

Properties of Reaction Products of Hydroxymethylated 2-Substituted 4,6-Diamino-s-triazines with Cotton

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Synopsis

A study has been made of the reaction products of hydroxymethylated 2-substituted (X) 4,6-diamino-s-triazines (MXT) with cotton fabrics in the presence of zinc nitrate as catalyst. The reagents used were MXT having the following substituents: methoxy (MMT), isopropoxy (MIPT), methyl (acetoguanamine) (MAG), monoethylamino [N-(2-ethyl)melamine] (MEM), monohydroxyethylamino [N-(2-hydroxyethyl)melamine] (MHEM), and dihydroxyethylamino [N,N-bis(2-hydroxyethyl)melamine] (MBHEM) groups. Trimethylolmelamine (TMM), dimethylolurea (DMU), dimethylolethyleneurea (DMEU), and dimethylolethyltriazone (DMET) were also used for comparison.

The molar ratio of total formaldehyde to 2-substituted 4,6-diamino-s-triazine (XT) residue in treated fabrics is larger in high-temperature curing than in low-temperature curing. In case of curing at 150°C for 5 min, MHEM and MBHEM crosslinked primarily with cellulose in a monomeric state, and the others in a oligomeric state. From these facts, the crosslinked structures were presumed. Infrared absorption spectra of the fabrics treated with MXT are discussed and a few physical properties of the fabrics are compared with those of the fabrics finished with TMM, DMU, DMEU, and DMET.

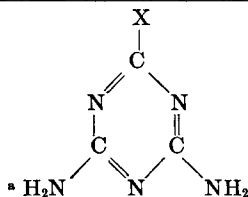
INTRODUCTION

Amino-s-triazine derivatives can be used as chemical modifiers of cellulosic fabric. Chemical modification of cellulosic fabric has been studied using hydroxymethylated amino-s-triazines for the purpose of obtaining shrink-proof,¹ crease-proof,² and hypochlorite-resistant crease-proof fabrics.³ The author and co-worker^{4,5} have studied the finishing of cotton fabrics using hydroxymethylated 2-substituted (X) 4,6-diamino-s-triazines (MXT) for the purpose of obtaining the crease-resistant agents which do not lessen the strength of treated fabrics, and revealed that MXT was good finishing agents which gave comparatively large crease recovery angles without a large fall in tearing strengths.

The present paper describes some investigations on the reactions of MXT with cotton fabrics by means of the pad dry-cure process at comparatively low temperature, on the polymerization degree of crosslinked MXT, infrared absorption spectra, tensile strengths, crease recovery angles, chlorine damage, chlorine retention, and evolution of free formaldehyde

TABLE I
Abbreviation and Melting Point of 2-Substituted (X) 4,6-Diamino-*s*-triazines,^a
Urea, Ethyleneurea, and Ethyltriazone

Compound	Abbreviation	X	mp, °C ^b
2-Methoxy-4,6-diamino- <i>s</i> -triazine	MT	CH ₃ O—	229-230 (229-230)
2-Isopropoxy-4,6-diamino- <i>s</i> -triazine	IPT	(CH ₃) ₂ CHO—	170-171 (170-171)
2-Methyl-4,6-diamino- <i>s</i> -triazine (Acetoguanamine)	AG	CH ₃ —	269-270 (269-270)
2-Monoethylamino- 4,6-diamino- <i>s</i> -triazine (N-(2-Ethyl)melamine)	EM	C ₂ H ₅ NH—	170-171 (171-172)
2-Monohydroxyethylamino- 4,6-diamino- <i>s</i> -triazine (N-(2-Hydroxyethyl)melamine)	HEM	HOC ₂ H ₄ NH—	224-225 (225-227)
2-Dihydroxyethylamino- 4,6-diamino- <i>s</i> -triazine (N,N-Bis(2-hydroxyethyl)melamine)	BHEM	(HOC ₂ H ₄) ₂ N—	201-203 (199-202)
2,4,6-Triamino- <i>s</i> -triazine (Melamine)	M	H ₂ N—	(353)
Urea	U		133 (133)
2-Imidazolidinone (Ethyleneurea)	EU		130-131 (131)
Tetrahydro-5-ethyl-2(1)- <i>s</i> -triazone (Ethyltriazone)	ET		175-176 (169-172)



in MXT-treated fabrics cured at 150°C for 5 min. The finishing agents used in the present study were hydroxymethylated compounds of 2-substituted 4,6-diamino-*s*-triazine (XT), shown in Table I. Comparison was also done with fabrics treated with such well-known agents as 2,4,6-tri(hydroxymethylamino)-*s*-triazine(trimethylolmelamine) (TMM), N,N'-bis(hydroxymethyl)urea(dimethylolurea) (DMU), 1,3-bis(hydroxymethyl)-2-imidazolidinone(dimethylolethyleneurea) (DMEU), and 1,3-bis(hydroxymethyl)tetrahydro-5-ethyl-2(1)-*s*-triazone(dimethylolethyltriazone) (DMET) as agent of structure similar to that of MXT.

EXPERIMENTAL

Preparation of Finishing Agents

2-Substituted (X) 4,6-diamino-*s*-triazines (XT) were synthesized from cyanuric chloride using the methods described by Controulis⁶ and Thurston.⁷ Tetrahydro-5-ethyl-2(1)-*s*-triazone(ethyltriazone) was synthesized in accordance with the methods described by Burk⁸ and Reid.⁹ 2,4,6-Tri-

TABLE II
Properties and Analytical Data of Finishing Agents

Finishing agent	X	F/XT ^a	mp, °C	MW ^b	F, % ^c	<i>n</i> ^d	<i>N_f</i> , %	<i>N_e</i> , % ^b
MMT	CH ₃ O—	2.5	120–122	215.3	34.43	2.47	32.43	32.53
MIPT	(CH ₃) ₂ CHO—	2.5	102–104	238.0	28.88	2.29	29.34	29.43
MAG	CH ₃ —	2.5	162–164	197.8	36.67	2.42	35.20	35.41
MEM	C ₂ H ₅ NH—	2.3	—	223.6	31.02	2.31	37.47	37.59
MHEM	HOC ₂ H ₄ NH—	2.3	—	240.7	29.33	2.35	34.82	39.91
MBHEM	(HOC ₂ H ₄) ₂ N—	2.3	—	283.9	24.53	2.32	29.68	29.61
TMM	H ₂ N—	3.3	153–156	215.6	41.46	2.98	83.93	38.98
DMU		2.2	126	120.1	49.90	1.99 ^e		23.34 ^e
DMEU		2.3	100–101	146.1	40.92	1.99 ^e		19.17 ^e
DMET		2.2	—	190.2	32.18	2.06 ^e		22.09 ^e

^a Molar ratio of formaldehyde (F) to XT, urea (U), ethyleneurea (EU), and ethyltriazone (ET) in the methylation.

^b Calculated value as compound with *n* moles of formaldehyde.

^c Determined by iodometric method.

^d Average degrees of formaldehyde substitution.

^e Calculated value as dimethylol compound.

amino-*s*-triazine(melamine), 2-methyl-4,6-diamino-*s*-triazine(acetoguanamine), urea, and 2-imidazolidinone(ethyleneurea) were obtained commercially and recrystallized.

