

## Degrees of Heterogeneity of Distribution of Formaldehyde Crosslinks in Cotton Cellulose\*

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### Synopsis

The distribution of formaldehyde crosslinks in cotton cellulose has been followed by electron micrographic analyses of fiber cross-sections and by kinetic analyses of rates of reactions of formaldehyde with cotton. Rapid and slow phases of the crosslinking reactions are indicated to extents which vary with the specific processes of reaction. A wide range in heterogeneity of distribution of crosslinks is found among the compositions investigated, the most heterogeneous distribution appearing in a high concentration of crosslinks in peripheral regions of the fiber. It is evident that additional substantial differences among the formaldehyde-crosslinked cottons are due to different extents of reaction of agent per accessible hydroxyl group.

### INTRODUCTION

The network structure of a semicrystalline fibrous polymer which is cross-linked in a heterogeneous reaction is strongly suspect of having a nonuniform distribution of linkages throughout the molecular and fibrous structures. Until clarification is achieved of the extent to which heterogeneous distribution of crosslinks occurs in such fibers, measurements of apparent frequency of crosslinks or effective elastic elements will have less than the desired significance.

Frick et al.<sup>1</sup> have observed that the expansion patterns of ultrathin cross-sections of crosslinked cottons are markedly different, depending upon whether the crosslinking reaction is conducted with the fibers in distended or collapsed condition. Reeves et al.<sup>2,3</sup> have explained the difference as one involving the absence (or deficiency) of interlamellar crosslinks for the distended fiber and the presence (or profusion) of these linkages for the fiber in the collapsed state. Whether this represents differences in distribution, in density, or in lengths of crosslinks has not been clarified. More obvious heterogeneity of distribution of crosslinks was observed by Frick et al.<sup>4</sup> in which localization of linkages appeared on the surface of the fiber

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when formaldehyde was applied under drastic conditions. This apparently caused considerable degradation of the cellulose. Further evidence of localization of crosslink development was encountered by Rowland et al.<sup>5</sup> for a cotton crosslinked in an acetic acid medium. Rowland and Post<sup>6</sup> interpreted the nonlinear behavior of a related formaldehyde-treated cotton in a Charlesby-Pinner treatment of sol-fraction data to indicate nonuniform crosslink distribution. On the basis of numerous studies of monofunctional reagents with cellulose<sup>7</sup> and also on an intuitive basis, heterogeneity of distribution of crosslinks from the exterior toward the interior of the fiber might be expected to be the logical consequence of diffusion-controlled reactions. The extent to which this situation occurs, if indeed it occurs at all, in crosslinked cottons which have been prepared under conventional and mild conditions of reaction is a matter of considerable interest.

This paper summarizes new evidence relative to extent of nonuniform distribution of crosslinks in cotton cellulose. Although a crosslinking agent of small molecular sizes might be expected to minimize heterogeneity in distribution of crosslinks, we have chosen to explore the problem with formaldehyde-treated cottons. Electron micrographs have been examined for direct evidence of nonrandom distribution of linkages, and kinetic data have been analyzed for indirect evidence.

## EXPERIMENTAL

Crosslinked cotton celluloses were prepared from desized, scoured, bleached 80 × 80 print cloth by employing formaldehyde under conditions representative of four different processes: aqueous system (designated form W), 7.6% CH<sub>2</sub>O, 12.2% HCl, 2.2% CH<sub>3</sub>OH, 78.0% H<sub>2</sub>O; nonaqueous system (designated form D), 5.5% CH<sub>2</sub>O, 5.5% HCl, 71.3% CH<sub>3</sub>COOH, 1.6% CH<sub>3</sub>OH, 16.1% H<sub>2</sub>O; vapor system (designated form V), paraformaldehyde-hydrochloric acid vapors; bake-cure process (designated form C), aqueous pad bath. Two processes were conducted in reagent systems characterized by higher concentrations of formaldehyde: form W', 16.0% CH<sub>2</sub>O, 14.6% HCl, 69.4% H<sub>2</sub>O; form D', 9.8% CH<sub>2</sub>O, 6.6% HCl, 66.0% CH<sub>3</sub>COOH, 17.6% H<sub>2</sub>O. Additional information on these reactions has been summarized by Rowland and Post.<sup>6</sup>

Changes in fiber morphology were followed by comparison of electron micrographs of (a) ultrathin cross-sections before and after immersion in 0.5M cupriethylenediamine hydroxide (cuene) for 30 min.<sup>8-10</sup> and (b) ultrathin sections of fibers which had been prepared by a modification of the methacrylate expansion technique to separate the fiber wall into layers.<sup>9-11</sup> Fibers from each treated fabric were compared with those from untreated controls and with fibers from samples at various levels of formaldehyde content in each series of treatments.

