

Investigation of the Catalyst in the Cellulose-DMEU Reaction. Part II. Physicochemical Studies of the Reaction*

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INTRODUCTION

In an earlier study of the effect of the catalyst in the cellulose-dimethylol ethyleneurea (DMEU) reaction,¹ evidence was obtained which indicated that the rate of the reaction varied with the catalyst and that the metal ion actually entered into the reaction, forming a coordination complex with the DMEU molecule through the formation of nitrogen-to-metal bonds. Damage during the chlorine scorch test appeared to be due to a free-radical mechanism in which this metallic complex was an important factor. In addition, infrared absorption spectra indicated that DMEU reacted with cotton preferentially at the primary alcohol group of the cellulose. The present investigation was undertaken as a continuation of these previous studies to provide a clearer insight into the significant behavior of the catalyst.

EXPERIMENTAL

DMEU was prepared in the laboratory according to the procedure outlined by Hoover and Vaala.² Found: m.p. 98°C., N 19.0%. Lit.: m.p. 99°C., N 19.1%.

Fabric samples were from 80 × 80 cotton print cloth (3.3 oz./sq.yd.) which had been desized, scoured, and bleached.

Inorganic salt catalysts included: (a) $MgCl_2 \cdot 6H_2O$, (b) $Zn(NO_3)_2 \cdot 6H_2O$, (c) $Mg(NO_3)_2 \cdot 6H_2O$, (d) $ZnCl_2$, (e) $CuCl_2$, and (f) $CdCl_2$. The salts were of analytical reagent grade.

Specimens of cloth were treated with an 8% aqueous solution of DMEU in the presence of each of the catalysts, keeping the concentration of the metallic ion constant. Two concentrations of metal ions were employed, 0.03M and 0.1M. The specimens at 0.1M were treated according to the procedure outlined previously.¹

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For the reaction rate studies at the 0.03*M* catalyst level, the treatment procedure was altered slightly in the curing step. Since the reaction rates were too high to differentiate at the usual curing temperature of 160°C., specimens were cured at 45, 55, and 65°C. for varying periods of time, then given an afterwash and allowed to drip-dry. Reaction rates for the cellulose-DMEU reaction catalyzed by 0.03*M* MgCl₂, Mg(NO₃)₂, ZnCl₂, and Zn(NO₃)₂ were determined by following changes in nitrogen and formaldehyde contents and changes in crease recovery properties. Nitrogen analyses were obtained by the Kjeldahl method. Formaldehyde determinations were made on the distillate obtained by distilling off 80–90% of the sulfuric acid-sodium sulfate mixture in which approximately 1 g. samples of the treated fabrics were digested. The spectrophotometric method with phenylhydrazine hydrochloride and potassium ferricyanide, described by Tanenbaum,³ was used to determine formaldehyde contents of aliquots of the distillate. Wrinkle recovery angles were determined with the Monsanto tester.⁴

Uniformity of reaction and extent of crosslinking were determined microscopically by examination (a) of specimens after 30 min. immersion in 0.5*M* cupriethylenediamine (cuene), for determination of extent of swelling or dissolution of the treated fibers, and (b) of specimens subjected to osmium tetroxide staining. Ultrathin sections (600–800 Å.) provided more detailed information on the extent of crosslinking. The techniques employed have been described previously.^{5–7}

The effect of ultraviolet radiation upon the cellulose-DMEU reaction product was investigated by subjecting specimens to the unfiltered radiation from a 500 w. Hanovia Special Lamp (#7400.11).^{*} Temperatures of the irradiated fabrics were measured with a calibrated copper-Constantan thermocouple, and damage due to retained chlorine on these and conventionally treated fabrics was determined by the AATCC "scorch test" method.⁸

Magnesium and zinc were quantitatively determined by the oxygen flask combustion technique and ethylenediamine tetraacetic acid.⁹ Zinc determinations were also made on cloth samples by line width spectrochemical analysis with a Littrow-type emission spectrograph.¹⁰

Infrared absorption spectra were obtained on a Perkin-Elmer Double Beam Spectrophotometer by the KBr disk technique of O'Connor, et al.¹¹

RESULTS AND DISCUSSION

In an attempt to establish the validity of observations made at the 0.03*M* catalyst concentration level, infrared spectra were obtained for cotton specimens that had been treated with DMEU in the presence of a higher concentration (0.1*M*) of the Mg or Zn salts as well as for specimens treated

^{*} Trade names have been used to identify material used in the work, and such does not imply endorsement or recommendation by the U.S. Department of Agriculture over other products not mentioned.

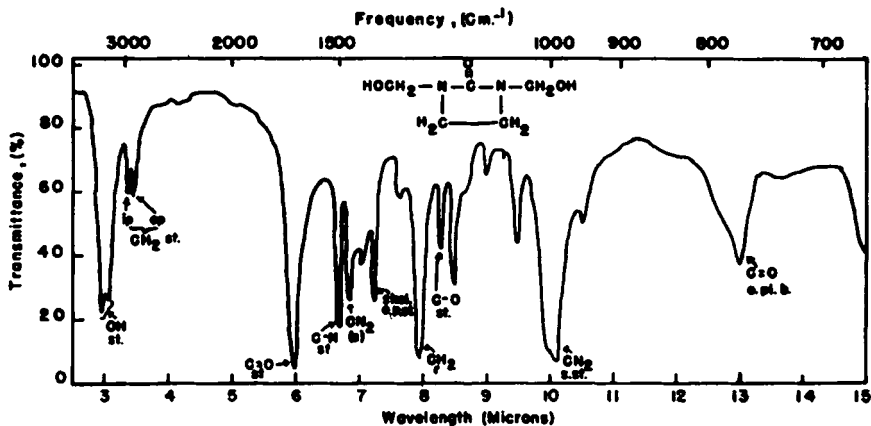


Fig. 1. Infrared spectrum of DMEU crystals by KBr disk method: (st) stretching; (i.p.) in phase; (o.p.) out of phase; (a) antisymmetric stretching; (r) rocking; (s.st.) symmetric stretching; (o.p.l.b.) out of plane bending.

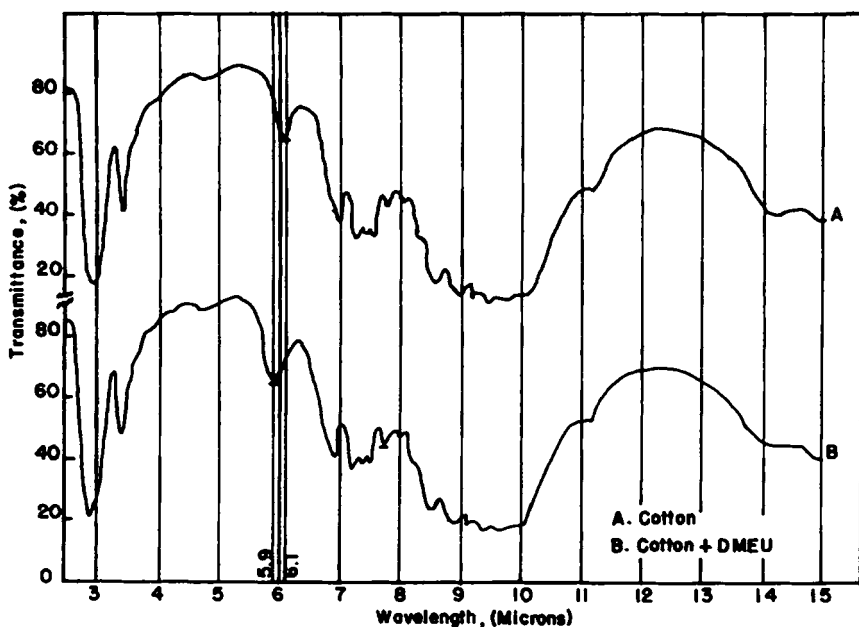


Fig. 2. Infrared spectra of untreated cotton and of cotton treated with DMEU in the absence of a catalyst. Underlining indicates observed changes in spectra.