Hydroxymethylation of melamine was carried out by the method in the literature,¹⁰ that is, about 37% formalin, which contained 3.3 moles of formaldehyde and was adjusted to pH 9.0 with sodium hydroxide, was added to 1 mole of melamine at room temperature. The mixture was heated under agitation to reach 70°C within 10 min to allow complete solution, and was further agitated for additional 10 min at 70°C after dissolution. Hydroxymethylation of MT, IPT, and AG was carried out at molar ratios of formaldehyde/XT = 2.5 by a similar method to melamine. Hydroxymethylation of EM, HEM, and BHEM was carried out at molar ratios of 2.3 as described above. These methylol compounds did not crystallize even at -20°C for a few weeks. Therefore, they were used in the syrupy state. Hydroxymethylation of urea, ethyleneurea, and ethyltriazone was carried out using the methods described by Kadowaki,¹¹ Hoover,¹² and Reid,⁹ respectively. Table II shows the analytical data of the finishing agents.

The cotton fabric used in the present study was a broad cloth woven with 60 counted yarn, which had been desized, scoured, and bleached.

Procedure

For finishing at low temperature, fabrics were immersed in the bath containing 10 g of agent and 0.0030 moles of Zn(NO₃)₂ in 100 ml aqueous solution, squeezed to give a wet pickup of 80%. This procedure was repeated three times. Predrying was performed on pinframes at 60°C for 7 min,

and curing, at 80–120°C for the time described. The fabrics were then washed in alkaline aqueous solution of Na_2CO_3 , 2 g, plus synthetic detergent 5 g/l. at 60°C for 20 min, rinsed, and air-dried. For high-temperature curing, fabrics were immersed in an aqueous solution of 10 g or 0.055 moles agent plus 0.0030 mole $\text{Zn}(\text{NO}_3)_2/100$ ml and cured at 150°C for 5 min. Other procedures were carried out similarly as in low-temperature curing.

Crease recovery angle was measured using the Monsanto method (ASTM D1295-60T), and tensile strength was measured for warp direction using an Instron tester at a speed of 10 cm/min. Nitrogen contents were determined by the Kjeldahl method, and total formaldehyde contents of the finished fabrics were determined by Roff's method.¹³ Add-on of resin was calculated from nitrogen and formaldehyde contents. Formaldehyde amounts liberated from the finished fabrics were determined according to JIS L-1041.¹⁴ Chlorine retained after bleach was measured by JIS L-1041 in the following way: the fabric sample was bleached in a 50:1 ratio of sodium hypochlorite aqueous solution (which contained 0.25% of available chlorine and was adjusted to pH 9.5) to sample at 25°C for 15 min and squeezed with a mangle to remove the excess solution. The bleached sample was then rinsed in a 50:1 ratio of distilled water to sample at 25°C for 2 min and squeezed to give a wet pickup of ca. 80%. This procedure was repeated five times and finally drip-dried at room temperature. Determination of chlorine contents in the bleached sample was performed according to the method described by Frick¹⁵ and Reid.⁹ The damage due to retained chlorine was determined by the AATCC scorch test method.¹⁶

Infrared absorption spectra of treated cotton samples were obtained on a Hitachi EPI-G3 spectrophotometer by the KBr disk technique.¹⁷ Determination of zinc contents in padded cotton fabrics was performed using an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Properties of Fabrics Cured at Low Temperature

Figure 1 illustrates the changes in N/N_0 (%) of MMT-, MIPT-, and MEM-treated fabrics against reaction time in min at 80°, 100°, and 120°C in the presence of zinc nitrate as catalyst, where N is the nitrogen content of fabrics cured and washed in alkaline solution and N_0 is the value for fabrics padded, predried, and unwashed. The value of N/N_0 at $t = 0$ is the degree of bound nitrogen in the fabrics washed in alkaline solution after predrying. Table III shows the content of finishing agents and of zinc padded on the fabrics which were unwashed after predrying. These fabrics were then cured at the temperature shown in Table III. It is difficult to give constant quantities of both finishing agent and catalyst to fabric in each padding process.

The amounts of finishing agents padded on the fabrics and cured at 80°C were approximately equal, ranging from 0.0428 to 0.0475 mole/100

g fabric, and so were the catalyst contents. Accordingly, the change in N/N_0 and crease recovery angles with time could be examined among three agents. After predrying, N/N_0 values of MMT, MIPT, and MEM were 13%, 24%, and 60%, respectively. On the other hand, an N/N_0 value of

TABLE III
Amounts of MXT and Catalyst on Fabric Measured After Predrying*

	Curing temp. 80°C	100°C	120°C
MMT, g(mole)/100 g fabric	10.1 (0.0469)	11.3 (0.0523)	13.9 (0.0646)
Zn(NO ₃) ₂ , g(mole)/100 g fabric	0.24 (0.0037)	0.29 (0.0046)
MIPT, g(mole)/100 g fabric	10.2 (0.0428)	12.0 (0.0505)	9.78 (0.0411)
Zn(NO ₃) ₂ , g(mole)/100 g fabric	0.23 (0.0035)
MEM, g(mole)/100 g fabric	10.6 (0.0475)	11.8 (0.0529)	13.1 (0.0586)
Zn(NO ₃) ₂ , g(mole)/100 g fabric	0.24 (0.0037)	0.24 (0.0037)

* Fabrics were padded in the bath containing MXT 10.0 g + Zn(NO₃)₂ 0.0030 mole/100 ml and squeezed 80% wet pick-up. MMT 10 g/100 ml = 0.464M, MIPT 10 g/100 ml = 0.420M, MEM 10 g/100 ml = 0.447M; (.....) = not analyzed.

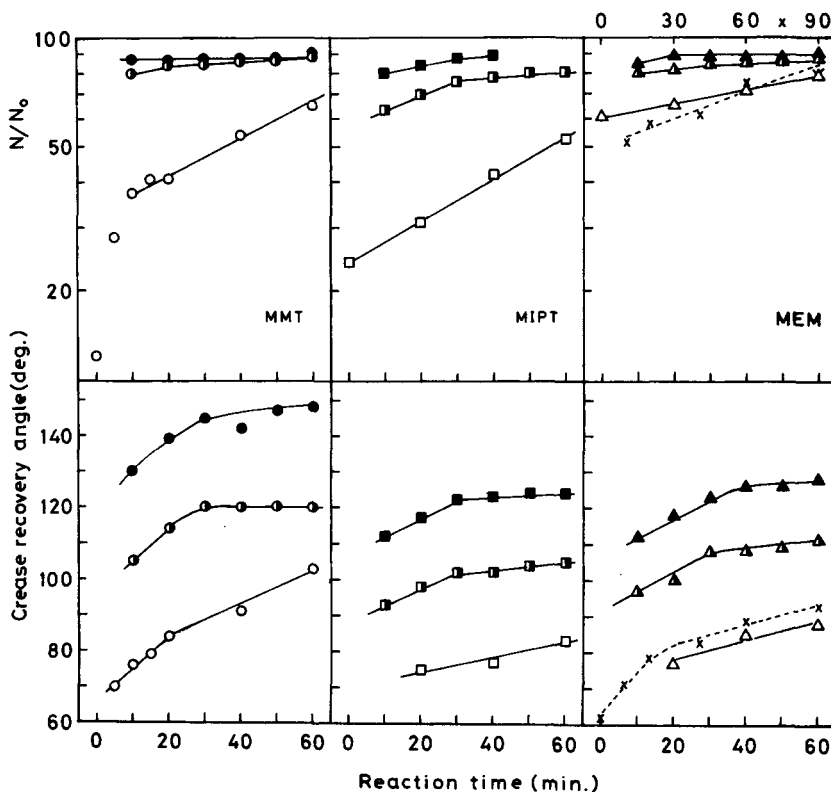


Fig. 1. Plots of $\log(N/N_0)$ and crease recovery angle vs. reaction time in the reaction of cotton fabrics with 10 g/100 ml MMT, MIPT, and MEM in the presence of 0.030M Zn(NO₃)₂ as catalyst: predrying, 60°C × 7 min; (○, □, △) reaction at 80°C; (●, ■, ▲) 100°C; (●, ■, ▲) 120°C; (×) predrying at 30°C and reaction at 80°C.

