Hydrolysis Mechanism of Crosslinks Formed Between Hydroxymethylated 2-Substituted 4,6-Diamino-s-triazines and Cotton

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Synopsis

Hydrolysis resistance and mechanism of reaction products of hydroxymethylated 2-substituted (X) 4,6-diamino-s-triazines (MXT) with cotton fabrics has been studied. Finishing reagents used were MXT having the following substituents: X = CH$_3$O— (MMT), (CH$_3$)$_2$CHO— (MIPT), CH$_3$— (MAG), C$_2$H$_5$NH— (MEM), HOC$_2$H$_4$NH— (MHEM), and (HOC$_2$H$_4$)$_2$N— (MBHEM). For comparison, trimethylolmelamine (TMM), dimethylolurea (DMU), dimethylolethyleneurea (DMEU), and dimethylolethyltriazone (DMET) were used. Hydrolysis was carried out in buffer and NaOH solutions of various pH's for 30 min at 80°C. The order of hydrolysis resistance of crosslinked reagents was determined from the nitrogen contents retained. It was as follows: pH 1, MROT < MRNT < MRT; pH $\geqq$ 2, MROT > MRT > MRNT; pH $\leqq$ 13, MROT > MRNT; pH 14, MROT < MRT < MRNT, where MROT is hydroxymethylated 2-alkoxy (MMT, MIPT), MRT is hydroxymethylated 2-alkyl (MAG), and MRNT is hydroxymethylated 2-alkylamino-4,6-diamino-s-triazine (MEM, MHEM, MBHEM). This fact can be explained in terms of the basicity constant (pK_b) of crosslinked MXT with cotton (approximately pK_b of 2-substituted 4,6-diamino-s-triazine (XT). The hydrolysis rates of crosslinked MMT, MAG, and MEM were determined at pH 2. The activation energies were 21.8 for MMT, 20.9 for MAG, and 21.0 kcal/mole for MEM.

INTRODUCTION

One of the qualities required for chemically modified cotton fabrics is resistance to hydrolysis of the resin. Therefore, many reports have been published on the hydrolysis resistance of crosslinked N-methylol-type finishes with cotton fabrics[1−9] and on the hydrolysis of their model compounds.[10−13] However, no triazine-type finish has been investigated except for crosslinked methylolmelamine with cotton.[3,14,15]

This paper is concerned with rates of hydrolyses of crosslinks formed between cotton and hydroxymethylated 2-substituted (X) 4,6-diamino-s-triazines (MXT),
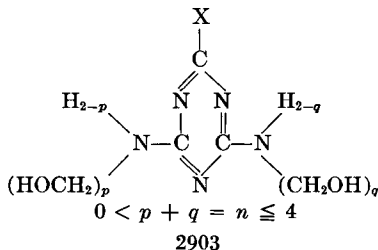
$$\begin{array}{c} X \\ | \\ C \\ \end{array}$$

H$_{2-p}$ and H$_{2-q}$, N—C C—N, (HOCH$_2$)$_p$ N   (CH$_2$OH)$_q$

$$0 < p + q = n \leqq 4$$

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TABLE I
Properties and Analytical Data of Finishing Reagents

Finishing reagent		F/XT[a]	mp, °C	% F[b]	n[c]	mol wt[e]	%N	
Abbreviation[f]	X						Found	Calcd.[e]
MMT	CH$_3$O—	2.5	120–122	34.43	2.47	215.3	32.43	32.53
MIPT	(CH$_3$)$_2$CHO—	2.5	102–104	28.88	2.29	238.0	29.34	29.43
MAG	CH$_3$—	2.5	162–164	36.67	2.42	197.8	35.20	35.41
MEM	C$_3$H$_5$NH—	2.3	.....	31.02	2.31	233.6	37.47	37.59
MHEM	HOC$_2$H$_4$NH—	2.3	.....	29.33	2.35	240.7	34.82	39.91
MBHEM	(HOC$_2$H$_4$)$_2$N—	2.3	.....	24.53	2.32	283.9	29.68	29.61
TMM	H$_2$N—	3.3	153–156	41.46	2.98	215.6	38.93	38.98
DMU		2.2	126	49.90[c]	1.99	120.1[d]		23.34[d]
DMEU		2.3	100–101	46.92	1.99	146.1[d]		19.17[d]
DMET		2.2	.....	32.18	2.06	190.2[d]		22.09[d]

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

[b] Determined by iodometric method.

[c] The average degree of formaldehyde substitution.

[d] The calculated value as dimethylol compound.

[e] The calculated value as compound with n moles of formaldehyde.

[f] MMT, Hydroxymethylated 2-methoxy-4,6-diamino-s-triazine; MIPT, hydroxymethylated 2-isopropoxy-4,6-diamino-s-triazine; MAG, hydroxymethylated 2-methyl-4,6-diamino-s-triazine (methylolacetoguanamine); MEM, hydroxymethylated 2-monoethylamino-4,6-diamino-s-triazine (methylol-N-(2-ethyl)melamine); MHEM, hydroxymethylated 2-monohydroxyethylamino-4,6-diamino-s-triazine (methylol-N-(2-hydroxyethyl)-melamine); MBHEM, hydroxymethylated 2-dihydroxyethylamino-4,6-diamino-s-triazine (methylol N,N-bis(2-hydroxyethyl)melamine); TMM, 2,4,6-tris(hydroxymethylamino)-s-triazine(trimethylolmelamine); DMU, N,N'-bis(hydroxymethyl)urea (dimethylolurea); DMEU, 1,3-bis(hydroxymethyl)-2-imidazolidinone (dimethylolethyleneurea); DMET, 1,3-bis(hydroxymethyl)tetrahydro-5-ethyl-2(1)-s-triazone (dimethylolethyltriazone).