in the presence of $0.03M$ $CuCl_2$ or $CdCl_2$ and cured at $160^\circ C$. Included, also, in this study was the product formed when DMEU and $CdCl_2$ reacted in the absence of the cellulose. The infrared absorption spectrum of DMEU crystals is shown in Figure 1. The spectra of Figure 2 are of the

untreated control and of cotton treated with DMEU in the absence of a catalyst. These are reproduced from an earlier paper¹ for purposes of comparison. The carbonyl stretching for DMEU crystals has been assigned to the band at 5.98μ and the C—N vibrations to that occurring at 6.65μ . Treatment of cotton with DMEU when no catalyst was used resulted in the disappearance of the absorbed water band occurring at 6.10μ in native cellulose, the appearance of a broad absorption at 5.95μ due to

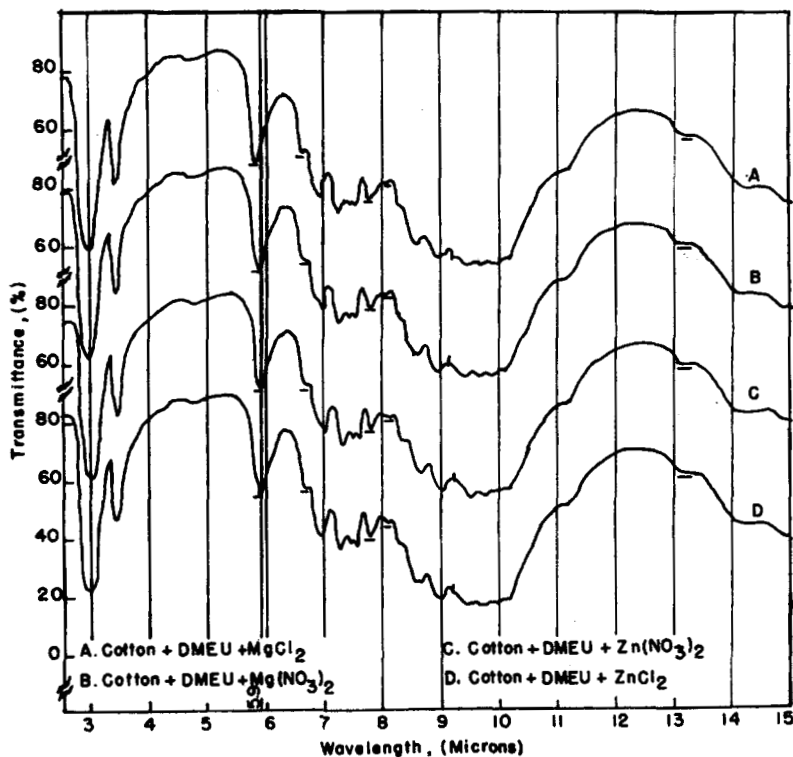


Fig. 3. Infrared spectra of cotton treated with DMEU in the presence of 0.1 M of various inorganic salt catalysts. Underlining indicates observed changes in spectra as a result of the presence of the catalyst.

the C=O stretching, and a slight broadening of the band at 7.78μ ascribed to OH deformation and/or CH₂ wagging in untreated cellulose.¹

In Figure 3 it can be noted that the addition of 0.1M of any of the Zn or Mg salt catalysts resulted in a sharpening and a shift of the C=O band to slightly shorter wavelengths (5.89 – 5.90μ), representing a total shift of 23 – 26 cm.^{-1} from the C=O band occurring in DMEU crystals at 5.98μ . In addition, Figure 3 shows: (a) the appearance of a shoulder at 6.65 – 6.75μ , attributed to a C—N vibration, (b) a further broadening of the peak at approximately 7.8μ and almost complete disappearance of the absorption

at 8.1μ , and (c) the indication of a shoulder at 13.10 – 13.30μ . These changes confirm those observed at the $0.03M$ catalyst concentration¹ and have again been interpreted as indicative of the formation of nitrogen-to-metal bonds and, thus, the existence of a coordination complex between the DMEU and catalyst.

The presence of the metal ion in the product was confirmed by quantitative Mg and Zn determinations on the treated samples which had received (a) only a mild alkaline afterwash (i.e., 0 launderings), (b) one laundering, and (c) 15 home-type launderings. The percentages of metal ions remaining on the treated fabrics are recorded in Table I. Because cotton itself, as well as the tap water used in laundering, contains Mg, it is difficult to establish accurately the origin of the Mg remaining in the treated fabric. Its presence, however, is definitely established by the analytical data of Table I which show only slight losses in the metal ion concentration as a result of laundering. In addition, after the first laundering, there is essentially no further change in the metal ion concentration as a result of further washing. In the case of $MgCl_2$, the apparent increase with additional laundering may be due to Mg ions in the tap water used.

TABLE I
Concentration of Metal Ion Remaining after Laundering in Cotton Printcloth Treated with DMEU in Presence of $0.1M$ Catalyst

No. of launderings	Mg, %		Zn, %			
			ZnCl ₂		Zn(NO ₃) ₂	
	MgCl ₂ ^b	Mg(NO ₃) ₂ ^b	(b)	(c)	(b)	(c)
0 ^a	0.18	—	0.13	0.23	0.33	0.47
1	0.13	0.12	0.28	0.18	0.36	0.19
15	0.18	0.08	0.29	0.16	0.32	0.20

^a Sample given only mild alkaline afterwash.

^b Analytical determination.

^c Spectrographic determination.

Figure 4 shows similar infrared absorptions of cotton specimens treated in the presence of $0.03M$ $CuCl_2$ and $CdCl_2$. In both cases the carbonyl band has again been shifted to higher frequencies, a peak appears at 6.67μ , the band at 7.78μ is slightly broadened, and a shoulder is indicated at 13.1 – 13.3μ . These shifts in the characteristic peaks of their absorption spectra were in the same direction as those noted when Zn and Mg salts catalyzed the reaction.

The reaction product of the DMEU– $CdCl_2$ system in the absence of cellulose produced the infrared absorption spectrum of Figure 5. It will be noted that there is a broad carbonyl band which has been shifted to higher frequencies (5.86 – 5.94μ), a shift of 11 – 34 cm.^{-1} from that occurring at 5.98μ in the spectrum of the DMEU crystals. The direction of the $C=O$

shift is in agreement with that noted when the cellulose was present, is indicative of the formation of nitrogen-to-metal bonds and thus indicates the formation of a complex between DMEU and the metal ion.

Absorptivities, calculated by the base line technique, were corrected for specimen add-ons, and sample weights contained in KBr disks. These cor-

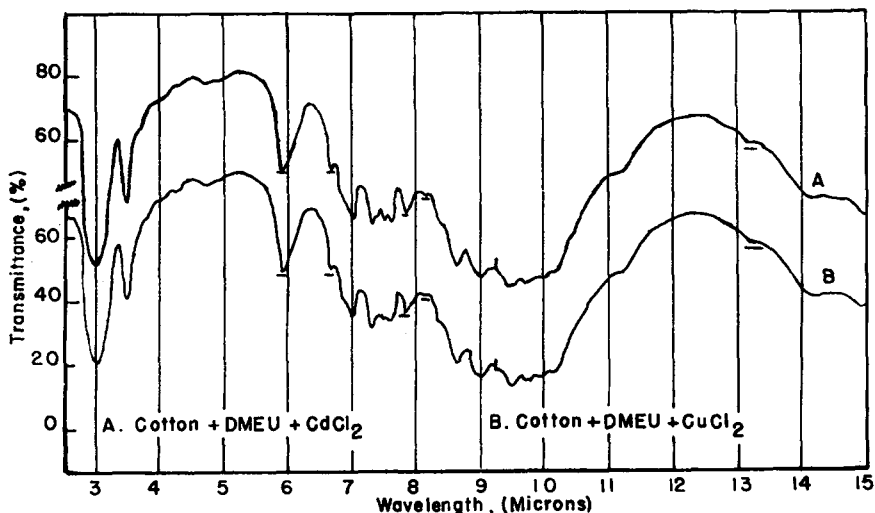


Fig. 4. Infrared spectra of cotton treated with DMEU in the presence of (1) 0.03 M CdCl₂ or (2) 0.03 M CuCl₂. Underlining indicates changes in spectra as a result of treatment.

