

Catalysis of the Reaction of Urea-Formaldehyde Precondensates on Cellulose*

RICHARD STEELE

Textile Research Laboratory, Rohm & Haas Company, Philadelphia, Pennsylvania

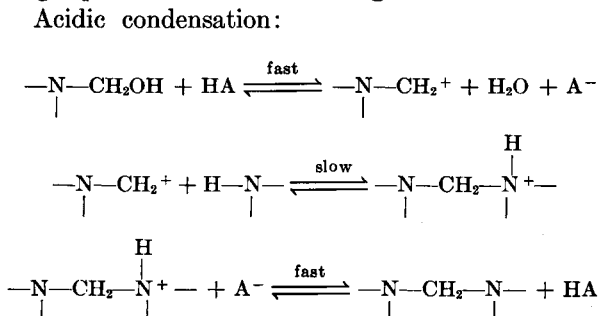
It has been customary in the application of monomeric urea-formaldehyde precondensates to cellulosic fabrics to use an acidic catalyst to accomplish the desired results of stabilization and creaseproofing. In the earliest days, organic acids were used, but these were supplanted relatively soon by the ammonium salts of certain strong mineral acids.¹ About fourteen years ago the use of amine salts was introduced, and more recently the use of metal salts, such as MgCl₂ or Zn(NO₃)₂, began. Within each of these classes there have been several commercial products offered which have found reasonable acceptance, and representatives of each are in current use.

The choice of a particular catalyst appears to be governed primarily by practical considerations involved in the actual application of the resin treatment and not by differences in the modification of fabric properties obtained. For example, Gagliardi² has suggested that the more important reasons for using a given catalyst in an individual mill are such things as efficiency, speed and uniformity of curing, bath stability, odor development, freedom from tendering, and freedom from yellowing or causing shade changes in dyeing. The first three of these are governed by the rate of the curing reaction, and the importance of the catalyst in this factor obviously depends on oven temperatures, fabric speeds, and other factors peculiar to a given industrial set-up. The other four are, in general, believed to result for the most part from side reactions which are not directly involved in producing the primary modification of fabric properties which the treatment is applied to obtain. Factors such as these can be extremely important in practice and can justify the considerable effort expended in the development and evaluation of new catalysts. However, relatively little informa-

tion is available in the literature on the role of catalysts in the reaction and how they may affect the end-product obtained. This paper is a brief review of what is known on the latter subject and a description of some new results in this field.

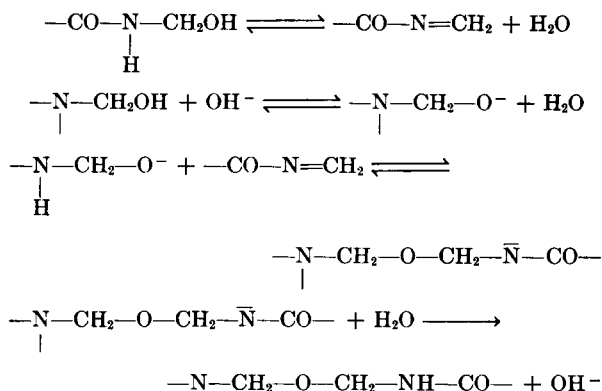
The reaction of urea and formaldehyde in aqueous solution has been investigated intensively by numerous workers in recent years, and their results have been reviewed comprehensively by Glauert.³ Both the addition reaction, which results in methylol ureas, and the condensation reaction, which yields the insoluble resinous products have been studied. The urea-formaldehyde "resins" used in textile finishing are mixtures of methylol ureas formed by the addition reaction and properly should not be called resins. We will call them precondensates. When these materials are condensed in solution under acid conditions, the products appear to be low molecular weight polymers of alternating methylene groups and urea residues. They may be linear or branched but are not cyclic, and contain free methylol groups. Condensation on the alkaline side has been studied less thoroughly, but in this case the links between urea residues seem to be chiefly methylene ether groups, —CH₂—O—CH₂—.

Considering the mechanisms proposed for the acidic⁴ and basic⁵ hydrolysis of resins, one might hypothesize that the corresponding condensations might proceed as in the following schemes.



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Basic condensation:



These reaction sequences, though they fit many of the observed facts, should be accepted with considerable qualification for the present.

When a catalyzed precondensate solution is dried down at moderate temperatures in a cellulosic fabric, one would expect condensation reactions to occur in much the same way as when the solution is in a beaker, at least until most of the water is evaporated. The fabric containing the lightly condensed resin deposited in it has somewhat improved crease recovery and is still soluble in cuprammonium hydroxide solution. If the catalyst used is acidic, as is the usual case, and the heat treatment intensified, a further reaction takes place, as evidenced by the resin becoming much more washfast, by the fabric becoming insoluble in cuprammonium hydroxide, and by a further enhancement of fabric crease recovery. The latter is particularly marked in the case of cotton fabrics. This further reaction, commonly called curing, is believed by many⁶⁻⁹ to involve reaction with the fiber. It is believed that reaction with the cellulose predominates over further reaction of the resin with itself for the following reasons. (a) Condensation of model methylol-urea compounds under acid conditions *in vitro* does not yield products containing $\text{---NH---CH}_2\text{---OCH}_2\text{---N---}$ linkages. (b) The number of cellulose hydroxyl groups available in a fiber containing 10% resin is at least five times the number of active hydrogens available on other resin molecules. The system, furthermore, is solid and dry so that the mobility of the resin molecules is restricted, and cellulose reaction sites should be more available to the resin molecules. (c) Finally, anhydrous acid conditions are known to promote *in vitro* the reaction of methylol compounds with alcohols.