TABLE II
Properties of Finished Fabrics

No. of finished fabric	Finishing reagent	X	N, %	Add-on, %	Crease recovery angle, (W)°
				Properties of finished fabric	
1	MMT	CH_3O-	3.35	9.2	114
4	M1PT	$(CH_3)_2CHO-$	2.62	7.9	135
5	MAG	CH_3-	3.56	8.2	138
8	TMM	H_2N-	3.97	8.6	150
10	MEM	C_2H_5NH-	3.60	8.8	144
12	MHEM	HOC_2H_4NH-	4.03	11.3	148
14	MBHEM	$(HOC_2H_4)_2N-$	3.04	10.0	148
15	DMU		1.86	7.3	155
18	DMEU		1.49	7.8	155
19	DMET		1.80	8.3	150

the effect of substituent X on the resistance of these finishes to hydrolysis, and differences between resistance of MXT finishes to hydrolysis and that of finishes of cotton treated with dimethylolurea (DMU), dimethylolethyleneurea (DMEU), dimethylolethyltriazone (DMET), or trimethylolmelamine (TMM).

EXPERIMENTAL

Reagents are listed in Table I, and fabrics treated with these reagents are shown in Table II. The details of the treatments have been reported previously.[16] Hydrolyses were performed in aqueous solutions buffered at various pH's in accordance with the method of Reeves[2] and Andrews.[3] The buffer solutions were prepared from the following reagents: pH 2; $0.2N$ HCl—$0.2N$ KCl, pH 4; $0.1M$ sodium citrate—$0.1N$ HCl, pH 10; $0.05M$ Na_2CO_3—$0.05M$ Na_2BO_3, pH 13; $0.1N$ NaOH, and pH 14; $1N$ NaOH.

The finished fabrics were exposed to the hydrolysis medium using a 1:50 ratio of sample to buffer solution under stirring for 30 min at 80° or 40°C in a three-necked flask with thermometer, condenser, and stirrer. After hydrolysis, the samples were washed in running water and air dried. Hydrolysis resistance was estimated primarily from retained nitrogen contents and also from crease recovery angles. Nitrogen contents were determined by the Kjeldahl method, and crease recovery angles (warp direction) were measured by the Monsanto method.

RESULTS AND DISCUSSION

Effect of pH on Hydrolysis Resistance

Samples were hydrolyzed in solutions of pH 1 for 30 min at 40°C, and of pH 2, 4, 10, 13, and 14 for 30 min at 80°C. Table III and Figure 1 show
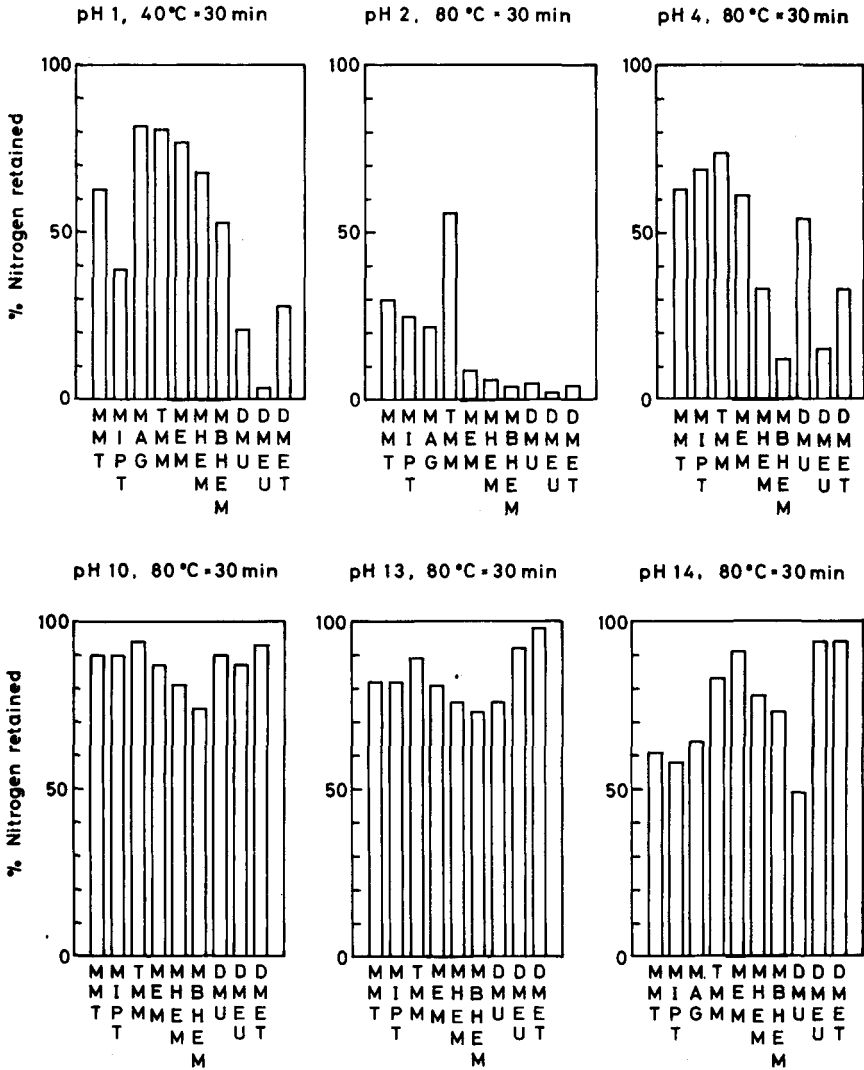
pH 1, 40°C ▪30 min   pH 2, 80°C ▪ 30 min   pH 4, 80°C ▪30 min