TABLE IV
 F/XT Molar Ratio of Fabrics Finished at Various Temperatures

Finishing agent	Curing, °C × min	N, %	XT, mole/100 g fab.	F, mole/100 g fab.	F/XT molar ratio
MMT	80 × 60	2.11	0.0303	0.0450	1.48
	100 × 60	3.25	0.0467	0.0746	1.60
	120 × 60	3.89	0.0560	0.0940	1.68
MEM	80 × 60	3.06	0.0365	0.0420	1.15
	100 × 60	3.97	0.0474	0.0645	1.36
	120 × 60	4.28	0.0510	0.0702	1.38

2.3% was obtained for the fabric which was padded in the bath of same concentration of MEM, dried at 30°C for 20 min, subsequently allowed to stand at 25°C for 5 hr, and washed in the same manner. This fact indicates that MEM combines much with fabric by predrying at 60°C for 7 min. The reactions of MMT, MIPT, and MEM with cellulose are likely to obey approximately first-order reaction in a period of 10 to 60 min ($N/N_0 = 37-65\%$), 0 to 60 min (24-52%), and 0 to 60 min (60-77%, real line, and 50-80%, broken line), respectively. For reference, the rate constants k , in min^{-1} , were calculated from the slopes of the lines by the least-squares method as follows: $k = 0.0109$ for MMT, 0.0130 for MIPT, and 0.00403 (real line) and 0.00521 (broken line) for MEM.

As described before, the amount of the bound agent during predrying was largest in MEM. This fact seems to indicate that the reaction rate of MEM with cellulose is larger than that of MMT and MIPT.

Curing at 80°C does not give large crease recovery angles as a whole, however, prolonged curing gradually increases N/N_0 values and also crease recovery angles. It takes about 60 min for N/N_0 to reach a definite value. In the reaction of MMT and MEM, the N/N_0 values of fabrics cured at 100°C for 20 to 60 min are approximately constant. In case of MIPT, it takes about 40 min for N/N_0 to reach a definite value. On the other hand, crease recovery angle does not increase even if curing is continued more than 30 min. In the reaction at 120°C, N/N_0 values of MMT- and MEM-treated fabrics do not increase even if curing is continued for more than 10 min. They do not increase even after 30 min in the case of MIPT. On the other hand, crease recovery angles increase until a curing time of 30 or 40 min. More prolonged curing, however, does not lead to an increase of the crease recovery angle. These facts show that the crosslinks of the combined agents with cellulose proceed gradually with continuation of curing, and only part of the total agents on fabric crosslinks with cellulose in the early stage before crease recovery angle reaches a constant.

Table IV shows molar ratios of $\text{CH}_2\text{O}/\text{XT}$ in the samples cured at 80°, 100°, and 120°C for 60 min. The ratios are larger in high-temperature curing than in low-temperature curing. A similar fact has been found in the reaction of DMEU¹⁸ with cellulose in the presence of zinc salts as catalyst. High-temperature curing favors the crosslinking formation of

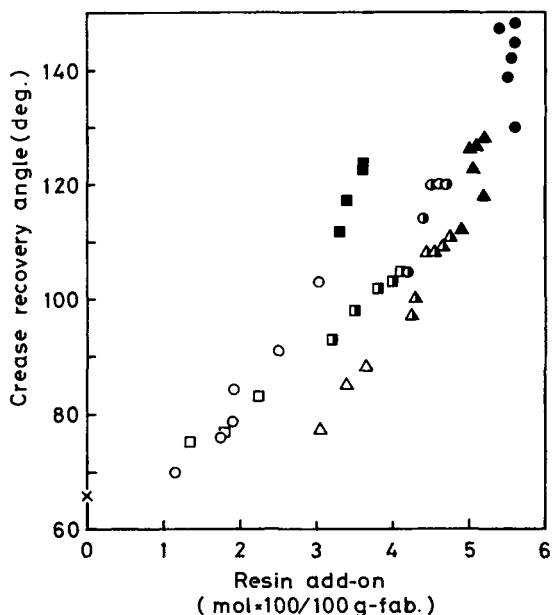


Fig. 2. Plots of crease recovery angle vs. resin add-on of cotton treated with MMT, MIPT, and MEM 10 g/100 ml in the presence of $Zn(NO_3)_2$ as catalyst: (○) MMT curing at 80°C; (●) MMT curing at 100°C; (●) MMT curing at 120°C; (□) MIPT at 80°C; (■) MIPT at 100°C; (■) MIPT at 120°C; (△) MEM at 80°C; (▲) MEM at 100°C; (▲) MEM at 120°C.

agents with cellulose rather than the methylene bond formation between methylol groups of the agents.

Figure 2 illustrates the plots of crease recovery angles against add-on of agents. The magnitude of crease recovery angles of the fabrics cured at the same temperature and with equal moles of agents is in the order MMT > MIPT > MEM. Formaldehyde contents and molar ratios of CH_2O/XT in the samples are larger in MMT-treated fabrics than in MEM-treated fabrics (see Table IV). These facts seem to show that the number of crosslinks is greater in the former than in the latter. Therefore, the crease recovery angle will become greater in the former than in the latter. In other words, it can be said that the smaller molar ratios of CH_2O/XT show longer crosslinks and give a smaller crease recovery angle.

Figure 3 illustrates IR spectra of the fabrics treated with MMT and MEM at 80°C for 60 min and of untreated cotton fabric. In the spectra of the treated cotton, a shoulder observed at 1640 cm^{-1} is of water absorbed in the fabric,^{19,20} and the bands at 1580 , 1480 , and 813 cm^{-1} are assigned, respectively, to ring CN stretching and/or NH deformation, to side chain CN breathing, and to triazine ring bending.²¹ The band at 1430 cm^{-1} is assigned to the CH_2 group of primary alcohol of cellulose,^{19,20} and its strength is smaller in treated fabric than in untreated fabric.

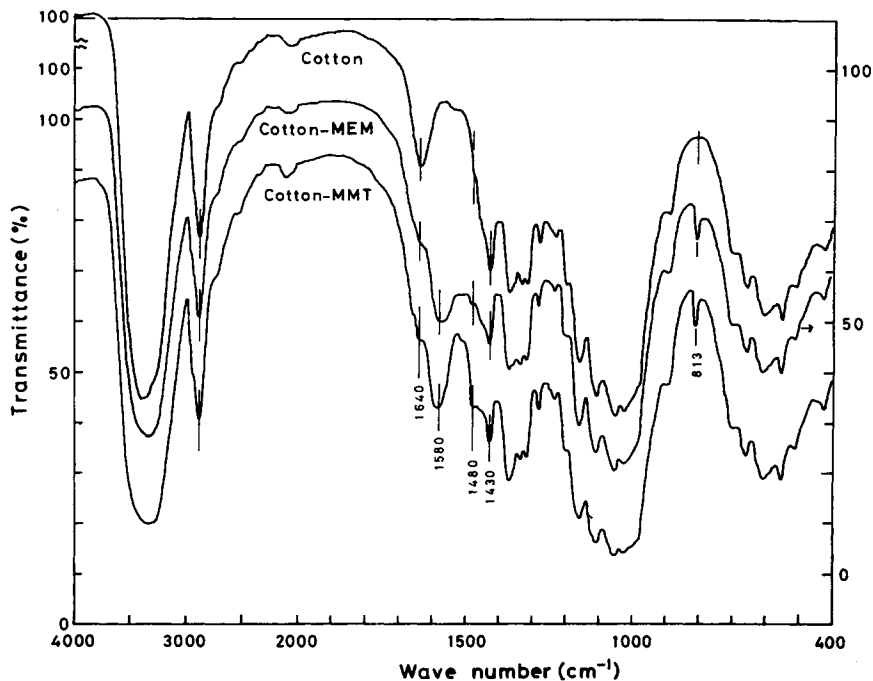


Fig. 3. IR spectra of untreated cotton and of cotton treated with MMT and MEM in the presence of 0.030M $Zn(NO_3)_2$. Curing, 80°C \times 60 min.