When a basic catalyst is used, it has been assumed^{2,10} that reaction with the fiber does not take

place during curing, and it will be shown below that this assumption is probably correct.

ACID CATALYSIS

The nature of the acid catalyst used does not affect the changes in fabric properties that can be produced with a given precondensate except insofar as it determines the amount fixed in the fabric, provided that the catalyst level is low enough to avoid hydrolytic damage. This was pointed out by Gagliardi and Nuessle¹¹ and appears to be confirmed by mill and laboratory experience. We have therefore chosen a single acidic catalyst, ammonium chloride, and investigated rather carefully its effect at various concentrations on the properties of cotton fabric treated with simple urea-formaldehyde resins.

Samples of desized 80 × 80 cotton printcloth were treated with aqueous solutions containing 10% freshly prepared dimethylol urea and various levels of ammonium chloride. They were padded on a heavy laboratory padder giving 80% wet pickup, stretched on pin frames at their original dimensions, dried at 115°C., and then cured for 10 min. at 150°C. The treated fabrics were analyzed for total and fixed resin by the acid hydrolysis method. Fixed resin was determined after washing the samples for 25 min. in a hot solution containing 0.07% sodium carbonate. The results are shown by the

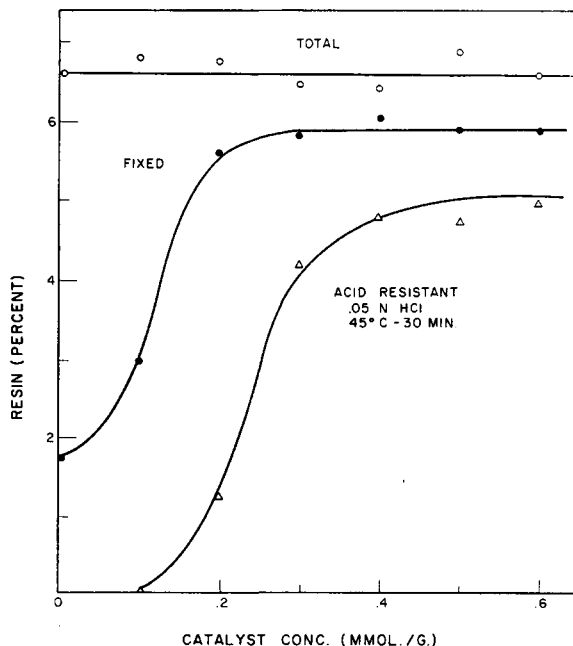


Fig. 1. Application of dimethylol urea to cotton printcloth at various levels of NH_4Cl catalyst.

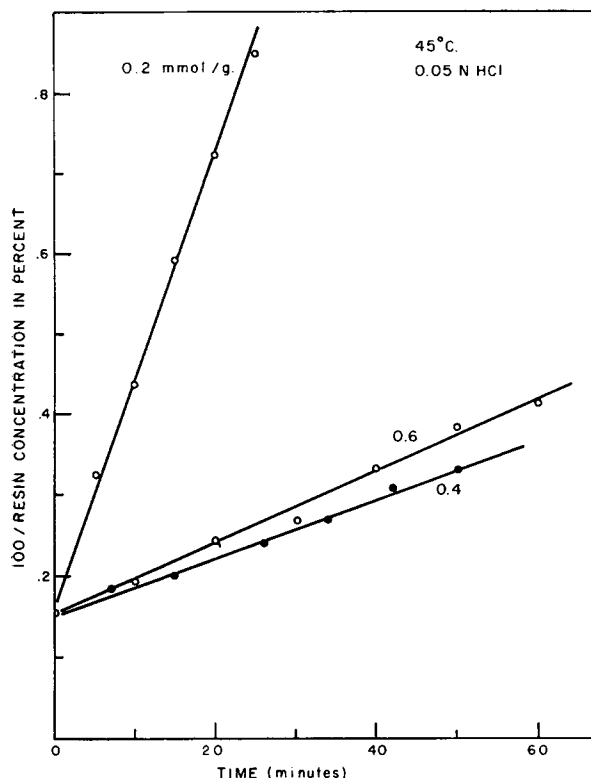


Fig. 2. Hydrolysis of dimethylol urea reacted on cotton printcloth with different levels of NH_4Cl as catalyst.

two upper lines in Figure 1. Catalyst concentration does not affect the total resin deposited on the treated fabric, but at least 0.2 mmole catalyst/g. precondensate is required to attain the maximum level of fixed resin.