## RESULTS AND DISCUSSION

Rowland and Post<sup>6</sup> have observed different degrees of efficiency in crosslinking cotton with formaldehyde in various processes of reaction. These may be the consequence of diffusion-controlled exclusion of reagent from some of the molecular species, the formation of crosslinks involving multiple units of reagent, or the consumption of agent in the formation of intramolecular linkages. The extreme case of low efficiency in crosslinking the molecular species in the series of formaldehyde-modified cottons examined by Rowland and Post was encountered with the form D' cotton which required 140 times the amount of agent calculated for network development in a model system. That there is a heterogeneity of distribution of crosslinks in this form D' cotton is shown in electron micrographs of thin cross-sections of these fibers. In a series of these cottons representing different formaldehyde contents, it is evident from fibers subjected to the expansion technique that there are substantial differences in crosslink density from the periphery of the fiber to the interior portion (Fig. 1). The resistance of the peripheral region in the sample of highest formaldehyde content (micrographs *A*) to undergo lateral expansion is indicative of crosslinks of intermicellar and interlamellar types among all the molecular species in this region. In the sample which represents the intermediate level of formaldehyde (micrographs *B*), it is apparent that the compact band at the periphery of the fiber has been ruptured by subsequent expansion of the noncrosslinked interior portion of the fiber during the specimen preparation. Even at the lowest level of formaldehyde content (micrographs *C*), there is evidence of a thin skin of crosslinked cellulose surrounding the fiber.

The nonuniform distribution of crosslinks in the form D' cottons is confirmed by the patterns of dissolution of the ultrathin fiber sections in cuene. The insoluble residues (Fig. 2) in all cases emphasize the relatively higher crosslink density on the surface of the fiber and decreasing depth of this region with decreasing formaldehyde content. In micrograph *A* there is a solid continuum of cellulose throughout the cross-section, but it is denser at the outer and inner peripheries of the cell wall than in the major area of the section. In the cross-section shown in micrograph *B* the residue inside the outer band appears stringy rather than continuous; and in micrograph *C* this interior residue is conspicuous by its absence.

The foregoing heterogeneity which involves a peripheral band of high crosslink density on the fiber sections is less apparent for form D cottons; similar heterogeneity was reported earlier by Rowland et al.<sup>5</sup> for fibers of this type containing 0.4% formaldehyde (0.022 moles of CH<sub>2</sub>O/AGU). Heterogeneity in our samples was observed in occasional fibers containing less than ca. 0.032 CH<sub>2</sub>O/AGU (0.6%). The expansion behavior of the form D fiber specimens was extremely variable, about half of the fiber cross-sections at the lower level of formaldehyde showing no response in the water-