Properties of Fabrics Cured at High Temperature

Table V indicates the properties of fabrics treated with various reagents at 150°C for 5 min in the presence of zinc nitrate as catalyst. MXT reagents give somewhat smaller crease recovery angles than the others. It can be said, however, that MEM, MHEM, and MBHEM give comparatively large crease recovery angles. The crease recovery angles of MEM-treated fabrics are larger than those of MMT- and MIPT-treated fabrics. This fact is contrary to the one observed in low-temperature curing. In high-temperature curing, the crosslinking reaction of MEM with cellulose takes place more likely than those of MMT and MIPT with cellulose. Also, MMT, MIPT, and MAG give somewhat smaller crease recovery angles than MEM, MHEM, and MBHEM. One of the causes will be explained as follows. The former reagents are crystalline; they were heated at 75–80°C for about 20 min in order to make solutions of 10–13 g MXT/100 ml water. Since part of the methylol groups were hydrolyzed by heating during the dissolution, formaldehyde was liberated and n decreased. Therefore, the crosslinks between cellulose and MXT decreased, and consequently the crease recovery angle seems to become somewhat smaller. TMM was dissolved in the same manner, but gave comparatively large crease recovery angle. Since n of TMM is 2.98, TMM is considered a three-functional agent. Therefore, the retained n is larger in TMM than

TABLE V
 Treating Condition and Properties of Finished Fabrics

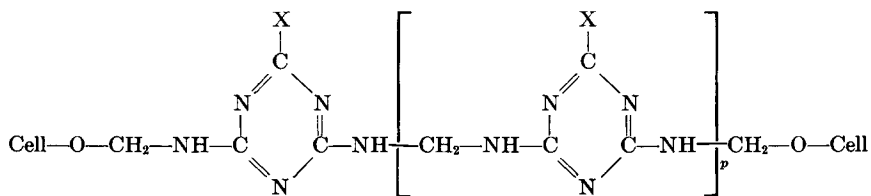
Fabric no.	Finishing agent	Treating soln.		Properties of finished fabric					
		Concn. g/100 ml	pH	Crease recovery angle, deg.	N, %	F, %	Add-on, %	F/MR ^a molar ratio	F/MR ^a <i>n</i>
1	MMT	12.0 ^b	4.5	144	3.33	2.52	9.2	1.77	0.71
2	MMT	10.0	—	140	3.59	2.58	9.8	1.68	0.68
3	MIPT	13.2 ^b	4.9	142	3.47	2.05	10.4	1.38	0.60
4	MIPT	10.0	4.9	135	2.62	1.58	7.9	1.41	0.62
5	MAG	10.8 ^b	5.8	138	3.36	2.18	8.2	1.52	0.63
6	MAG	10.0	—	135	3.33	2.22	8.2	1.48	0.61
7	TMM	8.0	—	149	4.20	2.92	8.9	1.95	0.65
8	TMM	8.0	—	150	3.97	2.66	8.6	1.88	0.63
9	MEM	11.8 ^b	6.6	147	5.18	3.07	12.6	1.66	0.72
10	MEM	10.0	6.5	144	3.60	2.15	8.8	1.67	0.72
11	MHEM	13.3 ^b	6.5	149	4.09	3.15	11.4	2.15	0.92
12	MHEM	10.0	6.3	148	4.03	3.16	11.3	2.19	0.93
13	MBHEM	15.9 ^b	6.4	152	3.95	2.99	13.0	2.12	0.91
14	MBHEM	10.0	6.2	148	3.04	2.27	10.0	2.09	0.90
15	DMU	8.0	4.1	155	1.86	3.33	7.3	1.67	0.84
16	DMU	10.0	4.1	155	2.00	3.46	7.7	1.62	0.81
17	DMEU	8.0	4.1	155	1.30	2.75	6.8	1.97	0.99
18	DMEU	10.0	4.1	155	1.49	3.22	7.8	2.00	1.00
19	DMET	10.0	4.7	150	1.80	2.75	8.3	2.13	1.03
20	DMET	12.0	4.7	145	2.11	3.27	9.8	2.17	1.05
21				66	—	0.02	—	—	—

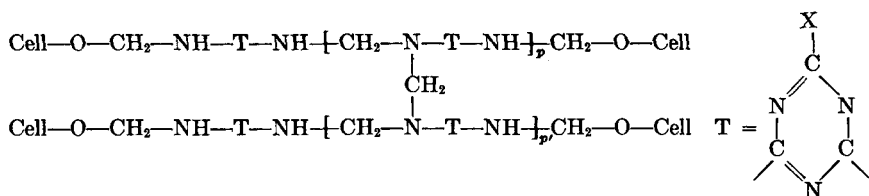
^a MR = Methylol residue.

^b These correspond to 0.55*M*; Zn(NO₃)₂ = 0.030*M*.

in MMT, MIPT, and MAG even if methylol groups did cleave a little. The somewhat larger crease recovery angle in TMM is thus explained.

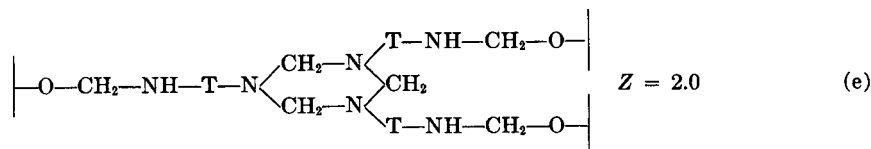
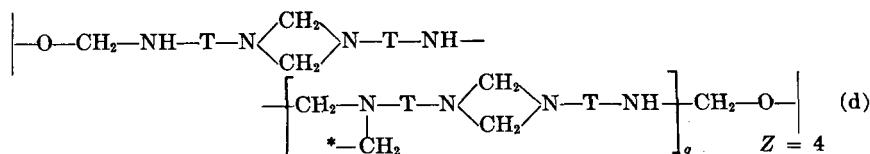
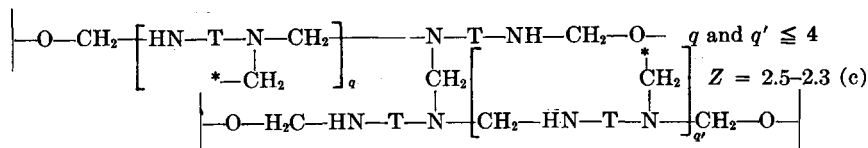
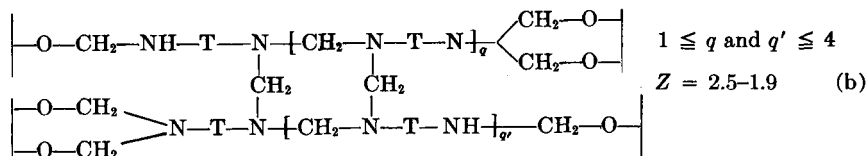
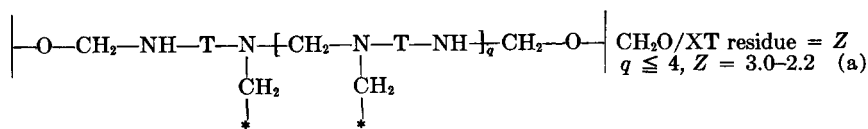
The molar ratios of formaldehyde to methylol residue (MR) in the fabrics finished with MXT and others at 150°C for 5 min were examined. Column 9 in Table VI shows the ratios, and column 10, the quotients of the molar ratios/*n*. In the reaction of MXT with cellulose, the structure of crosslinked MXT will be monomeric or oligomeric, as self-polycondensation of MXT will take place simultaneously. The molar ratio of CH₂O/XT is a measure which shows the degree of polycondensation. Since *n* of MXT is 2.29 to 2.47, MXT is considered mainly a mixture of di- and trimethylol compounds. Judging from the reaction products of DMEU^{15, 22, 23} and DMU^{24, 25} with cellulose, the reaction product of di-MXT with cellulose is presumed to be as follows:



