Δ) in presence of DMEU; (X) in absence of DMEU; DMEU concn., 100 g/l; drying, 100°C/3 min; curing, 150°C/3 min.

the loss in abrasion resistance during crosslinking must then be attributed to a combination of embrittlement together with molecular degradation of cellulose.¹⁴⁻¹⁸ With the new catalyst, however, the fraction of abrasion losses in crosslinked cotton brought about by embrittlement seems to constitute the major contribution. Sources of evidence are as follows: (a) Catalyst concentrations, in absence of DMEU, up to 15 ml/l., caused few if any losses in abrasion resistance, whereas the corresponding losses in the presence of DMEU were quite substantial. (b) The D.P. dropped by about 8% and 40% in the presence and absence of DMEU, respectively, at a catalyst concentration of 30 ml/l. Moreover, after removal of the crosslinks by mild acid hydrolysis, the fabric abrasion resistance was completely recovered. This will be discussed later in detail. (c) As will also be seen later, the catalyst behaves differently in the presence than in the absence of DMEU.

Time and Temperature

Figure 2 shows the crease recovery angle versus time of curing, whereas Figure 3 shows the change in water content of the fabric with time when the fabric was padded only with water and subjected to heat treatment at 100° and 120°C. It may be argued that the loss of water from samples of Figure 2 may not be identical with the corresponding loss in the samples of Figure 3, but the comparison indicates that the crease recovery is developed when crosslinking of the fabric occurs in the presence of a final moisture content of

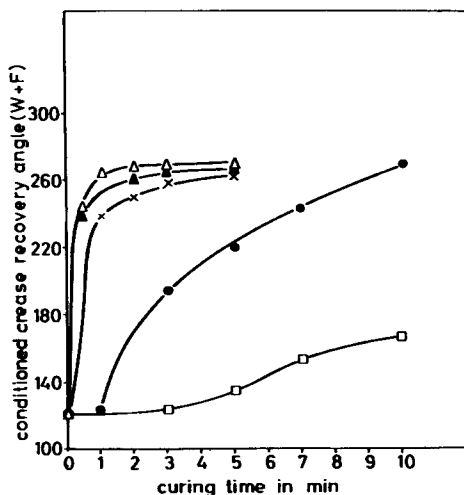


Fig. 2. Effect of temperature and time of curing on conditioned crease recovery of cotton treated with DMEU (100 g/l.) and the new catalyst (30 ml/l.): (○) original; (◻) 100°C; (●) 120°C; (X) 130°C; (▲) 140°C; (△) 150°C. No drying for fabrics heated at 100°C and 120°C; with other temperatures, fabric was dried at 100°C for 3 min before curing.

about 2%. The temperature is the main deciding factor to achieve the required moisture content of the fabric. Then the reaction starts independently of the temperature, but the rate of the reaction is determined by the temperature. This is, indeed, in full agreement with a Lewis acid catalysis.¹⁹

Among the techniques of easy-care cotton finishing is the pad-cure method. The latter involves padding the fabric at room temperature in a solution containing the N-methylol finishing agent along with a reactive catalytic system which allows curing, i.e., crosslinking, under low temperature. Figure 2 clearly illustrates that the pad-cure method can be applied with the new catalyst system. Mild curing at 120°C for 10 min produced a fabric with good resilience. The latter could be achieved by the conventional pad-dry-cure method (described in the experimental section) if curing was performed at 150°, 140°, and 130°C for 1, 2, and 3 min, respectively.

Concentration of the N-methylol Finishing Agent

The effect of DMEU concentration on crease recovery is shown in Figure 4. It is seen that increasing DMEU concentration up to 100 g/l. causes a significant enhancement in crease recovery. The latter increases marginally upon using higher concentrations.