The resistance of the resin to acid hydrolysis was also determined by measuring the resin remaining after the fabrics were extracted for 30 min. in 0.05N hydrochloric acid at 45°C. Maximum resistance to hydrolysis requires 0.3–0.4 mmole catalyst/g. precondensate. The rate of acid hydrolysis was determined more exactly for catalyst concentrations of 0.2, 0.4, and 0.6 mmole/g. A second set of fabrics was prepared as above. They were scoured to remove unfixed resin, and all three retained the same amount of fixed, water-insoluble resin. Then samples were hydrolyzed under the conditions given above for various times at 25, 45, and 65°C. If the reciprocal of the per cent resin remaining is plotted against time of hydrolysis, a straight line is obtained as shown in Figure 2, where the data for 45°C. are plotted. The slope of this line is a measure of the rate of reaction. The data do not give a straight line when plotted in accordance with first-order kinetics, although

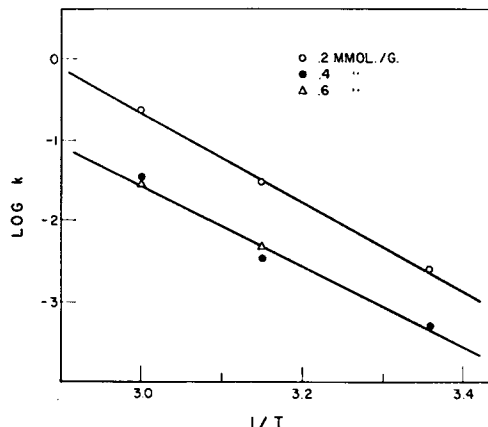


Fig. 3. Rate-temperature relationship for hydrolysis of dimethylol urea from cotton printcloth in 0.05N HCl.

the reaction must be pseudo first-order. The apparent second-order behavior must result from the effect of crosslinking on the accessibility of the sites of hydrolysis.

The slope of the line in Figure 2 is a measure of the rate of reaction. At each temperature the rates for the two higher catalyst concentrations were essentially the same and about one-sixth the rate for the low catalyst concentration. If these rate constants are plotted in the usual way suggested by the Arrhenius equation, as has been done in Figure 3, a pair of straight parallel lines is obtained. The activation energies calculated from these were

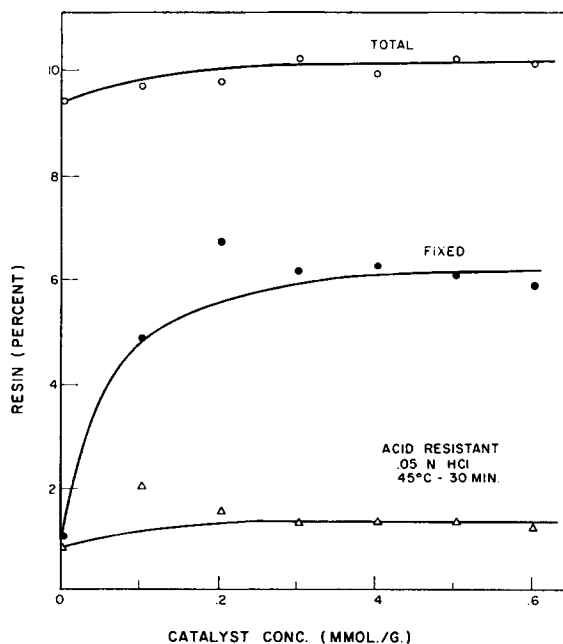


Fig. 4. Application of monomethylol urea to cotton printcloth at various levels of NH_4Cl catalyst.

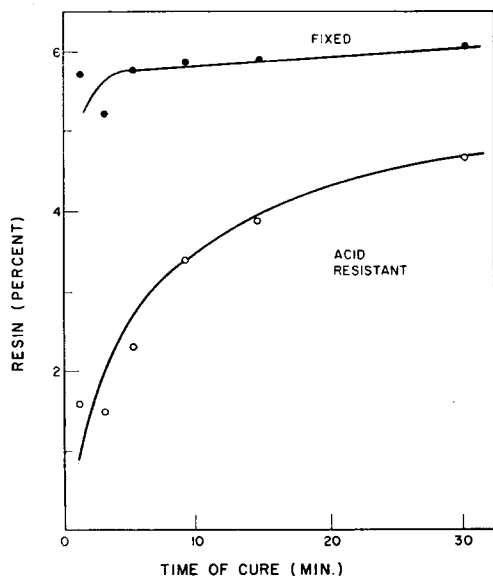


Fig. 5. Rate of curing of dimethylol urea on cotton printcloth at 135°C.

21.2 and 20.2 kcal./mole. These compare very well with the figure of 20.4 kcal. reported by Landquist¹² for the activation energy for hydrolysis of monomethylol and dimethylol ureas themselves, but it seems more likely that in the case of resin on cellulose that the rate-determining step may be breaking one end of a resin crosslink between two cellulose molecules, the other end being hydrolyzed rapidly. Thus in Figure 1 the insolubility of the resin applied to the fabric is brought about by single-ended reaction, and the acid resistance increases when extensive, double-ended, crosslinking reaction has been produced. The insolubilization and hydrolysis resistance of monomethylol urea is in agreement with this hypothesis. Figure 4 shows the results of an experiment with monomethylol urea carried out in the same way as that with dimethyl urea described above. This noncrosslinking precondensate can be reacted with the resin to be fast to washing but does not develop appreciable acid resistance, even at high catalyst levels.

The acid resistance of dimethylol urea catalyzed with ammonium chloride has a different rate of development during curing from the water insolubility, as shown in Figure 5. A 10% solution of dimethylol urea was applied to cotton printcloth with 0.3 mmole ammonium chloride/g. precondensate, and the padded samples were framed and put directly into the curing oven without preliminary drying. A lower cure temperature, 135°C., was used to accentuate the difference in rates of the two processes.