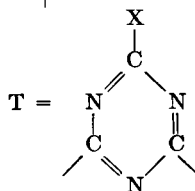


scheme 1: possible crosslinked structures of di-MXT with cellulose

Since the reaction products of tri-MXT with cellulose are complicated, many formulae are considered possible, of which some are shown in scheme 2:



* = OH, O-Cell, >N-T-



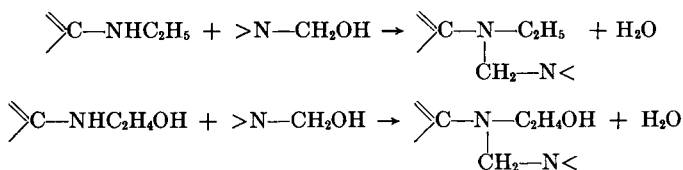
scheme 2: possible crosslinked structures of tri-MXT with cellulose

TABLE VI
Infrared Absorption Bands of 2-Methoxy-4,6-diamino-s-triazine and of Its Hydroxymethylated Compound

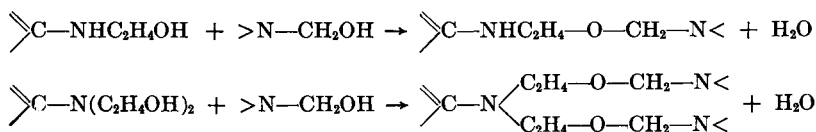
Absorption, cm^{-1} ,	Intensity*	2-Methoxy-4,6-diamino-s-triazine	Hydroxymethylated compound
3465	w	} NH_2 stretching	—
3410	s		—
3320	w		—
3140	s		—
3250—			
3400	s	—	OH st and/or NH st
2950	w	asym CH_3 st	sym CH_2 st and CH_3 st
1660	m	} NH_2 bend	—
1635	m		—
1595	s	—	ring $-\text{C}=\text{N}-$ st and/or NH d
1580	m	} ring $-\text{C}=\text{N}-$ st	—
1560	m		—
1510	m	—	asym CN st and/or CNH bend
1460	s, s	side chain CN br	side chain CN breathing
1370	s, s	$=\text{C}-\text{O}$	$=\text{C}-\text{O}$ and/or CN st of NCH_2
1210	m, m	NH_2 rocking	NH_2 rocking
1162	w	—	?
1140	m	?	—
1040	m	?	—
1010	s	—	$-\text{C}-\text{O}-$ st and/or OH deformation?
935	m	—	$-\text{C}-\text{O}-$ st and/or OH deformation?
895	m	—	$-\text{C}-\text{O}-$ st and/or OH deformation?
865	w	—	$-\text{C}-\text{O}-$ st and/or OH deformation?
810	s	ring bending	ring bending

* s = Strong; m = medium; w = weak.

Besides these products (schemes 1 and 2), crosslinked products of di-MXT with tri-MXT may be formed. In case of MEM and MHEM, the following reactions may also take place:



On the other hand, in the case of MHEM and MBHEM, the reaction

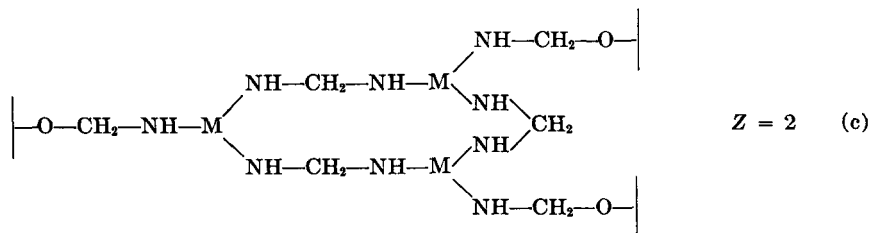
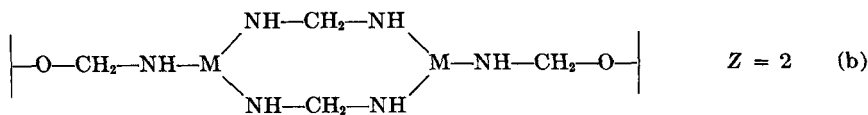
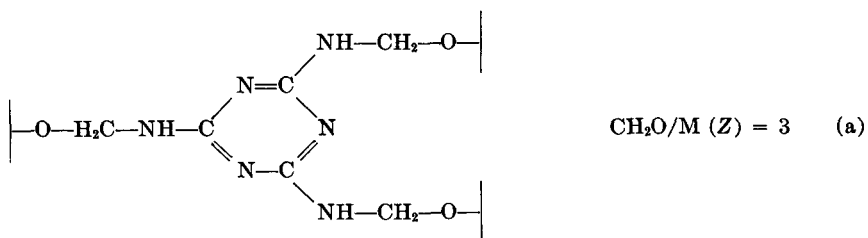


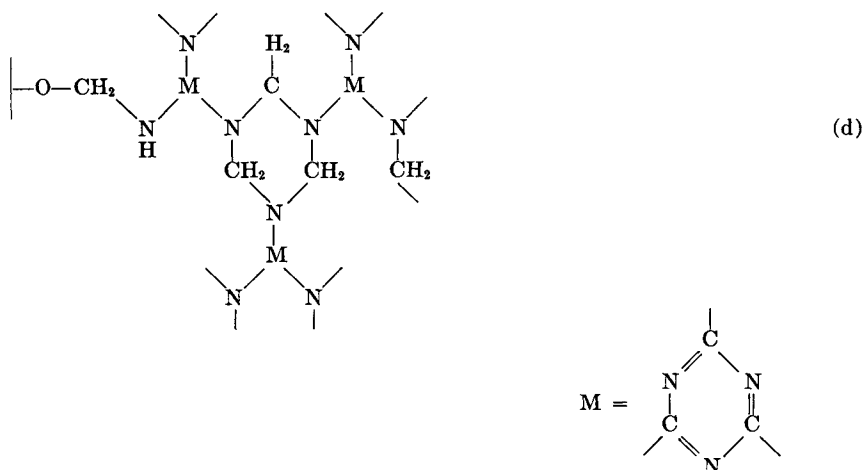
will scarcely take place, because the amount of hydroxyl groups of $\text{—NH—C}_2\text{H}_4\text{OH}$ or $\text{—NH(C}_2\text{H}_4\text{OH)}_2$ is very small compared to the total amount of $>\text{N—CH}_2\text{OH}$, —NH— , and $\text{—CH}_2\text{OH}$ groups of cellulose.