pH 10, 80°C ▪30 min   pH 13, 80°C ▪30 min   pH 14, 80°C▪30min

Fig. 1. Retention of nitrogen content as indicator for resistance of crosslinked finishing agents on cotton.fabrics retained after hydrolysis for 30 min at 40° and 80°C in buffer solutions of various pH's.

the changes in crease recovery angles and nitrogen contents retained, respectively, after the hydrolyses. Trimethylolmelamine shows greater resistance to acid hydrolysis when the bound nitrogen retained is the indicator than when the crease recovery angles are used as criteria. Andrews et al.[3] also have observed this fact, and reported that this may be due to hydrolytic cleavage of the crosslinks and subsequent formation of non-crosslinking polymer or melamine salt too insoluble to be extracted from the fabric under the conditions used.

The hydrolysis resistance of the crosslinked MXT will be as follows: pH 1, MROT < MRNT < MRT; pH 2–4, MROT > MRT > MRNT; pH 10–13, MROT > MRNT; pH 14, MROT < MRT < MRNT, where MROT is hydroxymethylated 2-alkoxy (MMT, MIPT), MRT is hydroxymethylated 2-alkyl (MAG), and MRNT is hydroxymethylated 2-alkylamino-4,6-diamino-s-triazine (MEM, MHEM, MBHEM).

In acid hydrolysis, the resistance order in pH 2–4 is the reverse of the one at pH 1; also in alkali hydrolysis, the order in pH 10–13 is the reverse of the one at pH 14. These facts are considered in the next paragraphs.

Mechanism of Acid Hydrolysis

Reeves[2] and Andrews[3] have proposed a mechanism for acid hydrolyses of crosslinks formed between amidemethylol compounds and cotton as illustrated in scheme 1:
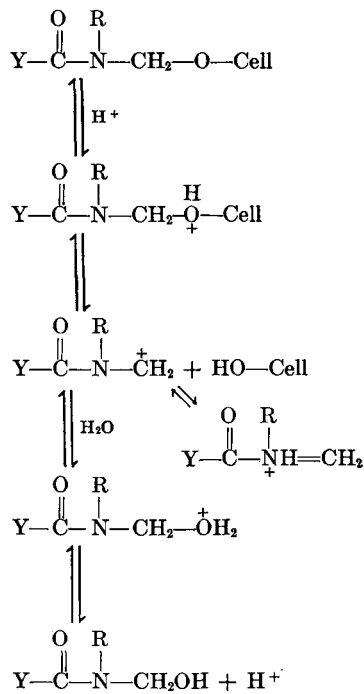
scheme 1: mechanism of acid hydrolysis

Proton attacks first on the ethereal oxygen between reagent and cellulose, and thus the acid hydrolysis is initiated. The electron density on the ethereal oxygen varies with the magnitude of inductive (I) and messomeric (M) effects of the accompanying groups Y and R. The greater the electron-releasing powers of the Y and R groups, the more easily the ether linkage is hydrolyzed.

Since the s-triazine ring is a resonance hybrid, the electron density on each atom of the ring varies with change in the M and I effects accompanying

TABLE III
Effect of Hydrolysis on Crease Recovery Angles (CRA) of Crosslinked Fabrics

	CRA (Warp)°		
		Hydrolyzed for 30 min at	
Finishing reagent	Original	pH 1, 40°C	pH 2, 80°C
MMT	144	103	75
MIPT	135	91	74
MAG	138	114	69
TMM	150	111	75
MEM	144	106	67
MHEM	148	110	67
MBHEM	148	90	68
DMU	155	83	77
DMEU	155	78	72
DMET	150	79	66

TABLE IV
pK_b of XT (25°C)[a]

X	pK_b
$CH_3O—$	10.46
$(CH_3)_2CHO—$	10.20
$CH_3—$	9.35 (9.4[b])
$H_2N—$	8.97 (9.0[b])
$C_2H_5NH—$	8.75 (8.77[b])
$HOC_2H_4NH—$	8.83
$(HOC_2H_4)_2N—$	8.70 (8.89[b])

[a] From ref. 24.
[b] From ref. 25.