The development of maximum resistance to acid hydrolysis with increasing catalyst parallels the modification in mechanical properties of the treated fabric. Figure 6 shows the changes in crease recovery and stress relaxation observed on the samples treated with dimethylol urea for the experiment in Figure 1. These tests were done on the unscoured samples so that all of them have the same total resin present in the fabric. It can be seen

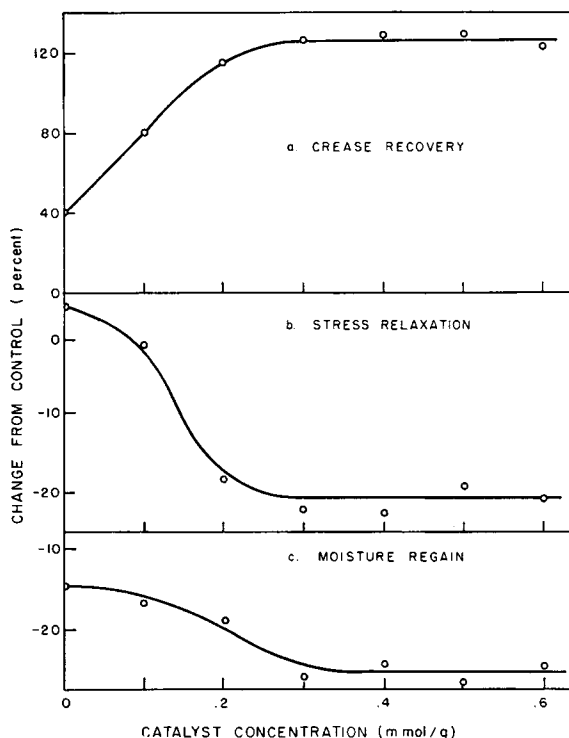


Fig. 6. Crease recovery, stress relaxation, and moisture regain of cotton printcloth treated with dimethylol urea at different levels of NH_4Cl catalyst, compared with values for untreated control fabric.

that treatment without catalyst, yielding about 2% of water-insoluble resin and 8% soluble, all of which is quite sensitive to acid hydrolysis, gives about 40% improvement in crease recovery. This is the order of enhancement obtained from monomethylol urea and other noncrosslinking materials. At higher catalyst levels, the crease recovery curve levels off at the high degree of crease recovery produced by crosslinking cotton.⁹ The changes in rate of stress relaxation follow the same pattern. The rate of stress relaxation was measured by the technique described elsewhere,¹² an initial extension of 3.5% being used. Here again, the uncatalyzed resin acts like monomethylol urea and yields a

small increase in the relaxation rate.¹³ The rate rapidly decreases as more catalyst is used and levels off at 0.3 mmole/g.

The moisture regain of these samples at standard testing conditions was also determined and is plotted in Figure 6c. Unlike the change in mechanical properties, the greater part of the effect in this case seems to be attainable with uncatalyzed resin, although there is still an inflection in the curve at the catalyst level where large changes occur in crease recovery and stress relaxation. This result is of interest in view of the theory held by some that crushproofing and stabilization of cellulose with resins is brought about by the deposition of resin particles which interfere with the solvation and plasticization of the cellulose molecules by water, thereby reducing molecular slippage when the fiber is strained and increasing the resilience. Reaction with the cellulose, if it occurs, is believed not to be extensive and therefore to be ineffective in producing the desired change in properties. This theory has been propounded principally by Elöd,^{14,15} his basic argument being that resin can be easily removed by mild chemical treatment (dilute acid, for example) which will not remove real chemical crosslinks such as those formed by formaldehyde.

Rotta and Allscher¹⁶ have also claimed to have found a procedure for leaching aminoplast resin out of cellulose. The treated fabric was placed in 20 times its weight of ethylene glycol, heated to 110°C., and kept at this temperature for 10 min. The extraction was repeated and then followed by a thorough wash in water. Sometimes a third extraction was necessary if the sample was still insoluble in cuprammonium solution. The data given by Rotta and Allscher are for cotton fabric treated with dimethylol urea. Since our experience has led us to believe that, in this case particularly, the reaction of the resin with the cellulose to form crosslinks is the most important process involved, as outlined in the discussion above, we have looked into this question further in the following experiment.

Four samples of treated 80 × 80 cotton printcloth were treated. Two were treated by the formula of Rotta and Allscher, and two by our usual treatment with ammonium chloride. The same dimethylol urea concentration was used in each case. One sample from each pair was cured under Rotta and Allscher's conditions and the other was given our ordinary laboratory cure. The details of treatment are given in Table I.

TABLE I

	Treating bath	Curing time, min.	Curing temp., °C.
Rotta and Allscher	80 g./l. DMU		
	8 g./l. urea	5	60
	8 g./l. NH ₄ NO ₃	5	110
	8 g./l. NH ₄ Ac		
Present work	80 g./l. DMU	5	60
	0.86 g./l. NH ₄ Cl	10	150

Swatches from each of these treatments were then extracted repeatedly with hot ethylene glycol in a 20:1 bath. The solvent was heated to 110°C. before adding the fabric. The samples were agitated in the hot bath for 10 min., removed, blotted, and then placed in a fresh portion of glycol. Samples for analysis were taken after one, two, and three extractions. Crease recovery was also obtained (Table II).