As described above, it is very difficult to presume crosslinked structures from the molar ratios of $\text{CH}_2\text{O/XT}$ ($= Z$). It can be said, therefore, that the Z values of 2.09 to 2.19 for MHEM- and MBHEM-treated fabrics indicate primarily the presence of monomeric crosslinks. Accordingly, these crosslinked structures will be mainly the mixture of products shown by scheme 1 ($p = 0$) and scheme 2a ($q = 0$). On the other hand, Z values of 1.38 to 1.67 for MMT-, MIPT-, MAG-, and MEM-treated cottons indicate the presence of polymeric crosslinks. From the crosslinked structures of DMEU^{15, 22, 23} and DMU,^{24, 25} it is presumed that q and q' in scheme 2a–e are not very large. Therefore, Z values are calculated to be 1.9 to 3.0 ($Z/n = 0.63$ to 1.0) by assuming q and $q' \leq 4$. From Table IV, Z/n for MMT-, MIPT-, MAG-, and MEM-treated fabrics are 0.61 to 0.72. Accordingly, these crosslinked structures seem to be mainly oligomeric ($p, p' \leq 4$) as shown by scheme 1 and a small amount of the crosslinks by scheme 2.

MMT, MIPT, and MAG were heated in order to obtain clear solutions. Since formaldehyde was liberated by the cleavage of methylol groups during dissolution, n decreased and approached 2. The crease recovery angle of a sample with small Z value is smaller than that with a large Z value.

Because TMM with $n = 2.98$ is a three-functional compound, many kinds of crosslinked structures can be presented. Scheme 3 shows comparatively simple structures among them:





scheme 3: possible crosslinked structures of TMM with cellulose

The molar ratios of Z treated fabrics are 1.88 to 1.95, i.e., approximately 2. The Z values for schemes 3b and c are 2.0, i.e., two of three methylol groups condense with the two methylol groups of another molecule, and another crosslinks with cellulose and or $-\text{NH}-$. Accordingly, crosslinked structures of TMM will involve the structures illustrated in schemes 3b and c and other complicated structures. As described before, formaldehyde was liberated due to the cleavage of methylol groups during dissolution of TMM, and n decreased a little. This fact seems to make the Z value slightly smaller than 2.0.

The reaction of DMEU and DMU with cellulose has been studied by many workers in the presence of various kinds of catalysts, and it has been reported that the Z value of DMEU-treated fabric is 2 in the presence of zinc nitrate.¹⁸ The observed Z value 2.0 in the present study also indicates primarily the presence of monomeric crosslinks and is consistent with the data observed by Ziifle.¹⁸ In case of DMU-treated cotton, Z was 1.62 to 1.67, indicating mainly the presence of oligomeric crosslinks. This is slightly larger than the values observed by Steel²⁴ and Mahta.²⁵ Zinc nitrate catalyst seems to induce more crosslinking with cellulose than NH_4Cl , MgCl_2 , $(\text{NH}_4)_2\text{SO}_4$, and other catalysts.

Infrared Absorption Spectra

Figures 4 and 5 illustrate IR spectra of MT, MMT, and of untreated cotton as well as of MXT-treated cotton fabrics. The absorption bands of MT and MMT were assigned by comparing their IR data with those of melamine,²⁶ *s*-triazine derivatives,²⁷ and trimethylolmelamine²¹ and are shown in Table VI. Assignments of the bands of cellulose were cited from the literatures^{19,20} and are shown in Table VII. Characteristic absorption bands of MXT-treated cotton at high-temperature curing were approxi-

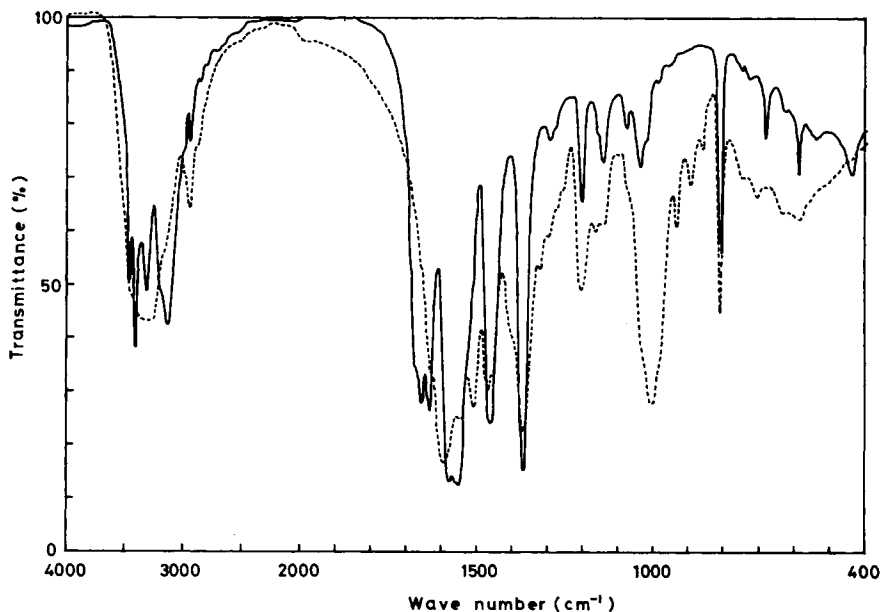


Fig. 4. IR spectra of 2-methoxy-4,6-diamino-*s*-triazine and of its hydroxymethylated compound (MMT): (—) 2-methoxy-4,6-diamino-2-triazine; (-----) MMT.

mately the same as the ones at low-temperature curing shown in Figure 3 and have been assigned in the foregoing paragraph. No absorption bands were observed at 1480 cm^{-1} in the spectra of MIPT-, MAG-, and MEM-treated cotton. Weak absorptions were observed at 1500 cm^{-1} in the spectra of MIPT- and MHEM-treated cotton, and shoulders at 1510 or 1460 cm^{-1} in MAG-treated cotton. They may be the absorption bands for the stretching of CN side chain. As a whole, the intensity of absorption at 1430 cm^{-1} in each spectrum was reduced greatly. This fact shows that MXT reacts preferentially with the primary hydroxyl of cellulose.

The intensities of 1430 cm^{-1} bands for MAG-, MIPT-, and MBHEM-treated cotton are larger than for MMT-, MEM-, MHEM-, and TMM-treated cotton. This fact indicates that the number of crosslinks in MAG and MIPT-treated cotton is smaller than in the latter. This is understandable from the fact that the crease recovery angles of the former are somewhat smaller than of the latter. The strength of the 1430 cm^{-1} band for MBHEM-treated cotton is as large as that of the MAG- and MIPT-treated ones. In the spectra of both *N,N*-bis(2-hydroxyethyl)melamine and MBHEM, an absorption band is observed at 1435 cm^{-1} ; this can be attributed to the side chain $\text{C}-\text{N}\begin{matrix} \text{C} \\ \diagdown \\ \text{C} \end{matrix}$. Therefore, the 1430 cm^{-1} band of MBHEM-treated fabric will be assigned to the stretching of the side chain and of the bending of $-\text{CH}_2-$. It is considered that the strength of the band would become, due to the overlap of the two bands, slightly greater for MBHEM-treated cotton than for MMT-, MEM-, MHEM-, and TMM-treated cotton in spite of the large crease recovery angle of the former.