a change in the X substituent. This change will be transmitted to the ethereal oxygen. Therefore, the magnitude of the electron density on the oxygen is dependent on the electron-releasing power of the X substituent. Table IV shows the pK_b values of XT. Judging from these values, the magnitude order of the electron density on the ethereal oxygen of crosslinked MXT is MRNT > MRT > MROT. (Although the pK_b values of crosslinked MXT cannot be measured, the magnitude order of those of MXT having an equal n is almost the same as the magnitude order of pK_b of XT. Because the pK_b values of MXT increase linearly with an increase in n, and the slopes of the lines (α) of MMT,[17a] MIPT,[17a] MAG,[17b] and methylolmelamine (MM)[17c] are 0.412, 0.279, 0.302, and 0.308, respectively, the order of pK_b of these MXT's used in this study is MMT > MIPT > MAG > TMM, and the order of pK_b of these crosslinked MXT's is considered the same. On the other hand, the magnitude order of pK_b for the crosslinked MRNT having approximately equal n's can be presumed to be almost the same for RNT, although the α's of MEM, MHEM, and MBHEM, the pK_b's of which are nearly equal, have not been determined.) Accordingly, the order of susceptibility to acid hydrolysis should

be MRNT > MRT > MROT. This is consistent with the observed susceptibility to hydrolysis in pH 2–4. The observed magnitude order of the resistance at pH 1, however, is approximately reverse of the one in pH 2–4. This fact can be explained as follows: XT is a weak base and is protonated in an acidic aqueous solution to give the conjugate acid.[18,19,20] Crosslinked MXT will also give its conjugate acid (II) similarly to XT in an acidic aqueous solution. In pH $\geq$ 2, the neutral molecule (I) and II will coexist and be hydrolyzed together. Therefore, the acid hydrolysis of crosslinked MXT will proceed via the following steps:

$$
\begin{array}{c}
\text{X} \\
| \\
\text{C} \\
\diagup \diagdown \\
\text{N} \qquad \text{N} \\
| \qquad \| \\
\text{C} \qquad \text{C} \\
\diagup \diagdown \diagup \diagdown \\
\text{Cell—O—H}_2\text{CHN} \qquad \text{N} \qquad \text{NHCH}_2\text{—O—Cell} \\
\text{I}
\end{array}
\qquad + \text{H}_3\text{O}^+ \quad \rightleftarrows
$$

$$
\begin{array}{c}
\text{X} \\
| \\
\text{C} \\
\diagup \diagdown \\
\text{H—N} \qquad \text{N} \\
| \qquad | \\
\text{C} \qquad \text{C} \\
\diagup \diagdown \diagup \diagdown \\
\text{Cell—O—H}_2\overset{+}{\text{CHN}} \qquad \text{N} \qquad \text{NHCH}_2\text{—O— Cell} \\
\text{II}
\end{array}
\qquad + \text{H}_2\text{O} \quad (1)
$$

$$\text{Cell—O—H}_2\text{CHN—T—NHCH}_2\text{—O—Cell} + \text{H}_3\text{O}^+ \rightleftarrows$$
$$\text{Cell—O—H}_2\text{CHN—T—N}\overset{+}{\text{H}}\text{CH}_2 + \text{HO—Cell} + \text{H}_2\text{O} \quad (2)$$

$$\text{Cell—O—H}_2\text{C}\overset{+}{\text{HN}}\text{=HT—NHCH}_2\text{—O—Cell} + \text{H}_3\text{O}^+ \rightleftarrows$$
$$\text{Cell—O—H}_2\text{C}\overset{+}{\text{HN}}\text{=HT—N}\overset{+}{\text{H}}\text{CH}_2 + \text{HO—Cell} + \text{H}_2\text{O} \quad (3)$$

$$\text{Cell—O—H}_2\text{CHN—T—N}\overset{+}{\text{H}}\text{CH}_2$$
$$\text{Cell—O—H}_2\text{C}\overset{+}{\text{HN}}\text{=HT—NHCH}_2 \qquad + \text{H}_2\text{O} \rightleftarrows$$

$$\text{Cell—O—H}_2\text{CHN—T—NH}_2$$
$$\text{Cell—O—H}_2\text{C}\overset{+}{\text{HN}}\text{=HT—NH}_2 \qquad + \overset{+}{\text{C}}\text{H}_2\text{OH} \quad (4)$$

$$
\text{where T} = \begin{array}{c}
\text{X} \\
| \\
\text{C} \\
\diagup \diagdown \\
\text{N} \quad \text{N} \\
| \qquad \| \\
\text{C} \quad \text{C} \\
\diagup \diagdown \diagup \diagdown \\
\qquad \text{N}
\end{array}
\quad \text{and HT} = \begin{array}{c}
\text{X} \\
| \\
\text{C} \\
\diagup \diagdown \\
\text{H—N} \quad \text{N} \\
| \qquad | \\
\text{C} \quad \text{C} \\
\diagup \diagdown \diagup \diagdown \\
\qquad \text{N}
\end{array}
$$

Reactions (2) and (3) are considered rate-determining steps, and the hydrolysis rate v_a is expressed[21] by eq. (5):

$$v_a = \frac{[\text{H}_3\text{O}^+]\{k_2[\text{H}_2\text{O}] + k_3K_1[\text{H}_3\text{O}^+]\}}{[\text{H}_2\text{O}] + K_1[\text{H}_3\text{O}^+]} (N_0 - x) \qquad (5)$$