TABLE II

Treating solution	Crease recovery, %	
	R. & A. cure	Present cure
Rotta and Allscher	62	64
Present work	65	77
Water control	32	36

The nitrogen analyses are plotted against number of extractions in Figure 7. It can be seen that for the fabric cured in our usual way, the ethylene glycol extractions have removed just about the proportion of the resin usually found to be water-

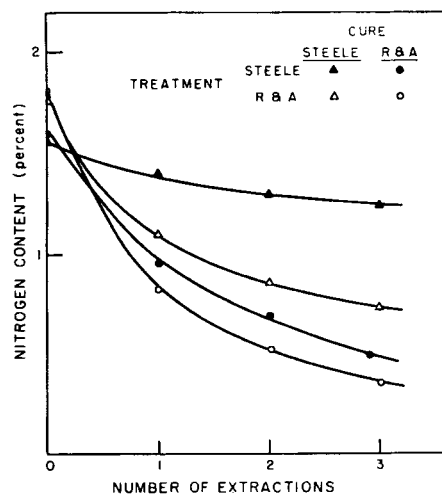


Fig. 7. Extraction of cotton printcloth treated with dimethylol urea with hot ethylene glycol.

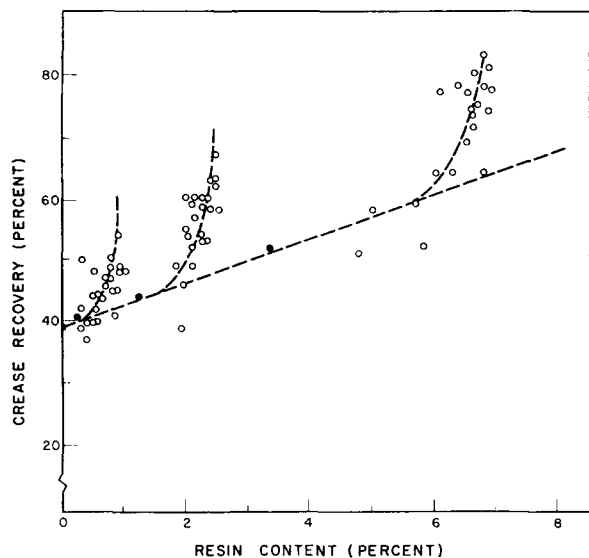


Fig. 8. Crease recovery of cotton printcloth treated with 2, 5, or 12% of dimethylol urea and various levels of acidic catalysts.

soluble. However, 80% of the nitrogen was removed from the fabric treated according to Rotta and Allscher's procedure, and it appears obvious that this treatment does not result in a satisfactory cure, and the extractability of the resin is to be expected. The intermediate position of the other two treatments would indicate that the poor cure is due both to the milder catalyst and to the lower curing temperature. The inadequate cure is also shown by the crease recovery data. Resin from

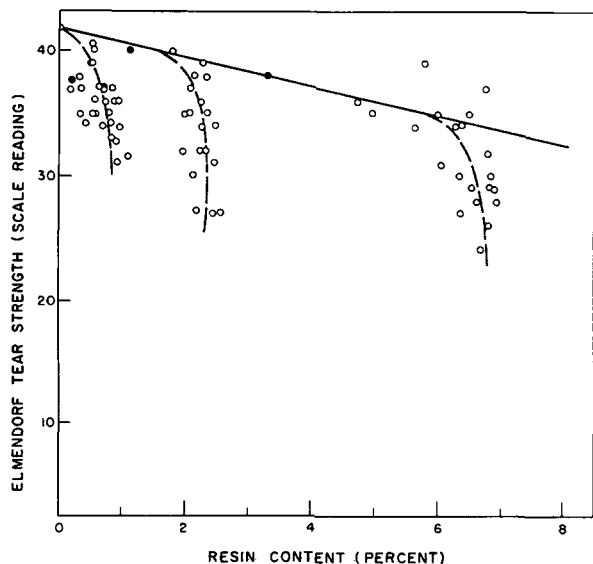


Fig. 9. Elmendorf tear strength of cotton printcloth treated with 2, 5, or 12% of dimethylol urea and various levels of acidic catalysts.

dimethylol urea applied under our normal laboratory conditions, which we believe are representative of those required for commercial production of the highly crease-resistant finishes used on cotton, is resistant to ethylene glycol extraction, and we believe this, like its effect on mechanical properties, is largely due to its reaction with the cellulose.

The concentration of an acid catalyst determines the efficiency of the resin application in terms of degrees of crease recovery per gram of added material. This is shown by the data in Figure 8, which were obtained in a number of experiments where various acidic catalysts were applied at a number of concentrations. Three levels of dimethylol urea were used, 2, 5, and 12%, and the treatments were carried out in the manner described above. The black points on the straight dashed line represent uncatalyzed control samples; the open points are various acid catalyst concentrations. The catalyzed samples not only result in a higher fixed resin content for a given application level but in considerably higher crease recovery values. The crease recovery enhancement is paralleled by loss of strength, as shown by the tear strengths in Figure 9. The branches on the curves in Figures 8 and 9 probably do not continue much beyond the points shown since all of the catalysts we have tested show a levelling off in crease recovery as the concentration increases, as shown in Figure 6a.