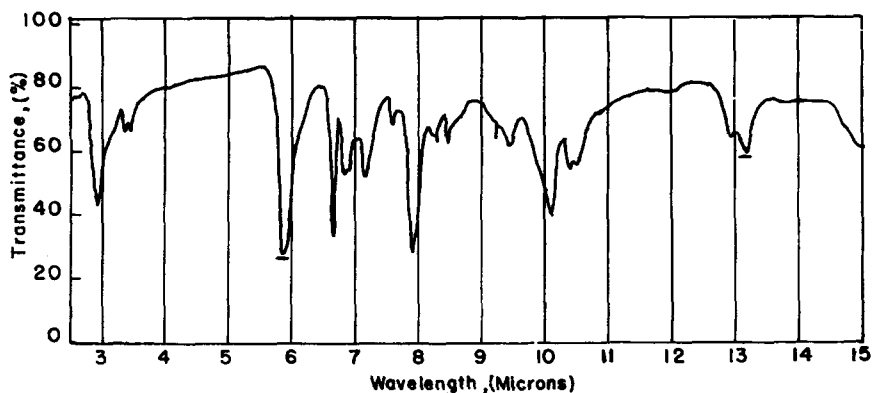


Fig. 5. Infrared spectrum of the reaction product of the DMEU-CdCl₂ system.

rected absorptivities, plotted in Figure 6 at different band positions for each of the specimens treated in the presence of 0.1M of Mg and Zn salts, show the effect of the treatment to be similar to that observed at the 0.03M catalyst level. (a) No shift occurred in the 3 μ or OH region as a result of

treatment, but absorptivities of the specimens treated in the presence of a catalyst were lower than those of the control and of the cotton specimen treated with DMEU when no catalyst was present. (b) There is very little change in the absorptivities in the 3.44μ or C—H region, but a considerable decrease in them at the 6.99μ region (CH_2 wagging in cotton cellulose). (c) No appreciable effect is noted at the 7.45μ absorption which is due to OH in-plane deformation. (d) However, DMEU treatment, in general, was accompanied by decreases in absorptivities in the 8.1 , 8.6 , 9.0 , 9.5 , and 11.1μ regions which, in untreated cellulose, have all been associated with CH_2 , C—O, OH, C—OH, antisymmetric in-phase ring stretching and C_1 group frequency vibrations.¹ Thus, the observed changes in absorptivities again seem to indicate preferential reaction at the primary alcohol group of the anhydroglucose unit. Changes in absorptivity of the OH stretching

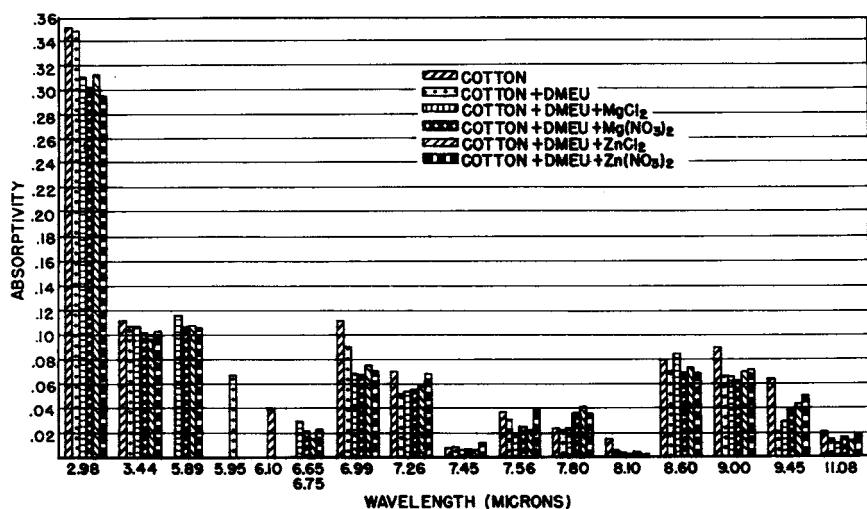


Fig. 6. Comparison of absorptivities of untreated cotton and of cotton treated with DMEU in the presence of various inorganic salt catalysts. Catalyst concentration = 0.1 M.

and CH_2 wagging bands (3.0 and 6.99μ respectively) have been evaluated as described¹ in Part I. The corrected absorptivities at 3.0 and 6.99μ for untreated cotton have been taken as initial measures of total hydroxyl groups and primary hydroxyl groups, respectively. Those for DMEU-treated samples have been taken as measures of total and primary hydroxyl concentrations remaining after reaction. Differences between the initial and final hydroxyl concentrations yield an estimate of the amounts of primary and total hydroxyls which have reacted during treatment. At the $0.03M$ concentration of all salts except $\text{Zn}(\text{NO}_3)_2$, the number of total hydroxyls reacted (millimoles per gram) as determined from decreases in absorptivities at 3μ was approximately equal to the number of primary hydroxyl groups reacted (millimoles per gram) as determined¹ from de-

TABLE II. Reactivity of Hydroxyl Groups at 0.1M Catalyst Concentration

	Absorptivities at:		Primary OH reacted		Total OH reacted		Secondary OH reacted	DMEU/HCHO crosslinks
	3 μ	6.99 μ	mm./g.	%	mm./g.	%		
Cotton ^a	0.338	0.111						
C + DMEU ^a	0.346	0.089	1.22	20.57	0.70	3.93	—	0.50
C + D + MgCl ₂	0.311	0.068	2.32	39.11	1.49	8.9	0	0.57
C + D + Zn(NO ₃) ₂	0.296	0.071	2.17	36.59	2.29	12.87	0	0.64
C + D + Mg(NO ₃) ₂	0.302	0.068	2.35	39.62	1.99	11.18	0	0.56
C + D + ZnCl ₂	0.313	0.075	1.99	33.55	1.39	7.81	0	0.74

^a Values taken from Table VII of Part I.¹

TABLE III. Physical Properties of 80 × 80 Cotton Printcloth Treated with 8% Aqueous DMEU in the Presence of 0.03M Catalyst

Catalyst	Breaking strength (warp), lb.	Elongation at break (warp), %	Crease angles (W + F),		Chlorine damage by breaking strength			Order of protection from Cl damage
			(W + F),		Cl (only), lb.	Cl + Se, lb.	Ret., %	
			Dry	Wet				
MgCl ₂ ^a	27.7	6.7	296	261	27.7	28.0	101.0	1
MgCl ₂ after 15 laund.	25.0	6.6	283	251	30.8	19.5	63.0	2
ZnCl ₂ ^a	29.5	6.5	277	251	31.1	15.9	51.0	3
ZnCl ₂ after 15 laund.	28.6	7.5	261	238	35.4	7.7	22.0	3
CdCl ₂	36.7	8.2	259	215	34.6	8.7	25.0	4
CdCl ₂ after 15 laund.	43.1	10.0	234	223	35.7	3.3	9.0	4
CuCl ₂	28.7	6.2	277	249	26.4	26.0	98.0	2
CuCl ₂ after 15 laund.	29.9	6.7	300	257	28.1	20.6	73.0	1