$$= k_a(N_0 - x) \qquad (5')$$

where K_1 is the equilibrium constant of reaction (1); k_2 and k_3 are the rate constants of reactions (2) and (3), respectively; k_a is the rate constant of acid hydrolysis; N_0 and x are the nitrogen contents of original treated fabric and the hydrolyzed amount, respectively; and k_2 will be larger than k_3.
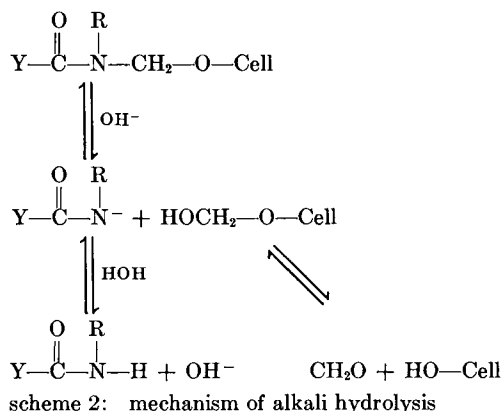
It is clear from eq. (5) that v_a decreases with increase in the K_1 value. From the pK_b value of XT, the order of the equilibrium constant of conjugate acid formation of XT with acid is RNT > RT > MROT. Therefore, the magnitude order of the K_1 value seems to be the same. If k_2 and k_3 do not vary much with change in X, the order of v_a should become: crosslinked MROT > crosslinked MRT > crosslinked MRNT, i.e., the order of hydrolysis resistance should become reverse to the one of v_a. In the hydrolysis in pH 2–4, however, the observed durability was in the order: crosslinked MROT > crosslinked MRT > crosslinked MRNT, which is contrary to the order described above. This fact shows that in pH 2–4, v_a is more influenced by k_2 and k_3 than K_1, and $k_2[\mathrm{H_2O}]$ is greater than $k_3K_1[\mathrm{H_3O^+}]$. That is, k_2 is considered the main factor controlling v_a of each crosslinked MXT. As the order of the electron-releasing power of X is —NR > —R > —OR, the order of the electron density on the ethereal oxygen of I becomes: crosslinked MRNT > crosslinked MRT > crosslinked MROT. Accordingly, the order of difficulty of an attack by proton, i.e., the order of acid hydrolysis resistance, is considered to be: crosslinked MROT > crosslinked MRT > crosslinked MRNT. The order of hydrolysis resistance in pH 2–4 agrees fairly well with the magnitude order of the pK_b of XT.

On the contrary, [II] ≫ [I] applies in pH ≤ 1, and thus $k_3K_1[\mathrm{H_3O^+}] > k_2[\mathrm{H_2O}]$ will be maintained. That is, k_3 is considered the main factor controlling v_a of each crosslinked MXT in pH ≤ 1. Due to the protonation of the ring, the order of the electron density on the ethereal oxygen of

$-\overset{+}{\mathrm{N}}\!\!=\!\!\mathrm{HT}\!\!-\!\!\mathrm{NHCH_2}\!\!-\!\!\mathrm{O}\!\!-\!\!\mathrm{Cell}$ (II) is: crosslinked MRNT < crosslinked MRT < crosslinked MROT. Accordingly, the order of hydrolysis resistance in pH ≤ 1 should become: crosslinked MRNT > crosslinked MRT > crosslinked MROT. The observed order at pH 1 was: crosslinked MRT > crosslinked MRNT > crosslinked MROT. The reason why the resistance of crosslinked MRT is not consistent with the above idea is not clear yet. The observed magnitude order of resistance at pH for crosslinks of MXT except for MAG is consistent approximately with the smallness order of pK_b of XT.
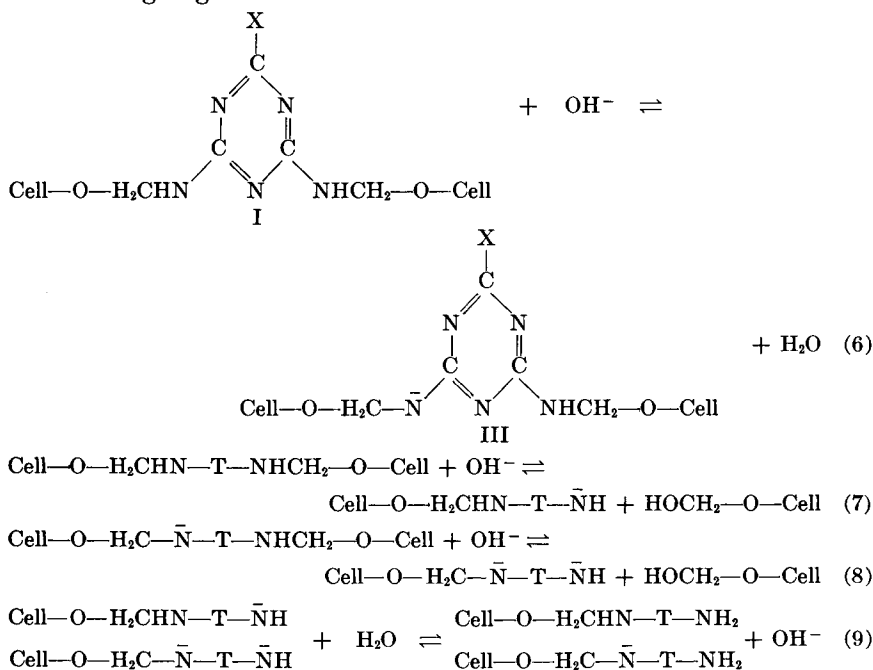
Thus, the observed data can be explained in terms of the idea described above.