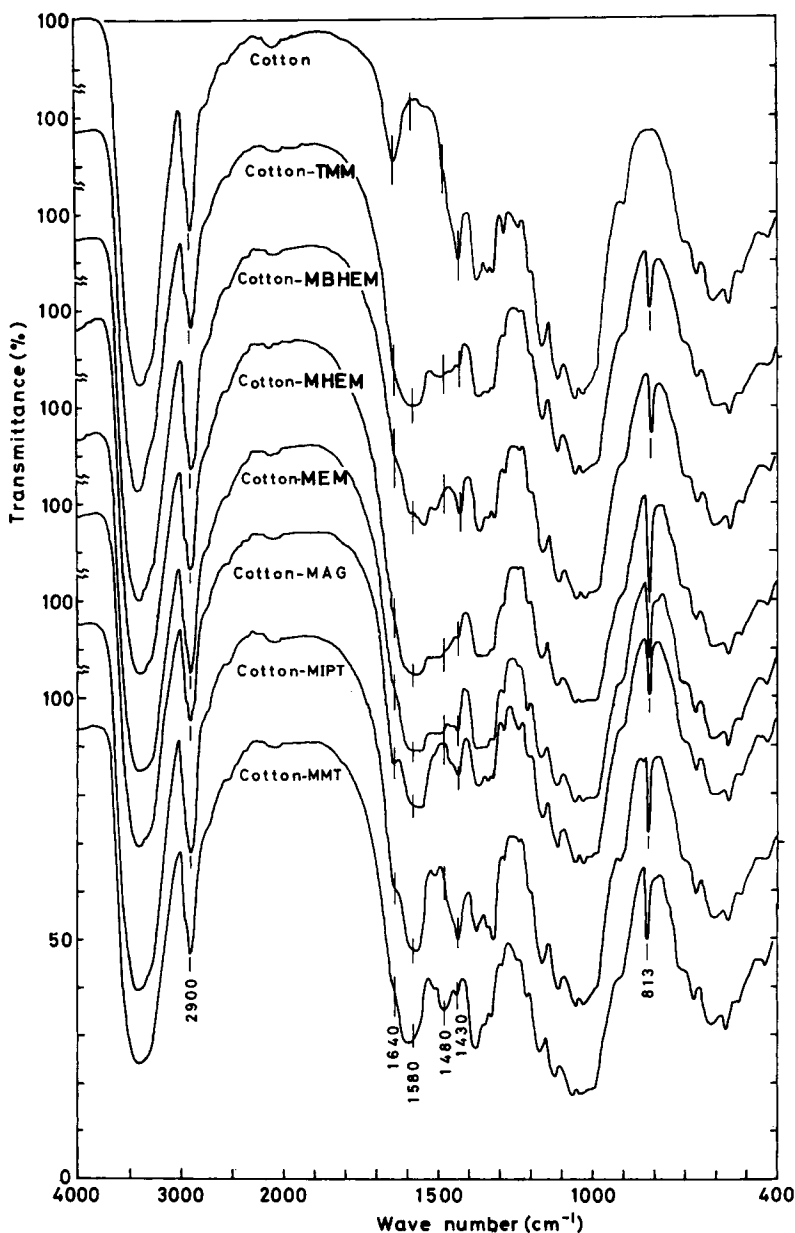


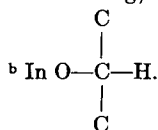
Fig. 5. IR spectra of untreated cotton and of cotton treated with MXT in the presence of $0.030M$ $Zn(NO_3)_2$ as catalyst. Curing, $150^\circ C \times 5$ min.

Figure 6 illustrates IR spectra of MMT-, MAG-, and MEM-treated cotton which were hydrolyzed for 30 min at $80^\circ C$ in buffer solution of pH 2. The nitrogen contents of MMT-, MAG-, and MEM-treated cotton are 1.01, 0.76, and 0.32, respectively. Acidic hydrolysis resulted in (1) re-appearance of the 1640 cm^{-1} band, (2) disappearance of the 1580 cm^{-1}

TABLE VII
Infrared Absorption Bands of Untreated and MMT-Treated Cotton Cellulose

Absorption, cm ⁻¹	Intensity ^a	Untreated cotton	Treated cotton
3345	s, s	total OH stretching	OH str and/or NH stretching
2899	s, s	CH stretching	CH stretching
1640	m	absorbed H ₂ O	—
1630	sh	—	absorbed H ₂ O and/or NH d
1590	s	—	NH d and/or ring st
1500	sh	—	CNH b and/or side chain st
1480	m	—	side chain CN breathing
1430	m, vw	CH ₂ bending	CH ₂ b and/or ring st
1370	vw, m	CH bending	CH b and/or C—N st of N—CH ₂ and/or =C—O—C
1340	vw, sh	C—OH in pl bending	C—OH in pl bending
1320	vw, vw	CH ₂ wagging	CH ₂ wagging
1282	w, vw	CH bending ^b	CH bending ^b
1235	vw, sh	unassigned	?
1205	sh, vw	OH in pl d	OH in pl d and/or NH r
1160	m, m	asym bridged O st	asy br O st; NH r; and/or CN st
1115	m	—	asy in phase ring st
1110	m	in-phase ring st	—
1055	m, m	C—O st	C—O st
895	vw, sh	C ₁ group: asy out of phase ring st	C ₁ group: asy out of phase ring st
813	m	—	Triazine ring bending

^a s = Strong; m = medium; w = weak, vw = very weak, sh = shoulder.



band and disappearance or great reduction of the 813 cm⁻¹ band, and (3) reappearance or great enlargement of the 1430 cm⁻¹ band. These facts indicate the severance of the ether linkages formed between cellulose and MXT. There is no essential difference in the IR spectra between native cellulose and the sample from which the crosslinked MXT was removed completely.

Chlorine Damage

Table VIII lists bleach tests with sodium hypochlorite, scorch tests, and chlorine retention. Tensile strengths of bleached MXT-treated fabrics are 16 to 17 kg/2.5 cm. DMU-, DMEU-, and DMET-treated fabrics show smaller tensile strength than MBHEM-, MHEM-, and MEM-treated ones, which have crease recovery angles approximately equal to the former. This fact seems to indicate that the substituent plays a part in preventing a fall in strength. DMET also has an ethyl group as the substituent, and the fall in the tensile strength is smaller for fabrics treated with it than with

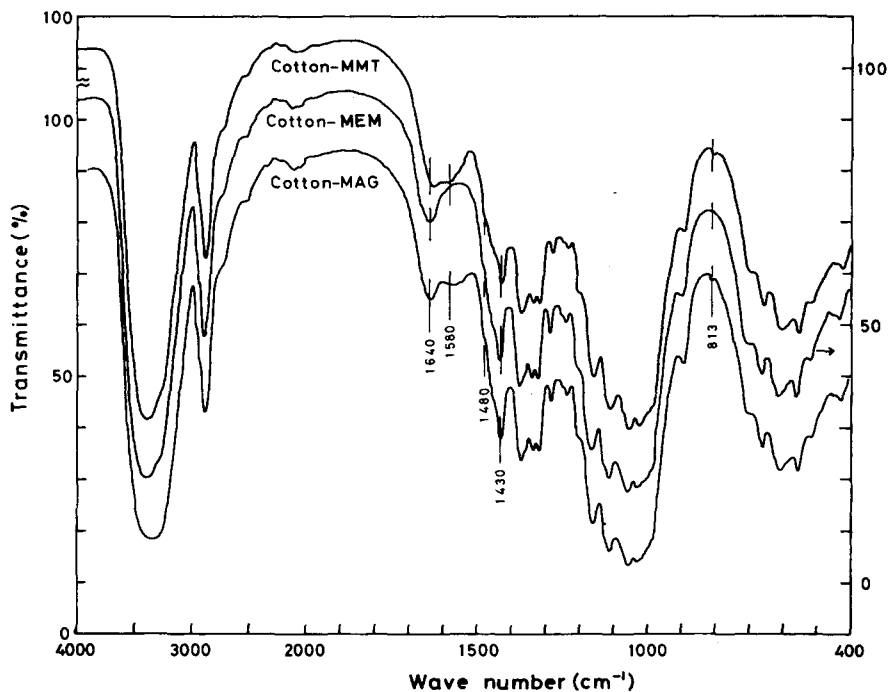


Fig. 6. IR spectra of the hydrolysis products of cotton treated with MMT, MAG, and MEM. Hydrolysis, pH 2, 80°C × 30 min.