The resistance to acid hydrolysis of cured dimethylol urea reaches a maximum at a higher catalyst level (0.3 mmole/g.) than that required to attain maximum fixation or crease recovery (0.2 mmole/g.), as shown in Figures 1 and 6. The latter figure, based on fixation and crease recovery data, was chosen by Steele and Giddings⁹ for their work on the composition of the cured resin. The present work suggested that this was perhaps not the best choice. This possibility was further checked by studying the resistance to alkaline hydrolysis of a series of samples prepared like those used in the experiment shown in Figure 1. The results are shown in Figure 10, and it is obvious that 0.2 mmole/g. of ammonium chloride does not give maximum resistance to dilute alkali. Moreover, this concentration is one where the alkali resistance is changing rapidly. (The low fixation obtained at 0.2 mmole/g. in this experiment also indicates that this level is too near the steep part of the curve to be satisfactory.)

This result means that the methylene to methylol ratio for the formaldehyde residues, as determined

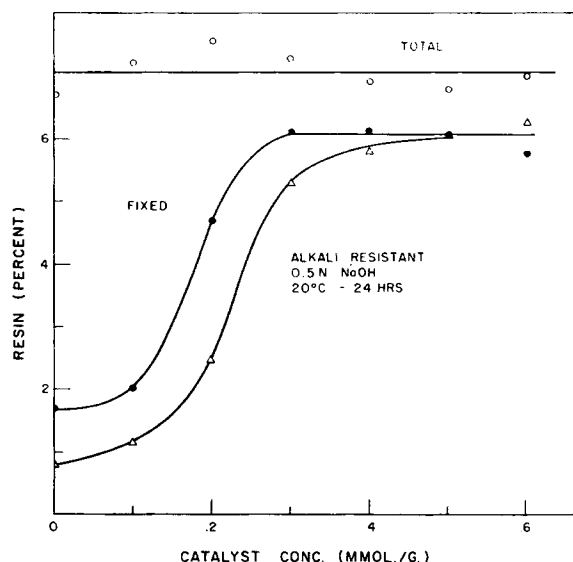


Fig. 10. Alkali resistance of dimethylol urea applied to cotton printcloth at various levels of NH_4Cl catalyst.

by alkaline hydrolysis, will depend on the catalyst level and that the conclusions as to the structure of the condensate put forth by Steele and Giddings are applicable only for the catalyst and level of it which they used. We have compared the amount of alkali-labile (methylol) formaldehyde in two samples which contained the same amount of resin but which were cured with 0.2 mmole/g. and 0.4 mmole/g. of ammonium chloride, respectively. The formaldehyde liberated in 0.5N NaOH at 20°C. was determined as a function of time.⁹ In both cases the hydrolysis of the susceptible formaldehyde was complete within one day, and no appreciable quantity was removed during the next nine days. In the case of the sample containing 0.2 mmole/g. of catalyst, about half of the formaldehyde present was liberated. With the higher catalyst level, only slightly more than 10% was freed. It is obvious that the earlier work needs to be extended to other catalyst concentrations.

ALKALINE CATALYSIS

As an example of alkaline catalysis of dimethylol urea, we have studied the use of sodium carbonate. There are many indications that this catalyst leads to a different product either *in vitro* or on fabric. Data on dimethylol urea cured with ammonium chloride or sodium carbonate on a watchglass are given in Table III. The catalyzed solutions of precondensate were dried down at 110°C., ground to a fine powder, and returned to

the oven for 24 hr. The solubility of the products was determined by refluxing them for 1 hr. in water, and their density was measured in gradient columns. The ineffectiveness of the alkaline

TABLE III

Properties of Dimethylol Urea Cured *in Vitro* for 24 hr. at 110°C. in the Presence of NH_4Cl or Na_2CO_3

Catalyst	Catalyst concn. mmole/g.	H_2O solubility, %	Density, g./cc.	
			Whole polymer	insoluble polymer
NH_4Cl	0.2	6.9	1.499	1.490
	0.4	11.3	1.490	1.491
Na_2CO_3	0.2	80.1	1.507	1.461
	0.4	90.4	1.519	1.471

catalyst in insolubilizing the polymer and the higher density of the soluble product are evident. Nitrogen and formaldehyde analyses of such products indicated formaldehyde/urea ratios of 1.3 for the acid catalyst and 1.4 for sodium carbonate.

Sodium carbonate is less efficient than ammonium chloride in insolubilizing dimethylol urea on fabric. The degree of conversion to insoluble resin with either catalyst also depends on other factors, such as curing conditions, but in general we have found that under comparable conditions, only two-thirds as much dimethylol urea is insolubilized in fabric by sodium carbonate as by ammonium chloride. Furthermore, with sodium carbonate catalysis, the cellulose remains soluble in cuprammonium hydroxide solution. In fact, the resin-treated fabrics frequently appear to dissolve even more readily than before treatment. This indicates that there are no alkali-stable crosslinks formed during the alkaline cure. The possibility of alkali-labile crosslinks can probably be ruled out also, since it was found that a scoured fabric containing 4.6% of dimethylol urea applied with sodium carbonate lost only 15% of its resin content after 5 hr. in 5N ammonium hydroxide and that its crease recovery (67%) was not diminished by this treatment. These observations make the presence of alkali-sensitive crosslinks very unlikely.