Mechanism of Alkali Hydrolysis

A mechanism of alkali hydrolysis of crosslinks of amidemethylol reagents has been proposed[3] as illustrated in scheme 2:

$$Y—\overset{O}{\overset{\|}{C}}—\overset{R}{\overset{|}{N}}—CH_2—O—Cell$$

$$\Updownarrow \; OH^-$$

$$Y—\overset{O}{\overset{\|}{C}}—\overset{R}{\overset{|}{N}}{}^- + HOCH_2—O—Cell$$

$$\Updownarrow \; HOH$$

$$Y—\overset{O}{\overset{\|}{C}}—\overset{R}{\overset{|}{N}}—H + OH^- \qquad CH_2O + HO—Cell$$

scheme 2: mechanism of alkali hydrolysis

Alkali hydrolysis is initiated by an attack of hydroxyl anion on the amide nitrogen. The greater the electron-releasing power of the Y and R groups, the greater becomes the electron density on the amide nitrogen. Therefore, the nitrogen becomes less susceptible to the attack by hydroxyl anion with increase in the electron-releasing power of the Y and R groups, and becomes more susceptible to the attack by hydroxyl anion with increase in the electron-withdrawing power of the two groups. For crosslinked MXT, the order of hydrolysis resistance in pH 10–13 was the reverse of the one at pH 14. This fact can be explained in terms of the following: XT produces conjugate base in an alkaline aqueous solution;[22] so does crosslinking MXT. Therefore, the alkali hydrolysis will proceed through the following stages:

$$\text{I} \qquad + \quad OH^- \; \rightleftharpoons$$

$$\text{III} \qquad\qquad + \; H_2O \quad (6)$$

Cell—O—H₂CHN—T—NHCH₂—O—Cell + OH⁻ ⇌

$$\text{Cell—O—H}_2\text{CHN—T—}\overset{-}{\text{N}}\text{H} + \text{HOCH}_2\text{—O—Cell} \quad (7)$$

Cell—O—H₂C—N̄—T—NHCH₂—O—Cell + OH⁻ ⇌

$$\text{Cell—O—H}_2\text{C—}\overset{-}{\text{N}}\text{—T—}\overset{-}{\text{N}}\text{H} + \text{HOCH}_2\text{—O—Cell} \quad (8)$$

$$\begin{array}{c}\text{Cell—O—H}_2\text{CHN—T—}\overset{-}{\text{N}}\text{H} \\ \text{Cell—O—H}_2\text{C—}\overset{-}{\text{N}}\text{—T—}\overset{-}{\text{N}}\text{H}\end{array} + \; H_2O \; \rightleftharpoons \begin{array}{c}\text{Cell—O—H}_2\text{CHN—T—NH}_2 \\ \text{Cell—O—H}_2\text{C—}\overset{-}{\text{N}}\text{—T—NH}_2\end{array} + OH^- \quad (9)$$

Both neutral molecule I and conjugate base III will coexist in pH 13 and will be hydrolyzed together. Reactions (7) and (8) are rate-determining steps, and alkali hydrolysis rate v_b is expressed by eq. (10):

$$v_b = \frac{[OH^-]\{k_7[H_2O] + k_8K_6[OH]^-\}}{[H_2O] + K_6[OH^-]}(N_0 - x) \tag{10}$$

$$= k_b(N_0 - x) \tag{10'}$$

where K_6 is the equilibrium constant of eq. (6); k_7 and k_8 are the rate constants of eqs. (7) and (8), respectively; k_b is the rate constant of alkali hydrolysis and $k_7 > k_8$. The order of the equilibrium constant of the conjugate base formation of XT with alkali will be ROT > RT > RNT. The magnitude order of the K_6 value will be the same as this. Accordingly, if k_7 and k_8 do not vary so much with change in the X, the order of v_b becomes: crosslinked MROT < crosslinked MRT < crosslinked MRNT. Therefore, the order of the resistance to alkali hydrolysis should be: crosslinked MROT > crosslinked MRT > crosslinked MRNT.

In pH 10–13, the observed order of the hydrolysis resistance was: crosslinked MROT > crosslinked MRNT, consistent with the consideration described above, and also agreed fairly well with the magnitude order of the pK_b value of XT.

On the contrary, [III] ≫ [I] and $k_8K_6[OH^-] \gg k_7[H_2O]$ will be maintained at pH 14. Accordingly, v_b at this pH is controlled primarily by reaction (8). The order of electron density on the nitrogen of —T—NH— of III is considered to be: crosslinked MRNT > crosslinked MRT > crosslinked MROT, which is the same as the magnitude order of the basicity of XT. Accordingly, the order of the hydrolysis resistance at pH 14 should be: crosslinked MRNT > crosslinked MRT > crosslinked MROT.

The observed data were in agreement with this order, and also the magnitude order of the hydrolysis resistance was fairly consistent with the magnitude order of the basicity of XT.