DMU, DMEU, and TMM. This can be attributed to the ethyl group of DMET. The substituents of MBHEM, MHEM, and MEM are likely to be more effective in preventing a fall in the tensile strength than a substituent of DMET. Tensile strength retention for MXT-treated fabrics after scorch is 92% to 100% and approximately equal to the values for DMU-, DMEU-, and DMET-treated fabrics.

Discoloration by scorch test is 4 to 5 for MEM- and 5 for other MXT-treated fabrics. They are approximately the same as the values for DMU- and DMEU-treated ones. The value for DMET-treated fabric is somewhat larger than for other samples. This fabric was already lightly colored brownish-yellow when cured. Chlorine retention is shown in columns 8 and 9 of Table VIII. The retention is the most in MAG-treated fabric. This will be attributed to large production of —NH— and —NH_2 due to the cleavage of methylol groups during the dissolution process of MAG in the preparation of the finishing bath, which required longer heating because of its smaller solubility. The retentions for other MXT-treated fabrics are approximately equal to those of DMU-treated fabrics.

Evolution of Free Formaldehyde

The amounts of formaldehyde liberated are shown in Table IX. These were measured by the following procedure. One gram of sample was placed

TABLE VIII
Chlorine Damage and Chlorine Retention of Finished Fabrics

Fab. no.	Finishing agent	MR ^a , mole × 100/100 g fab.	Crease recovery, deg.	Tensile strength after bleach			Chlorine retained		
				Cl only, kg/2.5 cm	Cl + scorch, kg/2.5 cm	Ret., %	Degree of color	g/100 g fabric	g/fab. containing 1 mole MR ^a
2	MMT	5.15	140	17.6	17.6	100	5	0.18 ₆	3.50
3	MIPT	4.95	142	15.7	15.5	99	5	0.20 ₃	4.19
6	MAG	4.82	135	16.7	15.4	92	5	0.47 ₈	9.92
7	TMM	4.99	149	13.5	11.5	85	4.5	0.18 ₉	3.78
9	MEM	6.16	147	16.0	15.0	94	4.5	0.18 ₉	3.06
11	MHEM	4.86	149	16.0	15.7	98	5	0.17 ₇	3.64
13	MBHEM	4.69	152	15.8	14.5	92	5	0.16 ₆	3.54
16	DMU	7.14	155	12.8	11.7	91	4.5	0.17 ₂	2.41
17	DMEU	4.64	155	13.5	13.2	98	5	0.12 ₇	2.74
19	DMET	4.28	150	14.6	14.7	100	3	0.14 ₆	3.42
	Blank	—	66	24.5	24.4	100	5	0.01 ₀	

^a MR = Methylol residue (XT, U, EU, ET residue).

TABLE IX
Formaldehyde Amounts Evolved from Treated Fabrics

Sample no.	Finishing agent	MR,* mole × 100/100 g fab.	Evolved CH ₂ O amount	
			g/100 g fab.	g/1 mole MR*
1	MMT	4.78	0.0111	0.232
4	MIPT	3.75	0.0131	0.349
5	MAG	4.82	0.0176	0.365
8	TMM	4.73	0.0212	0.448
10	MEM	4.29	0.0203	0.473
12	MHEM	4.79	0.0175	0.364
13	MBHEM	4.69	0.0186	0.397
16	DMU	7.14	0.0285	0.384
17	DMEU	4.64	0.0376	0.810
20	DMET	5.01	0.0364	0.726

* MR = Methylol residue (or XT, urea, ethyleneurea and ethyltriazone residue).

TABLE X
pK_b of XT (25°C)²⁸

X	pK _b
CH ₂ O—	10.46
(CH ₃) ₂ HCO—	10.20
CH ₃ —	9.35
H ₂ N—	8.97
C ₂ H ₅ NH—	8.75
HOC ₂ H ₄ NH—	8.83
(HOC ₂ H ₄) ₂ N—	8.70

in a conical flask containing 100 ml distilled water, which contained 1 ml of 1% aqueous solution of a nonionic surface-active agent. The flask was capped and allowed to stand at 40° ± 0.2°C for 1 hr with occasional shaking. After the solution was filtered, evolved formaldehyde was determined by the chromotropic acid method.

The order of the amounts of evolved formaldehyde from samples containing 1 mole of XT, urea, ethyleneurea, and ethyltriazone residue is as follows:

DMEU > DMET > MEM > TMM > MBHEM ≥ DMU >

MHEM > MAG > MIPT > MMT

DMEU and DMET resins are more liable to liberate formaldehyde than MXT resin. In case of MXT-treated fabric, the order of magnitude of formaldehyde liberated is approximately the same as the order of the basicity of XT (Table X), except for melamine.

SUMMARY

First, the reaction of MXT with cotton fabric was carried out at 80–120°C by the pad dry-cure technique in the presence of zinc nitrate as

catalyst, and the following results were obtained. The molar ratios of formaldehyde to XT residue (Z) in the reaction products of MMT and MEM with cotton fabrics at 80°, 100°, and 120°C for 1 hr increased as reaction temperature was raised. The ratios for MMT-treated fabrics were larger than for MEM-treated ones at the same temperatures. Crease recovery angles of fabrics containing equal resin concentrations were in the order of MMT- > MIPT- > MEM-treated fabric at the same temperatures.

Second, the reactions were performed at 150°C for 5 min in a similar way as described above, and the following was revealed. The quotients of Z/n for MHEM- and MBHEM-treated fabrics were 0.90 to 0.93, indicating primarily the presence of monomeric crosslinks, and for others they were 0.60 to 0.72, indicating the presence of oligomeric crosslinks. Generally, IR spectra of MXT-treated cotton indicated in a region a void of characteristic absorptions of cotton cellulose: (1) disappearance or great reduction of the 1640 cm^{-1} band ascribable to absorbed water, (2) great reduction of 1430 cm^{-1} band due to CH_2 bending of primary alcohol in cellulose, and (3) appearance of the 1580, 1480, and 813 cm^{-1} band, respectively, attributable to ring CN stretching and/or NH deformation, to side chain CN breathing, and to ring bending. Crease recovery angles were somewhat smaller for MXT-treated fabrics than for DMU- and DMEU-treated fabrics. Tensile strengths are, however, larger for the former than for DMU-, DMEU-, and DMET-treated ones. The retention of the strengths of the former after scorch test are 92% to 100%, and all approximately equal to the value of the latter, although chlorine retention was larger than that for DMU-, DMEU-, and DMET-treated ones. Formaldehyde evolved less from MXT-treated fabrics than from DMEU- and DMET-treated ones, and slightly less than, or almost the same as the DMU-treated one. Judging from the properties described above, it can be said that MMT, MEM, MHEM, and MBHEM are better finishing agents than DMU, DMEU, and DMET.

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