The conclusion that sodium carbonate does not catalyze the reaction of the resin with cellulose is also supported by the mechanical properties of the treated fabrics. It has been shown elsewhere that mono- and dimethylol ureas are quite different in the degree to which they modify cotton cellulose mechanically and that the difference seems to be due to the ability of the dimethylol compound to

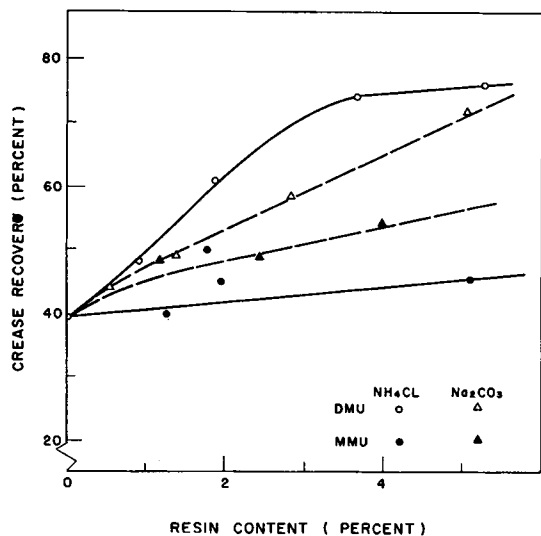


Fig. 11. Crease recovery of cotton printcloth treated with various levels of methylol ureas with NH_4Cl or Na_2CO_3 catalysis.

crosslink the fiber.⁹ When applied with sodium carbonate, these two reagents do not show this difference and have much more nearly equal effects. This is demonstrated by Figures 11 and 12, which show the crease recovery and strength of cotton printcloth treated with different levels of these two reagents and with either 0.1 mmole/g. of sodium carbonate or 0.2 mmole/g. of ammonium chloride. Preliminary experiments had shown that this level of sodium carbonate was sufficient to reach the maximum degree of resin insolubilization and fabric crease recovery. Later work indicated that

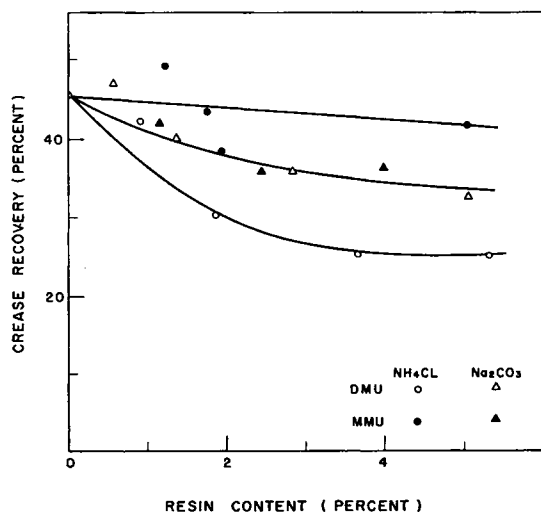


Fig. 12. Tensile strength of cotton printcloth treated with various levels of methylol ureas with NH_4Cl or Na_2CO_3 catalysis.

it may be a little low. The reagents were freshly prepared, and the samples were padded, framed, dried, and cured as described for the first acid-catalyzed samples described above. They were also scoured to remove unfixed resin.

The effects on tensile strength and crease recovery with ammonium chloride catalysis are similar to those reported earlier,⁹ dimethylol urea producing large changes and monomethylol urea small changes. With sodium carbonate catalysis both compounds give intermediate changes, being indistinguishable in the tensile strength produced under these conditions. This result indicates that the difference in functionality between the two reagents is minimized by alkaline catalysis and again indicates that reaction with the cellulose is not involved.

Although it seems unlikely that the alkaline catalyst brings about ether formation with the cellulose hydroxyls, it does result in greater insolubilization of the precondensate in fabric than *in vitro*. We have found that about 50% of the weight of applied dimethylol urea can be insolubilized on the fabric with sodium carbonate catalysis compared to 10–20% insolubility developed *in vitro*. Part of this difference may be due to the difference in extraction technique, the powder being refluxed for 1 hr. while the fabric was tumble-washed at 38°C. for 20 min. Goldschmidt, for example, prepared condensates under alkaline conditions which were soluble in hot water but insoluble in cold.¹⁷ However part of it may also be due simply to the mechanical trapping of polymer molecules in the fiber. The alkaline catalyst, like acidic ones,⁹ requires a "cure," not simply a drying, and we have found that, again as in the case of acid, there is no significant loss of formaldehyde when the dried fabric is cured. The alkaline cure is therefore presumed to occur by the mechanism given in the introduction which involves no loss in formaldehyde and leads to formation of a higher polymer containing methylene ether groups. The occurrence of methylene ether groups in basic condensations of urea-formaldehyde derivatives is supported by the work of Einhorn¹⁸ and Zigeuner.¹⁹ The polymerization of dimethylol urea with alkali to form molding compositions or lacquer ingredients was described by Walter.²⁰

The alkylation of methylol groups in aminoplast resins is not usually carried out under alkaline conditions, hot acidic anhydrous conditions being more favorable. The latter are comparable to the normal acid curing of resins on cellulose. We have found one report of alkaline catalysis in forming the

lower alkyl ethers of methylol urea.²¹ The products were not characterized by any of the usual criteria, such as analytical or melting point data, and the results claimed are so contrary to normal experience as to suggest the desirability of a closer examination of the products.