Different N-Methylol Finishing Agents

The ability of the new catalyst to expedite reactions of various N-methylol finishing agents with cellulose may be realized from Table I. The data indicate that reaction of N-methylol finishing agents examined with cellulose occurred in the presence of the new catalyst. However, the extent of reaction depends upon the nature of the N-methylol compound. Based on these data, the following order may be cited: dimethylolethyleneurea \geq dimethyloldihy-

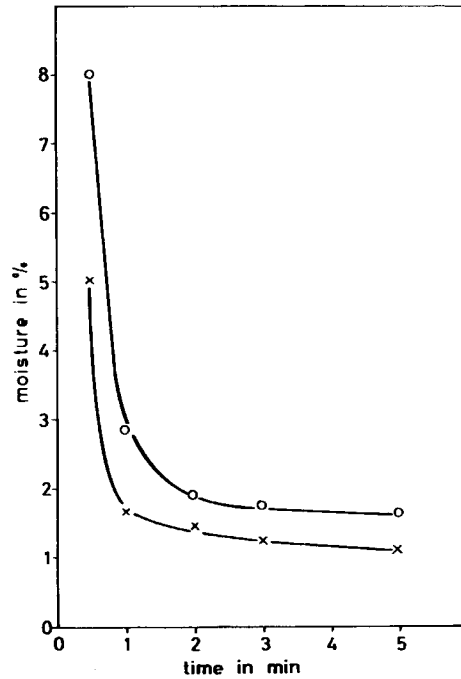


Fig. 3. Moisture content of cotton fabric impregnated to ca. 65% pickup of water, as a function of time of heating in an air-circulating oven: (O) 100°C; (X) 120°C.

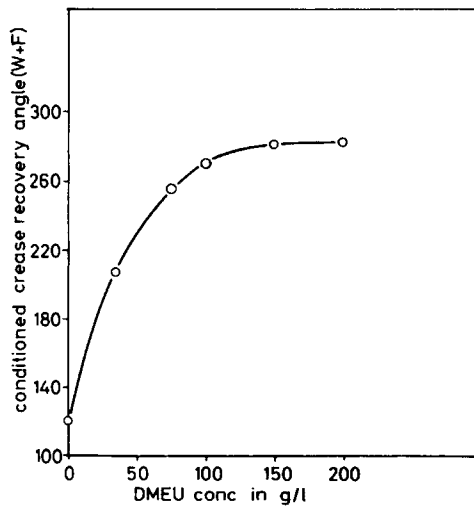
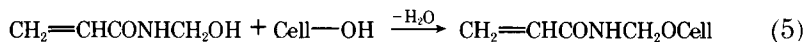


Fig. 4. Effect of DMEU concentration on conditioned crease recovery of cotton fabric: concentration of the new catalyst, (30 ml/l.); drying, 100°C (3 min); curing, 150°C/3 min.

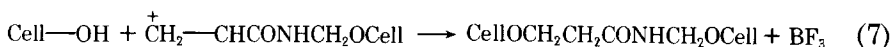
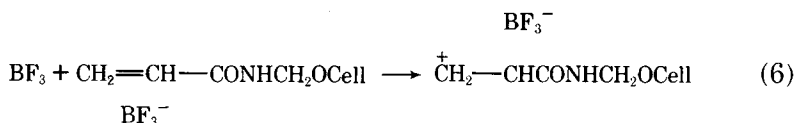
droxyethyleneurea > dimethylolpropyleneurea > mixture of dimethylolurea and dimethyloethyleneurea > dimethylol-4-methoxy-5,5-dimethylolpropyleneurea > modified dimethylolurea > dimethyloethyl carbamate > N-methylolacrylamide.

Of course, the N-methylolacrylamide should be excluded from this order

since it reacts as a monofunctional compound under normal acid conditions to yield acrylamidomethylated cellulose,^{20,21} eq. (5):



Despite this, the crease recovery obtained with N-methylolacrylamide under the influence of the new catalyst is much greater than that obtained with other catalysts.^{20,21} This suggests a crosslinking reaction via a cationic mechanism due to the presence of BF_3 complexes in the new catalyst. Attachment of BF_3 to the doubly bonded carbon atoms of the pendent acrylamidomethyl groups results in a carbonium ion, eq. (6), which can react with cellulose hydroxyls, eq. (7):



The losses in abrasion resistance observed upon using different N-methylol compounds are proportional to the improvement in crease recovery (Table I). The slightly higher loss in abrasion resistance observed with dimethyloldihydroxyethyleneurea compared with dimethylolethyleneurea is in agreement with previous work²² and could be associated with a more rigid crosslinked cellulose structure due to the polyfunctionality of dimethyloldihydroxyethyleneurea.