Judging from the pK_b value, crosslinked MEM should be susceptible to hydrolysis more than crosslinked MHEM. The observed data, however, are contrary to this presumption. This can be attributed to the difference in crosslinked structure between MEM (mainly oligomeric crosslinks) and MHEM (mainly monomeric crosslinks),[16] because the amount of —CH_2—O—Cell in the former is less than that in the latter, and —CH_2—O—Cell is more easily hydrolyzed than the N—CH_2—N group.[23]

Comparison of Hydrolysis Resistance of Crosslinked MXT, DMU, DMEU, and DMET

The hydrolysis resistance of crosslinked DMET in pH 2–4 is greater than that of crosslinked MBHEM, nearly equal to that of crosslinked MHEM, and smaller than the resistance of crosslinked MEM. On the other hand, the resistance at pH 1 is smaller than the resistance of all crosslinked MXT. It has been reported that the amino group of triazone is only weakly basic and does not form a stable salt with strong electron-withdrawing property.[3]

Perhaps this can be attributed to a larger pK_b of ethyl triazone than that of XT. Therefore, the resistance to alkali hydrolysis is considered larger in crosslinked DMET than in crosslinked MXT. Due to the very weak electron-withdrawing property of the ethyleneurea ring, the resistance to acid hydrolysis is smaller in crosslinked DMEU than in MXT, but the resistance to alkali hydrolysis is larger.

The resistance to acid hydrolysis is greater in crosslinked DMU than in DMEU and DMET, but the resistance to alkali hydrolysis is smaller. This fact has been reported as a result of intramolecular H bond formation between the amide hydrogen and the ethereal oxygen.[3]

Comparing these results with crosslinked MXT, the resistance to acid hydrolysis is in the order crosslinked MXT > DMET > DMEU > DMU, and the resistance to alkali hydrolysis is: crosslinked DMET > DMEU > MXT > DMU. MXT finishing reagents are very stable to acid hydrolysis.

Effect of Temperature on Acid Hydrolysis Rate

Acid hydrolysis rates of crosslinked MMT, MAG, and MEM were determined. Hydrolysis was carried out in buffer solution of pH 2 at 40°, 60°, and 80°C. Figure 2 illustrates the plots of log N/N_0 (N_0, N are the nitrogen contents in the original and the hydrolyzed fabrics, respectively) against time. Although a few plots deviated slightly from the line, all plots showed good linearity. The rate constants k_a were calculated from the slopes of these straight lines, and they were indicated in Table V. The order of k_a is: crosslinked MEM > MAG > MMT at the given temperature. The reason for this order has already been explained.

The nitrogen content of crosslinked MIPT is considerably smaller in the hydrolysis at 60°C compared with that at 80°C (Fig. 3). This fact is due
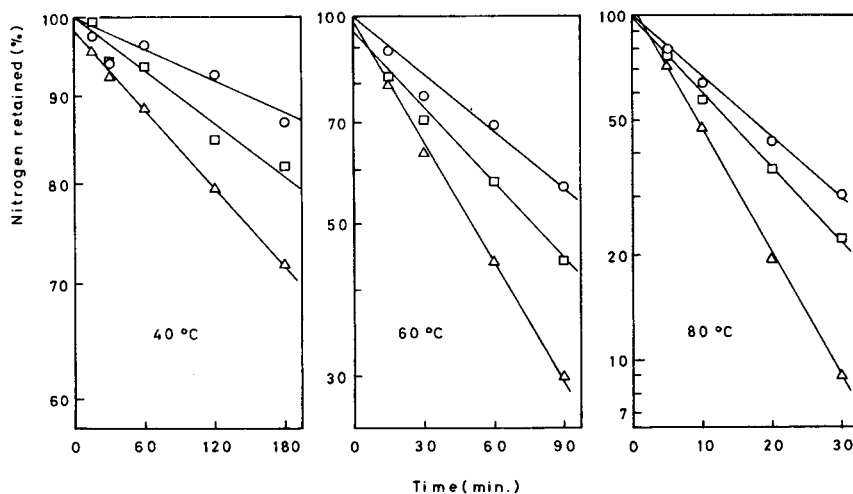

Fig. 2. Plots of log N/N_0 vs. time for hydrolysis of crosslinked MMT, MAG, and MEM with cotton fabrics in buffer solution of pH 2: (O) MMT; (□) MAG; (△) MEM.

TABLE V
Hydrolysis Rate Constants k_a of Crosslinked MXT's

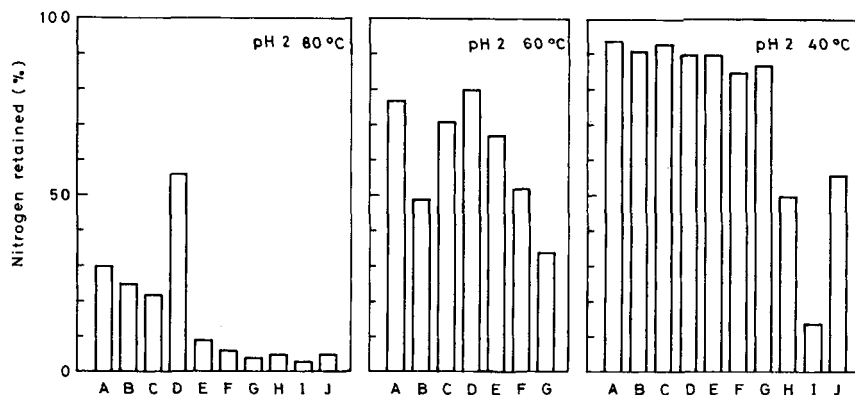| MXT	$k_a \times 10^4$, min^{-1}		
	40°C	60°C	80°C
MMT	7.04	59.2	378
MAG	11.1	75.3	468
MEM	19.4	135	831

Fig. 3. Nitrogen content retained after hydrolysis for 30 min at 80°, 60°, and 40°C in buffer solution of pH 2: (A) MMT; (B) MIPT; (C) MAG; (D) TMM; (E) MEM; (F) MHEM; (G) MBHEM; (H) DMU; (I) DMEU; (J) DMET.

probably to the nonuniform treatment. The order of nitrogen content of the other crosslinked MXT's in the hydrolysis at 60°C is nearly equal to that at 80°C.