It should also be pointed out that the mechanism proposed for the basic condensation accounts for the failure of alkaline catalysts to condense dimethylol ethylene urea on cellulose, since this precondensate cannot form the necessary methylene imine intermediate.

CONCLUSION

The condensation of dimethylol urea on cellulose with typical acidic and basic catalysts may be summarized as follows. During drying with either catalyst a low degree of polycondensation occurs. Formaldehyde is lost to about the same extent in either case. The resin product is extractable by water, and the fabric is soluble in cuoxam solution. When the ammonium chloride-catalyzed system is cured at a higher temperature, the resin and fabric are insolubilized, because the acid catalyst promotes the formation of ether linkages between the condensate and the cellulose. With sodium carbonate, a further condensation of the resin takes place, so that part of it is insolubilized in the fabric by mechanical entrapment, but it does not react with the cellulose so that the latter remains soluble in cuoxam. No formaldehyde loss occurs during curing with either catalyst.

The acid-cured resin-treated fabric is crosslinked and has a high degree of crease recovery with a proportional loss in tensile strength. The alkali-catalyzed product has a lower crease recovery and higher strength. The resin deposited in it is of intermediate effectiveness in changing the physical properties. It is not so effective as the crosslinking resin formed by acid-catalyzed curing, but is more effective than the low molecular weight polymer formed by simply drying the precondensate in the fabric. The alkaline-cured polymer is more effective than the latter probably because the alkaline cure causes a further condensation of the polymer in the fabric.

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Synopsis

The reaction of dimethylol urea on cotton cellulose at 150°C. has been studied with NH₄Cl and Na₂CO₃ as catalysts. With the ammonium salt, 0.2 mmole/g. precondensate was required to attain the maximum level of fixed resin, while maximum resistance to hydrolysis by dilute acid required 0.3-0.4 mmole/g. The acid resistance is attributed to the crosslinking of the fiber, which is primarily responsible for the changes produced in resilience and other physical properties. The application of monomethylol urea with NH₄Cl does not lead to changes in acid resistance or physical properties such as are attributed to crosslinking. Catalysis with Na₂CO₃ does not appear to lead to crosslinking with dimethylol urea, since the treated cellulose remains soluble in cuprammonium hydroxide. There is very little difference in the effectiveness of monomethyl and dimethylol ureas for changing physical properties when they are applied with the alkaline catalyst. It is suggested that the curing step with Na₂CO₃ leads to further condensation through methylene ether linkages rather than to reaction with the cellulose substrate.

Résumé

La réaction de la diméthylol-urée sur la cellulose de coton à 150°C a été étudiée en présence de NH₄Cl et Na₂CO₃ comme catalyseurs. Avec le sel d'ammonium, 0,2 mmol./g. de précondensat furent nécessaires pour atteindre le niveau maximum de résine fixée, tandis que la résistance maximum à l'hydrolyse par les acides dilués nécessitait 0,3 à 0,4

mmol./g. La résistance aux acides a été attribuée au pontage de la fibre qui est en premier lieu responsable des changements produits dans l'élasticité et dans les autres propriétés physiques. L'application de monométhylol-urée avec NH_4Cl ne mène pas à des changements dans la résistance aux acides ou dans les propriétés physiques, suffisants pour être attribués au pontage. La catalyse avec Na_2CO_3 ne semble pas conduire au pontage avec la diméthylol-urée, puisque la cellulose traitée reste soluble dans l'hydroxyde de cuprammonium. Il y a très peu de différence dans l'efficacité des monoéthylol et diméthylol-urée pour faire varier les propriétés physiques lors de leur application en présence du catalyseur alcalin. On suggère que le traitement au Na_2CO_3 mène à une condensation ultérieure par des ponts méthylénique éthers plutôt qu'à une réaction avec le substrat cellulosique.

Zusammenfassung

Die Reaktion von Dimethylolharnstoff mit Baumwollcellulose wurde bei 150°C mit NH_4Cl und Na_2CO_3 als Katalysatoren untersucht. Von dem Ammoniumsalz waren

0,2 mMol/g. Präkondensat erforderlich, um die Höchstausbeute an fixiertem Harz zu erreichen, während der maximale Widerstand gegen Hydrolyse durch verdünnte Säure mit 0,3 bis 0,4 mMol/g erreicht wurde. Die Säurebeständigkeit wird auf Vernetzung der Faser zurückgeführt, was primär für die Änderung der Elastizität und anderer physikalischer Eigenschaften verantwortlich ist. Die Anwendung von Monomethylolharnstoff gemeinsam mit NH_4Cl führt zu keiner Änderung der Säurebeständigkeit oder von physikalischen Eigenschaften, die einer Vernetzung zuzuschreiben sind. Katalyse mit Na_2CO_3 scheint mit Dimethylolharnstoff nicht zur Vernetzung zu führen, da die behandelte Cellulose in Kuprammonhydroxyd löslich bleibt. Es besteht sehr wenig Unterschied in der Wirksamkeit von Monomethylol- und Dimethylolharnstoff in bezug auf Änderung physikalischer Eigenschaften bei Anwendung mit dem Alkalikatalysator. Es wird angenommen, dass die Behandlung mit Na_2CO_3 zu weiterer Kondensation durch Methylenätherbrücken und nicht zur Reaktion mit dem Cellulosesubstrat führt.

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