^a Values taken from Table V of Part I.¹

creases in absorptivities at 6.99μ . Only with $\text{Zn}(\text{NO}_3)_2$ did the decrease in total hydroxyls significantly exceed the decrease in primary hydroxyls. In this investigation it was again found that the decrease in total hydroxyl groups was equal to the decrease in number of primary hydroxyl groups when $0.03M$ CuCl_2 or CdCl_2 catalyzed the reaction. The striking parallel in these two quantities at the $0.03M$ catalyst level suggests that, no matter where the truth lies in this debatable question, there can be no doubt that the two quantities are intimately related to each other and have a common origin. Similar data showing the decreases in hydroxyl groups at the $0.1M$ catalyst concentration are recorded in Table II. These data indicate that reaction with primary hydroxyls was in every case less than at the $0.03M$ catalyst level. Also, at this higher catalyst concentration, the calculated number of total hydroxyls that reacted was less than the calculated number of primary hydroxyls in every case except that of $\text{Zn}(\text{NO}_3)_2$. This probably indicates less crosslinking by monomers or at least that some O—H or N—H groups are formed simultaneously as the primary hydroxyl groups of cellulose react at the higher catalyst concentration. The results are similar to those obtained at the $0.03M$ catalyst concentration in that the percentage of hydroxyl groups reacting, as calculated from infrared data, exceeds that determined from nitrogen analyses as necessary for reaction with DMEU. Again, therefore, it is postulated that some of the hydroxyls have reacted with liberated formaldehyde and some with DMEU. An alternative explanation may be that the absorptivity at 6.99μ of untreated cotton is not a measure of all primary hydroxyls but only of an undetermined portion of the total primary hydroxyls of cellulose.

Preliminary analyses of the product of the CdCl_2 -DMEU reaction carried out in the absence of cellulose showed the presence of 3.31% H, 20.00% C, and 7.99% N. Theoretical values of these three elements based on a 1:1:1 ratio of DMEU, CdCl_2 , and HCHO in the complex are 3.33% H, 19.98% C, and 7.77% N.

The importance of the metallic complex in the problem of chlorine scorch damage is reflected in other physical test data obtained for cotton specimens treated with DMEU in the presence of $0.03M$ CdCl_2 , CuCl_2 , MgCl_2 , or ZnCl_2 (See Table III). Data are shown for samples which had been given only the mild alkaline afterwash as well as for those which had received an additional 15 home-type launderings.¹ It will be noted that prior to chlorination the properties of all of the treated specimens, regardless of the catalyst employed, were of the same order of magnitude and were equally good. After chlorination and scorch, however, samples could be separated according to the degree of protection against chlorine damage afforded by the different metal ions in the catalysts. The last column of Table III provides rankings based upon the amount of protection against chlorine damage and, proceeding from greatest to least, shows the catalysts to assume the following order: $\text{Mg} \geq \text{Cu} > \text{Zn} > \text{Cd}$. Similar rankings are assumed by the catalysts if their dry crease angles after 15 launderings are used as a basis for comparison. Data in Table III, therefore, also indi-

cate some correlation between the durability of the crosslink formed and the degree of protection afforded by the catalyst against chlorine damage. The catalyst which provides the highest dry crease angle after laundering shows the greatest resistance to damage. Data in Part I indicated that chlorine damage was caused during heating by a free-radical mechanism. The data of Table III tend to confirm these earlier observations since, if ranked according to their ability to act as free-radical traps, the metals would assume the same order as indicated above.

Further support of the free-radical mechanism was obtained through a series of experiments with ultraviolet radiation. A specimen of 80 × 80 cotton printcloth which had been treated with DMEU in the presence of 0.03M ZnCl₂ by the procedure described earlier¹ was given 15 home-type launderings, then subdivided into 6 specimens, and given further treatment as follows: (a) none, (b) chlorinated, (c) chlorinated and scorched by AATCC method, (d) chlorinated and exposed to ultraviolet light for 20

TABLE IV
Effects of After-treatment on Strength and Elongation*

Sample no.	After-treatment	Breaking strength (warp), lb.	Elongation at break (warp), %
1	DMEU control (R)*	36.7	7.5
2	R + chlorinated (R + Cl)	35.2	7.9
3	R + Cl + scorched	6.7	—
4	R + Cl + exposed to U.V.	15.1	5.3
5	R + Cl + oven-cured at 98°C.	36.0	7.5
6	R + exposed to U.V.	37.6	7.7

* 80 × 80 printcloth treated with 8% DMEU in the presence of 0.03M ZnCl₂, dried at 60°C., cured at 160°C., process-washed, and laundered 15 times. R = resin.

min., (e) chlorinated and heated in an oven at 98°C. for 20 min., and (f) exposed to ultraviolet light for 20 min. The temperature attained upon exposure to the ultraviolet lamp for 20 min. was 98°C. Breaking strengths and elongations at break determined on each of the treated specimens are recorded in Table IV. Chlorination alone had no deleterious effect upon the strength and elongation at break of the resin-treated fabric, a result which confirms earlier findings.¹ Nor did exposure to the ultraviolet lamp for 20 min. or subsection for a similar time to a temperature comparable to that attained by the fabric when subjected to ultraviolet radiation (98°C.) have any effect upon these fabric properties. However, those specimens which had been chlorinated and subsequently scorched (at 365°F. for 30 sec.) or had been chlorinated and then exposed to the ultraviolet light became yellow in color and did suffer extensive loss of breaking strength and a considerable decrease in elongation at break. Photochemical dissociation is a well-known method of producing radicals, and the behavior exhibited

by the samples exposed to the ultraviolet light indicates that a free-radical reaction has been initiated by the ultraviolet radiation. Similarity of effects between chlorinated samples exposed to ultraviolet light and those subjected to scorching indicate a similar mechanism, thus supporting the conclusion that chlorine damage during heating is a result of the formation of free radicals.

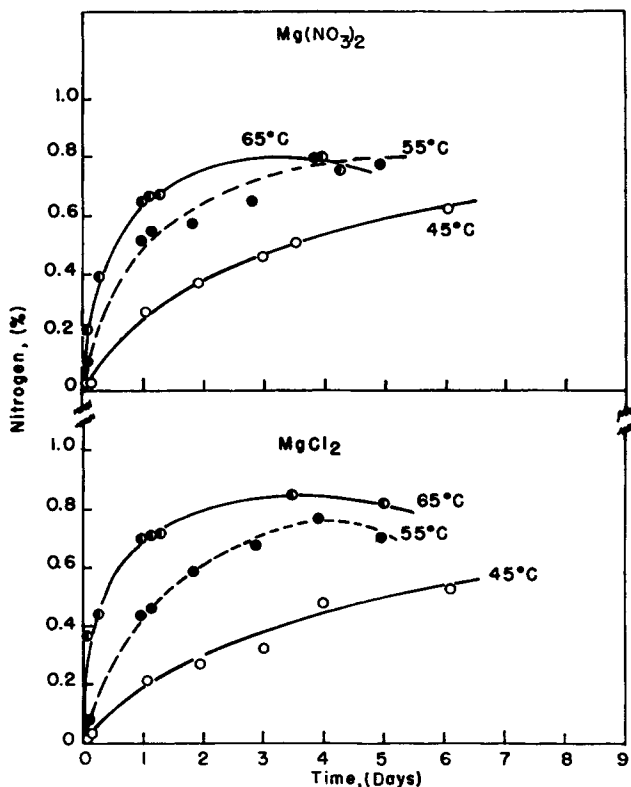


Fig. 7. Changes in nitrogen content with reaction time for cotton treated with DMEU in the presence of .03 M magnesium salts at 45, 55, and 65°C.