The plots of log k_a versus $1/T$ show good linearity (Fig. 4); from these lines, the activation energies for acid hydrolysis were calculated to be 21.8, 20.9, and 21.0 kcal/mole for crosslinked MMT, MAG, and MEM, respectively. Among these values, differences are negligible. Figure 5 illustrates the plots of log k_a versus σ_m. It has been previously shown that the linear correlation is observed between pK_b of XT and σ_m (Fig. 6).[24] It was found that the former plots showed approximately equal grade linearity to the latter and were in conformity with the Hammett relationship. The slope of the line $|\rho|$ decreases as the temperature is raised.

SUMMARY AND CONCLUSION

The hydrolysis resistance of crosslinked MXT was investigated. The orders of the resistance at pH 1 and 14 were the reverse of the orders in pH 2–4 and 10–13, respectively. A possible explanation is that crosslinked MXT produces conjugate acid in acidic media and base in alkaline media. The resistance of crosslinked MXT to acid hydrolysis was larger than the resistance of crosslinked DMU, DMEU, or DMET, but its resistance to alkali hydrolysis was a little smaller than the resistance of crosslinked DMEU or DMET, and was larger than the resistance of DMU.
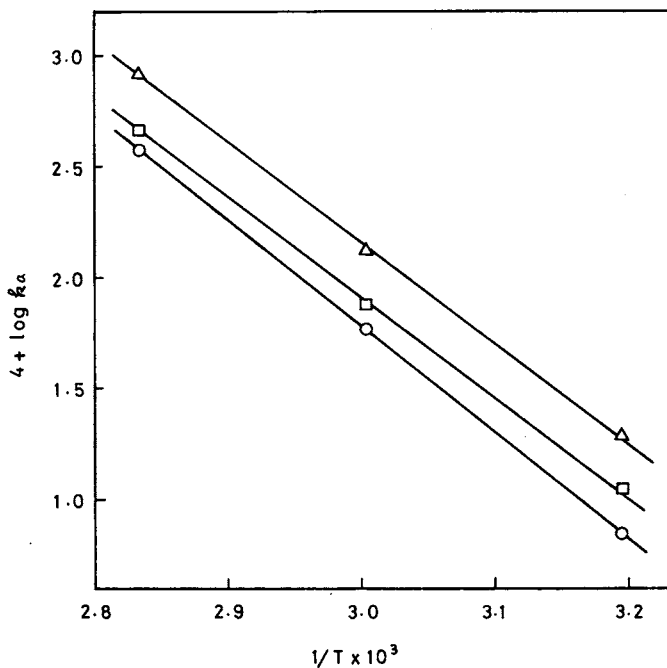
Fig. 4. Plots of log k_a vs. $1/T$ for hydrolysis of crosslinked MMT, MAG, and MEM with cotton fabrics: (O) MMT; (□) MAG; (△) MEM.
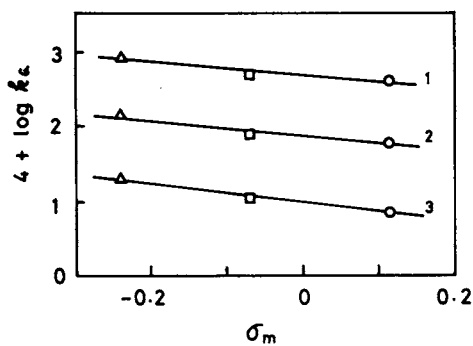

Fig. 5. Plots of k_a vs. Hammett constant σ_m: (O) MMT; (□) MAG; (△) MEM; (1) 80°C, $\rho = -0.957$; (2) 60°C, $\rho = -0.984$; (3) 40°C, $\rho = -1.099$.
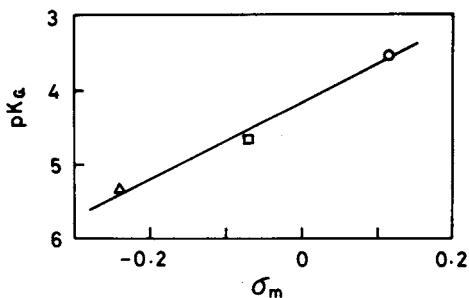

Fig. 6. Plots of pK_a of XT vs. σ_m: X = (O) CH₃O—; (□) CH₃—; (△) C₂H₅NH—.

The hydrolysis rate constants k_a of crosslinked MMT, MAG, and MEM were determined. They were in the order: crosslinked MEM > MAG > MMT. The activation energies for crosslinked MMT, MAG, and MEM were 21.8, 20.9, and 21.0 kcal/mole, respectively. The Hammett relationship was observed between log k_a and σ_m at the given temperature.

Generalizing various properties of treated cotton fabrics (that is, crease recovery angle, tensile strength, chlorine retention and chlorine damage, evolution of formaldehyde, etc.)[16] and resistance to hydrolysis, it can be said that MXT's are better finishing agents than DMU, DMEU, or DMET. MMT and MIPT are especially good finishing agents.

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