Abrasion Resistance Versus Crease Recovery

Crosslinked cottons having different crease recovery angles were tested for abrasion resistance. These cottons were obtained by changing the concentra-

TABLE I
Ability of the New Catalyst to Expedite Reactions of
Various N-Methylol Compounds with Cellulose^a

N-Methylol compound	Crease recovery angle (W + F)	Loss in abrasion resistance, %
Dimethylolethyleneurea	270	19.8
Dimethyloldihydroxyethyleneurea	265	22.0
Dimethylolpropyleneurea	250	18.0
Dimethylolethyl carbamate	210	11.6
Dimethylol-4-methoxy-5,5-dimethylpropyleneurea	220	10.5
Modified dimethylolurea	250	18.5
Dimethylolurea + dimethylolethyleneurea	245	15.6
N-Methylolacrylamide	200	8.7
None	122	4.0

^a N-Methylol compound, 100 g/l.; mixture of dimethylolurea and dimethylolethyleneurea, 50 g/l. each; catalyst concn., 30 ml/l.; padding to 65% wet pickup; drying 100°C for 3 min; curing 150°C for 3 min.

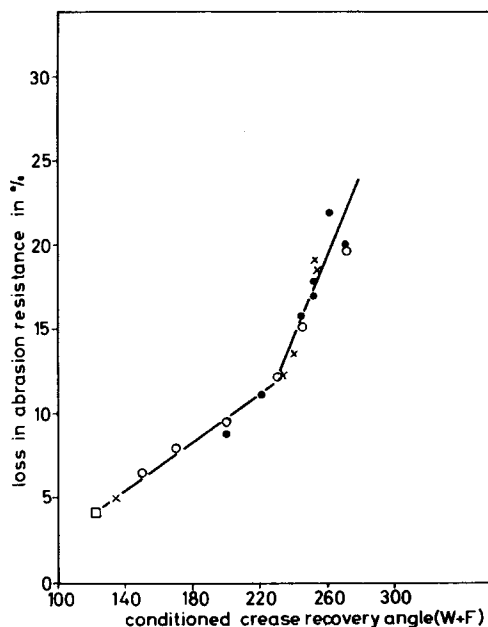


Fig. 5. Relation between conditioned crease recovery and per cent loss in abrasion resistance of cotton fabrics treated with N-methylol finishing agent in presence of the new catalyst under various conditions: (O) by changing catalyst concentration; (X) by changing curing temperature; (●) by using different N-methylol finishing agents; (□) untreated cotton.

tion of the new catalyst and temperature of curing as well as by using different N-methylol compounds. The crease recovery angles are plotted against loss in abrasion resistance in Figure 5. Obviously, there are two distinct straight lines with different slopes. While the first line has a slope of 0.7, the second line requires a slope of 2.5. Indication of this is that regardless of the conditions used or the N-methylol finishing agent employed in the finishing treatment, the abrasion resistance is reduced significantly after the fabric has acquired a certain level of crease recovery. Above this, the cotton fabric seems to be very rigid, thus losing relatively much of its abrasion resistance.

Comparison of the New Catalyst With Conventional Catalysts

Some properties of crosslinked cotton catalyzed by the new catalyst are compared with the corresponding properties of crosslinked cottons catalyzed by conventional catalysts (Table II). It is clear that the pH of the finishing bath has practically no effect on fabric properties. Fabric properties of crosslinked cotton catalyzed by the new catalyst are generally better than those of crosslinked cotton catalyzed by ammonium salts. The same holds true with respect to the metal salts, but to a lesser degree.