Reaction rates at 45, 55, and 65°C. for the cellulose-DMEU reaction when catalyzed by 0.03M MgCl₂, Mg(NO₃)₂, ZnCl₂, or Zn(NO₃)₂ were determined by following changes in nitrogen and formaldehyde contents as well as changes in crease recovery properties of the treated cotton printcloth. Figure 7 shows the change in nitrogen content with time at each of the three temperatures for the Mg salts. Based upon previous findings at high temperature of cure, the maximum amount of bound nitrogen obtained under the existing experimental conditions was approximately 1.0% when a catalyst at either 0.006, 0.03, or 0.10M concentration was used and 0.5% when no catalyst was present. In Figure 8 typical curves for the Mg salt

catalysts show the reaction to be pseudo first order when followed to $\frac{2}{3}$ completion, based upon these nitrogen contents. Similar treatment of data obtained with catalysis by zinc salts showed the reactions also to be pseudo first order when followed to $\frac{2}{3}$ completion. However, the faster rates of reaction with both zinc salts necessitated sampling for analysis at much shorter time intervals as the reaction reached $\frac{2}{3}$ completion within a matter of hours rather than days. Similarly shaped curves were obtained

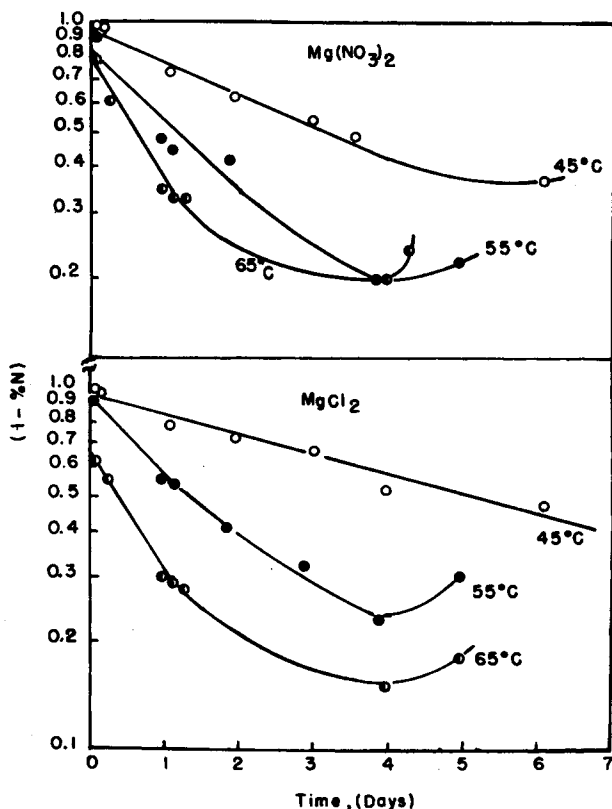


Fig. 8. Typical semilogarithmic graphs of (1-% N.) vs. reaction time for cotton treated with DMEU in the presence of 0.03 M magnesium salt catalysts.

when changes in formaldehyde content and dry crease recovery properties of the treated fabrics were examined. The maximum formaldehyde content at completion of the reaction at high temperature of cure, obtained in earlier work, was 2.3% when a catalyst was employed and 0.6% when one was not. When fabric treated at the 0.03M catalyst concentration was cured at 160°C., the ratio of per cent formaldehyde to per cent nitrogen, determined analytically, was always approximately 2.1, regardless of catalyst used. This ratio corresponds to what would result from monomeric

crosslinks of DMEU. In the low-temperature rate studies, it was of interest to note that the ratio was greater than 2 only in the early stages of the reactions catalyzed by the zinc salts. With all other products the ratio varied from 1.5 to 1.8, and indicates polymeric links, probably some dimeric crosslinks which would give a ratio of 1.1 accompanied by some formaldehyde crosslinks. Maximum dry crease angles previously obtained were 290° (W + F) in the former case and 200° (W + F) in the

TABLE V
Specific Reaction Rate Constants for Cellulose-DMEU Reaction in Presence of Various 0.03M Inorganic Salt Catalysts

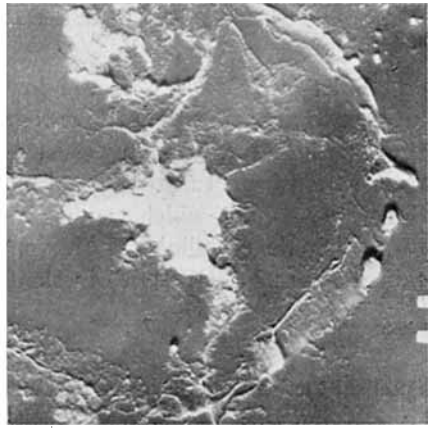
Catalyst	Temp., °C.	N, %	Specific reaction rate constants, $k \times 10^6 \text{ min.}^{-1}$ based upon	
			HCHO, %	Dry crease angles
None (DMEU alone)	45	1.9	2.5	—
	55	4.3	3.4	—
	65	11.6	8.0	—
MgCl ₂	45	8.8	9.4	7.5
	55	32.1	20.6	19.5
	65	50.9	37.0	44.7
Mg(NO ₃) ₂	45	13.7	9.9	7.0
	55	31.1	29.9	15.3
	65	52.0	31.6	52.4
ZnCl ₂	45	67.2	27.0	211
	55	63.3	89.2	131
	65	229.0	335.0	128
Zn(NO ₃) ₂	45	444	288	220
	55	519	397	472
	65	640	397	744

latter. Specific reaction rate constants computed by the method of least squares on the basis of a first-order reaction over $\frac{2}{3}$ of the reaction are shown in Table V, and relative rates calculated from them by using the rate of MgCl₂ as a basis are recorded in Table VI. The catalysts, when ranked according to greatest to least effect upon the reaction rates, follow the order: Zn(NO₃)₂ > ZnCl₂ > MgCl₂ = Mg(NO₃)₂. It is also evident that, as the reaction temperature was increased from 45 to 65°C. differences between the relative rates obtained with Zn and Mg salts diminished.

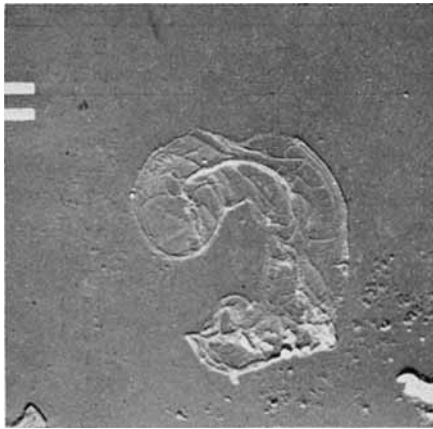
Additional evidence of the differing rates of reaction when Mg or Zn salt catalysts were employed was afforded by microscopical examination of the swelling behavior of the treated fibers which had been immersed for 30 min. in cuene or had been subjected to staining with osmium tetroxide. It has been found at this laboratory that the extent of combination of the crosslinking agent with the cellulosic molecule is reflected by the degree of swelling and dissolution of the treated fibers.⁵⁻⁷ Figure 9a shows the cross



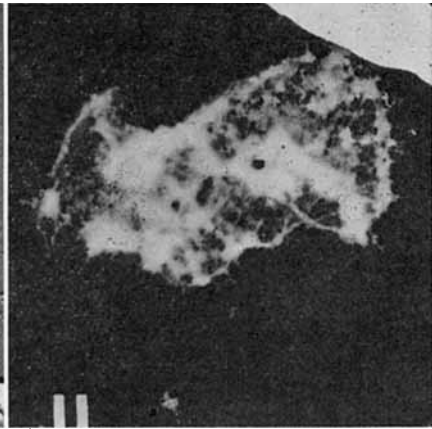
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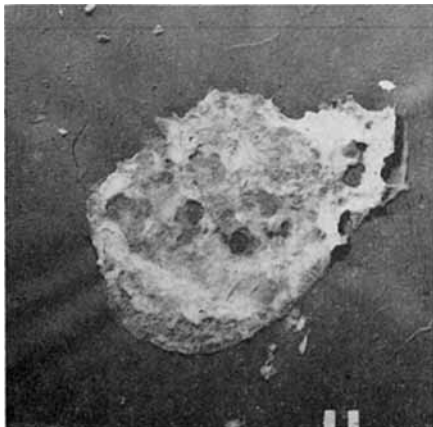
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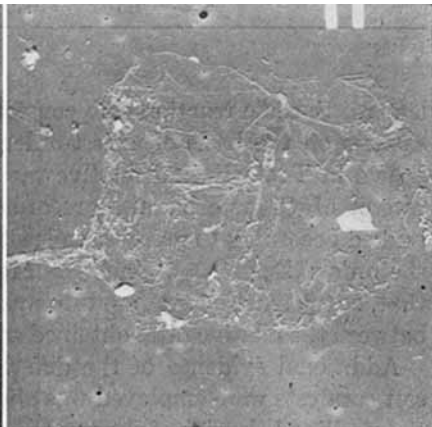
(1)



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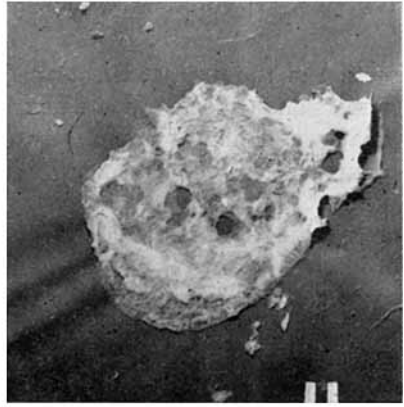
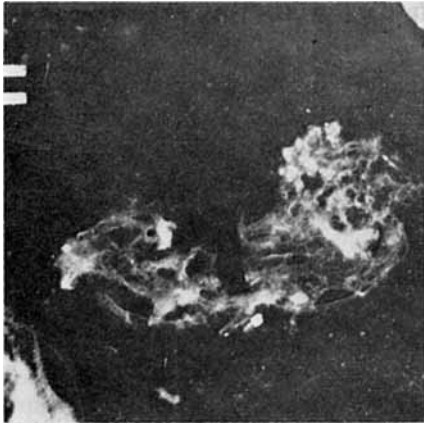


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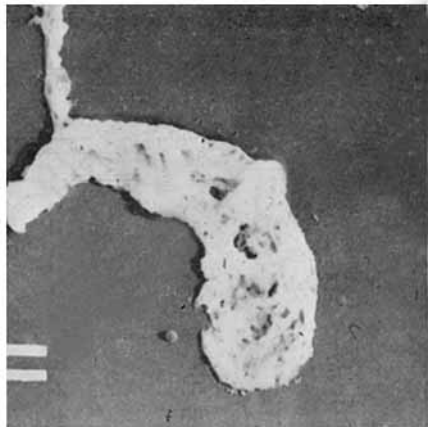
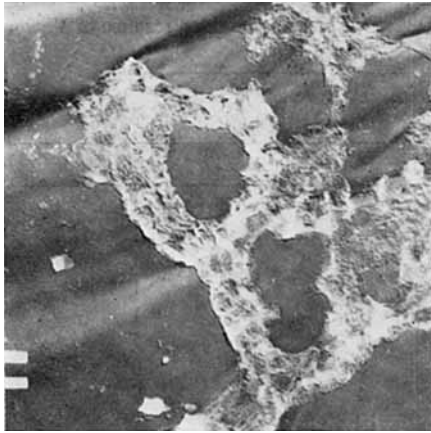


(4)

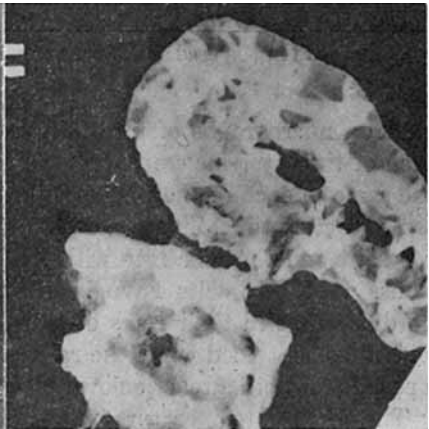
Fig. 9. Electron micrographs of ultrathin sections of the cotton fiber: (9A) untreated cotton fiber; (9B) untreated cotton fiber after 30 min. immersion in cupriethylenediamine, (9C) cotton fiber treated at 45°C. with DMEU in the presence of 0.03M of the designated catalyst (reaction time = approximately 200 min.) after 30 min. immersion in Cuene. Catalysts: (1) $Mg(NO_3)_2$; (2) $Zn(NO_3)_2$; (3) $ZnCl_2$; and (4) $MgCl_2$. Magnification 3240 \times .



45°C.



55°C.



65°C.

(A)

(B)

Fig. 10. Electron micrographs taken after 30 min. immersion in Cuene of ultrathin sections of cotton fiber treated with DMEU in the presence of 0.03 M MgCl_2 and 0.03 M $\text{Zn}(\text{NO}_3)_2$ at 45, 55, and 65°C. (10A) MgCl_2 at reaction time of 1500 minutes; (10B) $\text{Zn}(\text{NO}_3)_2$ at reaction time of 200 min. Magnification: 3240 \times .

section of the untreated cotton fiber and Figure 9b shows the fiber after immersion in cuene. When no treatment has been applied, the fiber swells greatly and almost completely dissolves in cuene. When reaction has occurred, the cellulosic material is not dissolved but swells to a degree dependent upon the frequency of the crosslinks formed. With extensive crosslinking there is little swelling and dissolution. In these studies it is of interest to note that, even at the lowest temperature and shortest time, some very slight amount of crosslinking has occurred with each catalyst. Owing to differing rates, the extent of reaction as the catalysts vary should differ and, then, presumably should be reflected by varying degrees of crosslinking in cross-sectional views of the treated fibers. Figure 9c shows

TABLE VI
Relative Reaction Rates of the Cellulose-DMEU Reaction in the Presence of Various
0.03M Inorganic Salt Catalysts

Catalyst	Temp., °C.	Relative reaction rates* based upon:		
		N, %	HCHO, %	Dry crease angle
MgCl ₂	45	1	1	1
	55	1	1	1
	65	1	1	1
Mg(NO ₃) ₂	45	1	1	1
	55	1	1	1
	65	1	1	1
ZnCl ₂	45	8	3	30
	55	2	4	6
	65	4	10	3
Zn(NO ₃) ₂	45	50	30	30
	55	20	20	23
	65	10	10	16

* Rates with MgCl₂ used as basis of comparison.

electron micrographs of ultrathin sections of fiber treated at 45°C. with each of the catalysts employed. The time of reaction was approximately the same in each of the photographs, 200 min. It is obvious that for the same reaction time, Zn salts promote a greater amount of crosslinking than Mg salts and that the rate with Zn(NO₃)₂ exceeds all others. Cross sections, when Mg salts have been used as catalysts, appear to indicate no differences in their rates of reaction. These results are in agreement with those obtained when the relative rates were determined by assuming a pseudo first-order reaction over $\frac{2}{3}$ completion.