The outstanding loss in abrasion resistance observed with NH_4Cl could be associated with the presence of free HCl brought about by both hydrolysis of the salt and reaction of the latter with free formaldehyde in the treating solution or liberated via dissociation of the methylol groups of the finishing agent. Besides catalyzing crosslinking, HCl has a very detrimental effect on the cellulose chains.²³ $\text{NH}_4\text{H}_2\text{PO}_4$ works by the same mechanism, yet the acid lib-

erated is H_3PO_4 , which confers on cellulose a much lower degradation than HCl does.

With the metal salt catalysts, i.e., $MgCl_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, the situation is different. Carbonium-immonium ions necessary for the reaction with cellulose are produced through complexation with the N-methylol compound²⁴⁻²⁸; no free acid is liberated. Since the new catalyst is a mixture of $MgCl_2 \cdot 6H_2O$ and $BF_3 \cdot 2CH_3COOH$, the catalytic action of $MgCl_2 \cdot 6H_2O$ would be expected to follow the mechanism reported in the literature.²⁴⁻²⁸ Boron trifluoride, on the other hand, is likely to form complexes with water, dimethylformamide, and the N-methylol compound, e.g., eqs. (1) and (2). These complexes dissociate into a proton H^+ and a negatively charged counterion $(BF_3X)^-$. The proton catalyzes the crosslinking reaction via a carbonium ion mechanism. That is, the new catalyst functions by a cooperating mechanism between weak and strong Lewis acid catalysts.

The differences in loss in abrasion resistance of crosslinked cottons catalyzed by the new catalyst or by metal salt catalysts could be interpreted in terms of the amount of formaldehyde liberated during curing and the mode of reaction of the formaldehyde with the cellulose. Intermolecular reaction confers further rigidity on cellulose and, therefore, greater loss in abrasion resistance. This case has been reported for $MgCl_2 \cdot 6H_2O$. With zinc nitrate, the reaction of formaldehyde with cellulose has been reported to be mainly intramolecular.²⁹ This seems also to be the case with the new catalyst (see below).

The comparison (Table II) between the catalyst effect in presence and absence of DMEU implies that the ammonium salt catalyst in absence of

TABLE II
Comparison of the New Catalyst with Others^a

Catalyst	Catalyst concn.	pH of bath	Curing min/°C	N, %	HCHO, %	Crease recovery angle (W + F)	Loss in abrasion resistance, %	D.P.
Ammonium chloride	4 g/l.	4.2	5/140	1.14	2.6	266	b (5.2)	984 (1668)
Ammonium dihydrogen phosphate	4 g/l.	4.3	5/140	1.19	2.7	257	23.0 (5.0)	1464 (1693)
Magnesium chloride	12 g/l.	6.1	5/150	1.05	3.0	261	27.0 (7.5)	1360 (1047)
Zinc nitrate	10 g/l.	6.2	5/150	1.03	2.7	265	23.4 (14.8)	1450 (605)
New catalyst	30 ml/l.	3.0	3/150	1.03	2.7	270	19.8 (10.9)	1550 (960)
Untreated cotton						122	4.0	1688

^a Cotton fabric was padded twice with a solution containing 100 g/l. DMEU plus the amount of catalyst indicated in the table to a wet pickup of ca. 65%, dried at 90°C for 4 min, and cured under the conditions shown in the table.

^b Could not stand the abrasion test. Values in parentheses indicate the effect of catalyst only on abrasion resistance and D.P.

DMEU had practically no effect on abrasion resistance and D.P. This suggests that the hydrolysis of the salt is followed by evaporation of the liberated acid and/or the inability of the acid so generated to attack cellulose while the latter is in an almost dry state. Nevertheless, extension of the cellulose chains resulting from heating the cellulosic material at elevated temperature^{17,30} cannot be ruled out.

With the other catalysts, the reduction in D.P. and abrasion resistance follows the order zinc nitrate > new catalyst > magnesium chloride. During curing, zinc nitrate seems to complex with cellulose rather than bound to the cellulose hydroxyls by secondary valence forces.¹⁸ Such complexation alters the behavior of zinc nitrate salt. It is likely that decomposition occurs more readily, with the liberation of nitrogen oxides and oxygen, which then attack the cellulose. This is not the case with magnesium chloride. Complexation of the latter takes place via secondary valence forces. Decomposition of the salt is not likely to occur under the conditions studied. Its degradative effect would, therefore, rely on its behavior as a weak Lewis acid. On the other hand, the initial low pH of the treating solution as well as the contribution of BF₃ complexes in hydrolyzing cellulose would account for the moderate degradation observed with the new catalyst.

With the exception of crosslinked cotton catalyzed by ammonium salts, the D.P. of the crosslinked cotton is much higher than that of cotton treated with the catalyst only (Table II), indicating less cellulose degradation during crosslinking. The acid attack on cellulose is perhaps moderated via contribution in catalysis of reaction between methylol groups and cellulose hydroxyls.

Acid Hydrolysis

The susceptibility of crosslinked cottons catalyzed by different catalysts toward acid hydrolysis is summarized in Table III. Acid hydrolysis removed essentially all DMEU residues, leaving an only insignificant amount of formaldehyde. The latter depends on the nature of the catalyst used.

A previous report²⁹ has shown that less formaldehyde is evolved with mag-

TABLE III
Some Properties of Cotton Crosslinked with DMEU Using Different Catalysts Before and After Acid Hydrolysis^a

Catalyst	Before hydrolysis				After hydrolysis ^b				Reduction in D.P. after hydrolysis, %
	N, %	HCHO, %	Loss in abrasion resistance	D.P.	N, %	HCHO, %	Loss in abrasion resistance	D.P.	
Ammonium chloride	1.14	2.6	^c	984	0.06	0.54	7.8	858	12.8
Ammonium dihydrogen phosphate	1.19	2.7	23	1464	0.02	0.27	4.7	1227	16.2
Magnesium chloride	1.05	3.0	27	1360	0.02	0.09	4.5	1140	16.3
Zinc nitrate	1.03	2.7	23.4	1450	0.01	0.23	5.2	1216	16.0
New catalyst	1.03	2.7	19.8	1550	0.00	0.42	3.8	1297	16.3
Untreated cotton	—	—	4.0	1688	—	—	4.0	1421	15.8

^a Treatment as shown in Table II.

^b Hydrolysed 30 min at 80°C with urea-phosphoric acid (5% urea, 1.5% H₃PO₄).

^c Could not stand abrasion test.

nesium chloride than with zinc nitrate catalyst. Furthermore, reaction of liberated formaldehyde with cellulose in the presence of magnesium chloride is essentially intermolecular, whereas in the presence of zinc nitrate the reaction is presumed to be intramolecular. The present data (Table III) would, therefore, suggest that hydrolysis of the intermolecular formaldehyde occurs more easily than the intramolecular formaldehyde. Reaction of liberated formaldehyde with cellulose in the presence of the new catalyst also seems to be intramolecular since a relatively substantial amount of formaldehyde was found after hydrolysis.

The D.P. of crosslinked cottons before and after hydrolysis showed that, regardless of the catalyst used, there is a drop in D.P. after hydrolysis (Table III). With the exception of crosslinked cotton catalyzed by ammonium chloride, the percent reduction in D.P. of all crosslinked cottons examined is equal to that of untreated cotton. The relatively higher resistance of crosslinked cotton catalyzed by ammonium chloride could be associated with partial removal of the accessible cellulose by acid attack, i.e., the catalyst, during curing.

Abrasion resistance of crosslinked cottons before and after hydrolysis showed clearly that, with the exception of crosslinked cotton catalyzed by ammonium chloride, the abrasion resistance of the fabric could be recovered practically unimpaired after removal of the crosslinks.

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