The effect of temperature on the rate of reaction may be discerned from the cross-sectional views of treated fibers shown in Figure 10. Figure 10a shows the cross sections of samples treated in the presence of MgCl₂ catalyst for approximately 1500 min., and Figure 10b shows similar sections with Zn(NO₃)₂ catalyst for approximately 200 min. It is evident that in-

TABLE VII
 Enthalpies, Entropies, and Free Energies of Activation at 45°C. of the Cellulose-DMEU Reaction in the Presence of Various 0.03M Inorganic Salt Catalysts

Catalyst	Enthalpy ΔH^* , kcal./mole, based on:			Entropy ΔS^* , cal./mole, based on:			Free energy ΔF^* , kcal./mole, based on:		
	% N kcal	% HCHO	Crease angle	% N	% HCHO	Crease angle	% N	% HCHO	Crease angle
MgCl ₂	19.3	15.2	19.7	-26.6	-39.4	-24.8	27.7	27.7	27.8
Mg(NO ₃) ₂	14.8	14.7	22.3	-40.0	-40.6	-17.5	27.5	27.7	27.9
ZnCl ₂	13.6	27.8	5.6	-40.5	+2.7	-63.4	26.1	27.0	25.8
Zn(NO ₃) ₂	4.0	3.5	13.4	-66.8	-69.2	-38.6	25.3	25.6	25.7

creasing the temperature from 45 to 65°C. caused an increase in the extent of crosslinking because of the faster reaction rate but that the differences between the amounts of crosslinking (i.e., extent of reaction) at the higher temperatures (between 55 and 65°C.) diminished, indicating that the rates of reaction become more nearly alike, a result observed from the relative rates computed earlier on the basis of a pseudo first-order reaction.

Ultrathin sections in some instances have indicated two types of swelling. Some sections ballooned and became thin, having the appearance of having been crosslinked in the swollen condition; others swelled only slightly, a large amount of material remaining, and had the appearance of having been crosslinked in a dry or collapsed state. The two types of swelling indicate that two types of crosslinks are present in the structure of the treated fibers.

Enthalpies, entropies, and free energies of activation of the system computed at 45°C. from the data are recorded in Table VII. The enthalpy of activation, ΔH^* , was calculated from the following formula:

$$k = (PZ) \exp \left\{ -\Delta H^*/RT \right\}$$

where k is the specific reaction rate constant (PZ) is the frequency factor, R is the molar gas constant, and T is the absolute temperature. The graph of $\log k$ versus $1/T$ was linear and, from the slope of the least-square line through the data, ΔH^* was computed.

The entropy of activation was computed from the equation:

$$\Delta S^* = R[\ln k_1 - \ln(KT/h) + \Delta H^*/RT - 1]$$

where k_1 is the specific reaction rate constant in reciprocal seconds, ΔH^* is the enthalpy of activation obtained from the slope of the line through the graph of $\ln k$ versus $1/T$, R , K , and h are the molar gas, Boltzman, and Planck constants, respectively.

The free energy of activation was calculated from the relationship:

$$\Delta F^* = \Delta H^* - T\Delta S^*$$

The free energies of activation when Mg salts catalyze the reaction are essentially equal and slightly exceed those obtained when Zn salts were employed, that for $ZnCl_2$ being about 1 kcal. greater than that of $Zn(NO_3)_2$. Although ΔF^* does not vary greatly with the catalyst, the widely different entropy changes confirm the hypothesis that the metal ion enters the reaction, forming a transition state complex. The free energies of activation (ΔF^*) for all of the catalysts except $ZnCl_2$ are the same, regardless of the method by which they were determined. Enthalpies and entropies of activation, however, vary according to whether changes in nitrogen or formaldehyde contents or crease angles were followed. This seems to suggest different reaction mechanisms with respect to the complex formation as the catalyst varies. If one assumes that the change in bound nitrogen is indicative of the ease with which DMEU crosslinks are formed and the change in formaldehyde as indicative of the ease of formation of formal-

dehyde-type crosslinks as well as of DMEU crosslinks, then it would appear that $\text{Mg}(\text{NO}_3)_2$ and ZnCl_2 behave similarly with respect to DMEU crosslinks. Comparatively, the restrictions upon the freedom of motion of the molecules of the activated complex involving the DMEU crosslinks are least when MgCl_2 catalyzes the reaction and greatest when $\text{Zn}(\text{NO}_3)_2$ is employed. On the other hand, formaldehyde entropy changes show a similarity between the two Mg salts and indicate that the restrictions upon the freedom of motion of the molecules of the activated complex involving the formaldehyde-type crosslinks are least in the case of ZnCl_2 and greatest in the case of $\text{Zn}(\text{NO}_3)_2$. The greater the increase in disorder of the transition state complex over that of the reactants, the greater the entropy change; and the greater the entropy change, the more loosely bound the complex. Consideration of entropy changes for each catalyst, as determined from both nitrogen and formaldehyde contents, seems to indicate that with MgCl_2 the DMEU transition state complexes are more loosely bound or less ordered than the formaldehyde-type. With $\text{Mg}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$, both types of complexes are equally ordered. With ZnCl_2 , however, the formaldehyde-type complex seems to be more loosely bound and is the only one showing an increase in entropy over the reactants. This suggests the possibility that dissociation of the activated complexes occurs by the breaking of different bonds, depending upon the catalyst employed.

Consideration of only the enthalpies of activation computed from changes in dry crease recovery properties would lead to an apparent reversal in the rates of the reaction when catalyzed by zinc salts. That is, it appears from these data that ZnCl_2 , having the smallest enthalpy of activation, would proceed at a faster rate than the reaction catalyzed by $\text{Zn}(\text{NO}_3)_2$ if entropies of activation were neglected. However, the higher negative entropy change obtained in the case of ZnCl_2 would indicate that the reactant molecules must experience a greater increase in orientation when ZnCl_2 catalyzes the reaction. These results do not appear to be in accord with those observed with changes in nitrogen and formaldehyde content. It is conceivable, however, that these apparent discrepancies are due to the fact that crease recovery properties result from the formation of both DMEU and formaldehyde-type crosslinks, and since nitrogen and formaldehyde data suggest the possibility of different mechanisms for the dissociation of the activated complexes with the different catalysts, changes in crease angles might not necessarily accurately reflect the reaction mechanism. It is realized that additional research is needed to determine accurately the extent of reaction of cellulose with formaldehyde as well as with formaldehyde donors, and to establish the exact nature of the transition state complexes between metallic ions and the reagent, before definite conclusions may be drawn. Nevertheless, the above data definitely establish the metallic complex as an important intermediate in the treatment of cotton with DMEU to produce "durable wash-wear finishes." Emphasis in future work will be placed upon spectrophotometric methods of evaluating these transition state complexes.

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Synopsis

In a continuation of a previously reported investigation into the effect of the catalyst in the cotton cellulose-DMEU reaction, experiments were performed in which the four inorganic salt catalysts originally studied, $MgCl_2$, $Mg(NO_3)_2$, $ZnCl_2$, and $Zn(NO_3)_2$, were employed at the higher metal ion concentration of 0.1M, and $CuCl_2$ and $CdCl_2$ were employed at 0.03M concentration. Data from infrared absorption spectra of the treated cotton products were in agreement with those obtained at the 0.03M catalyst concentration, again indicating that the catalyst entered into the reaction, forming a coordination complex through the formation of nitrogen-to-metal bonds between the catalyst and the DMEU molecule. Similarly, it was again indicated that reaction with DMEU takes place preferentially at the primary alcohol group of the anhydroglucose unit. Analyses of IR data indicated a higher degree of crosslinking, and thus fewer terminal O—H or N—H groups at the 0.03M catalyst than at the 0.1M catalyst concentration. Further evidence of complex formation was obtained from infrared spectra of the product of the $CdCl_2$ -DMEU reaction carried out in the absence of cellulose. Supplemental physical data obtained on products of reactions catalyzed with $CdCl_2$ and $CuCl_2$ at the 0.03M level, when compared with those obtained on products catalyzed with $MgCl_2$ and $ZnCl_2$, supported the earlier hypothesis that chlorine damage during heating was dependent upon the ability of the metallic complex to act as a free-radical trap. Additional support for the free-radical mechanism was obtained when treated cloth subjected to chlorination and exposed to ultraviolet radiation suffered the same discoloring and degradative effect as cloth chlorinated and subsequently scorched according to the usual AATCC method. Reaction rates of the cellulose-DMEU reaction at 45, 55, and 65°C. with each of the four catalysts at the 0.03M concentration were determined by following changes both in nitrogen and formaldehyde content as well as in crease recovery properties. The reaction was found to be pseudo first order when followed to $\frac{2}{3}$ completion, and the catalysts, when ranked according to greatest to least effect upon the reaction rates, followed the order: $Zn(NO_3)_2 > ZnCl_2 > MgCl_2 = Mg(NO_3)_2$. Enthalpies, entropies, and free energies of activation have confirmed the earlier hypothesis that the metal ion enters into the reaction, forming a transition state complex.

Résumé

Pour faire suite aux travaux sur l'effet du catalyseur dans la réaction de la cellulose de coton DMEU, des nouvelles expériences ont été effectuées dans lesquelles les quatre catalyseurs inorganiques étudiés antérieurement: $MgCl_2$, $Mg(NO_3)_2$, $ZnCl_2$ et $Zn(NO_3)_2$ ont été employés à des concentrations en ion métallique plus élevée, de $0.1M$ et les $CuCl_2$ et $CdCl_2$ à une concentration de $0.03M$. Les données du spectre d'absorption I.R. du coton traité étaient en accord avec ceux obtenus à une concentration en catalyseur de $0.03M$; ceci indiquait que le catalyseur prenait part à la réaction en formant un complexe de coordination par un lien métal-azote entre le catalyseur et la molécule DMEU. De même, il fut montré que la réaction avec DMEU prenait place préférentiellement sur le groupe alcool primaire de l'unité anhydroglucose. Les données de l'analyse I.R. indiquent un plus haut degré de pontage et aussi moins de groupes terminaux OH et NH à une concentration $0.03M$ en catalyseur qu'à une concentration en catalyseur de $0.1M$. On obtenait une autre évidence de la formation de complexe grâce au spectre I.R. du produit provenant de la réaction $CdCl_2$ -DMEU effectuée en l'absence de cellulose. Les données physiques supplémentaires obtenues sur les produits de réaction catalysées par $CdCl_2$ et $CuCl_2$ à concentration $0.03M$ comparées à celles obtenues sur les produits de réaction catalysées par $MgCl_2$ et $ZnCl_2$ confirment l'hypothèse antérieure que la détérioration due au chlore durant le chauffage dépendait de la capacité du complexe métallique à piéger les radicaux libres. Un argument additionnel pour le mécanisme par radicaux libres était obtenu quand le tissu soumis à la chloration et exposé aux radiations U.V. subissait la même décoloration et le même effet de dégradation que celui qui avait été chloré et subséquemment brûlait superficiellement, ceci étant en accord avec la méthode usuelle AATCC. Les vitesses de réaction de la cellulose-DMEU à 45 , 55 et $65^\circ C$ avec chacun des quatre catalyseurs à une concentration $0.03M$ ont été déterminées en suivant les changements dans la teneur en azote et formaldéhyde aussi bien que dans les modifications des propriétés de récupération. La réaction était du premier ordre apparent quand elle avait atteint une conversion au $2/3$; les catalyseurs, classés par ordre décroissant de vitesses de réactions, du plus important au moins efficace: $Zn(NO_3)_2 > ZnCl_2 > MgCl_2 = Mg(NO_3)_2$. Les enthalpies, entropies et énergies libres d'activation ont confirmé l'hypothèse antérieure suivant laquelle l'ion métallique entre dans la réaction en formant un état de transition complexe.

Zusammenfassung

In Fortsetzung einer schon früher mitgeteilten Untersuchung über den Einfluss des Katalysators auf die Baumwollcellulose-DMEU-Reaktion, wurden weitere Versuche mit einer höheren Metallionenkonzentration der ursprünglich als Katalysator verwendeten vier anorganischen Salze— $MgCl_2$, $Mg(NO_3)_2$, $ZnCl_2$ und $Zn(NO_3)_2$ —, nämlich $0,1M$, und mit $CuCl_2$ und $CdCl_2$ bei der Konzentration $0,03M$ durchgeführt. Die infrarot-absorptionsspektroskopischen Ergebnisse an behandelten Baumwollprodukten standen mit den Befunden bei der Katalysatorkonzentration $0,03M$ in Einklang, was wieder dafür spricht, dass sich der Katalysator an der Reaktion durch Bildung eines Koordinationskomplexes über Stickstoff-Metallbindungen zwischen Katalysator und der DMEU-Molekel beteiligt. In ähnlicher Weise konnte auch gezeigt werden, dass die Reaktion mit DMEU bevorzugt an der primären Alkoholgruppe der Anhydroglucose stattfindet. Die IR-Ergebnisse ließen bei der Katalysatorkonzentration $0,03M$ einen höheren Vernetzungsgrad und damit eine geringere Anzahl endständiger OH- oder NH-Gruppen erkennen, als bei $0,1M$. Weitere Hinweise auf Komplexbildung lieferte das Infrarotspektrum des Produkts der in Abwesenheit von Cellulose ausgeführten $CdCl_2$ -DMEU-Reaktion. Zusätzliche physikalische Daten, die an Reaktionsprodukten bei $CdCl_2$ - und $CuCl_2$ -Katalyse bei $0,03M$ erhalten worden waren, lieferten beim Vergleich mit den Daten von Produkten der $MgCl_2$ - und $ZnCl_2$ -Katalyse eine Stütze für

die frühere Hypothese, dass die Schädigung durch Chlor während des Erhitzens von der Fähigkeit des Metallkomplexes, als Abfänger für freie Radikale zu wirken, abhängt. Zusätzliche Belege für den Radikalmechanismus wurden bei Chlorierung und Ultraviolettbestrahlung von behandeltem Zeug erhalten, wobei der gleiche Verfärbungs- und Abbaueffekt auftrat wie bei chloriertem Zeug, das nachher entsprechend der üblichen AATCC-Methode gesengt worden war. Die Reaktionsgeschwindigkeit der Cellulose-DMEU-Reaktion wurde bei 45, 55 und 65°C mit jedem der vier Katalysatoren bei der Konzentration 0,03 M durch Verfolgung der Änderung des Stickstoff- und Formaldehydgehaltes sowie der Änderung der Knitterfestigkeit bestimmt. Bis zu $\frac{2}{3}$ des vollständigen Umsatzes verlief die Reaktion nach erster Ordnung; nach abnehmendem Einfluß auf die Reaktionsgeschwindigkeit geordnet, ergab sich folgende Reihenfolge der Katalysatoren: $\text{Zn}(\text{NO}_3)_2 > \text{ZnCl}_2 > \text{MgCl}_2 = \text{Mg}(\text{NO}_3)_2$. Durch die gemessene Aktivierungsenthalpie, entropie und freie Energie wurde die frühere Hypothese bestätigt, dass das Metallion in die Reaktion durch Bildung eines Übergangszustandskomplexes eingreift.

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