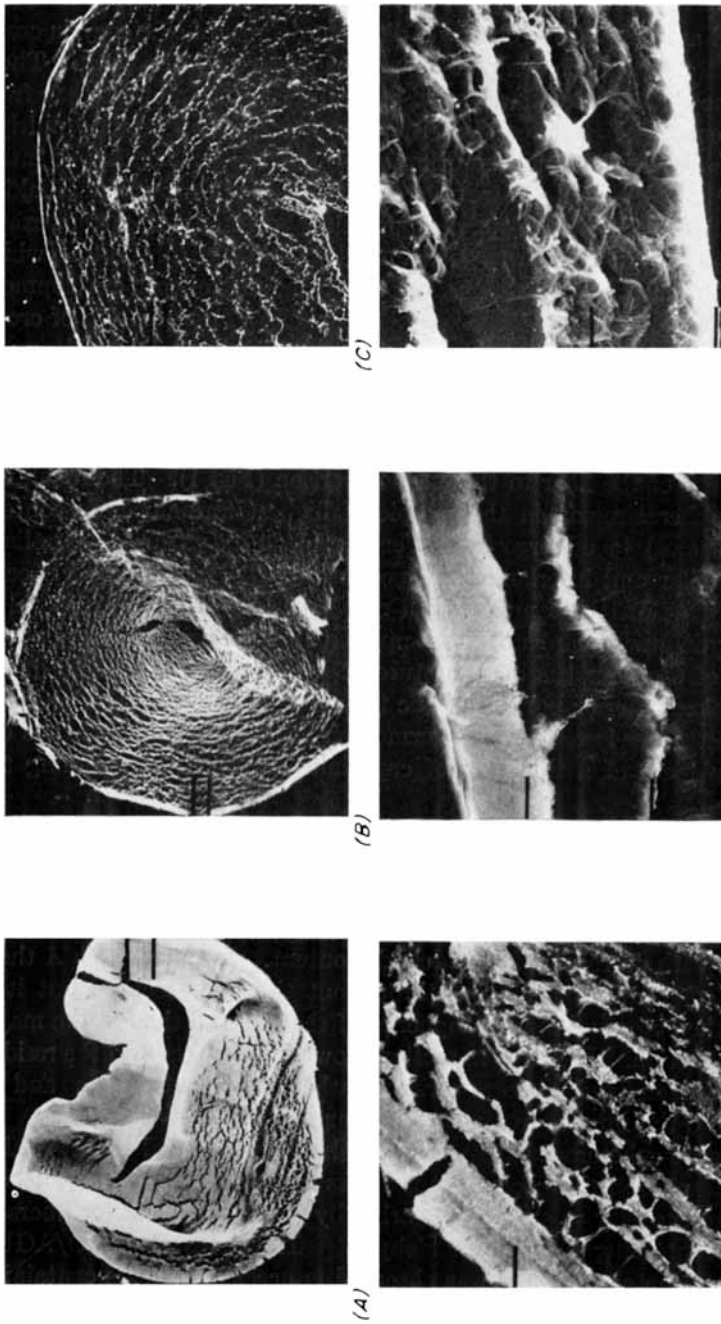


Fig. 1. Electron micrographs of cross-sections of form D' cotton fibers at low and high magnifications. Percentages of formaldehyde and moles of formaldehyde per AGU are: (A) 1.44, 0.078; (B) 0.69, 0.037; (C) 0.21, 0.011. The distance between markers is 1  $\mu$ .

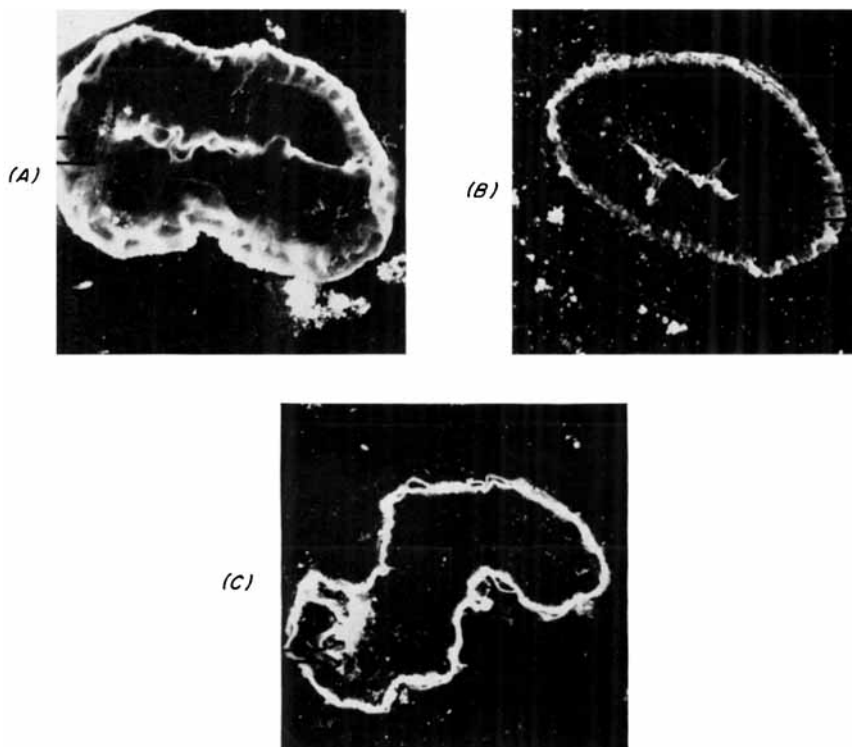


Fig. 2. Electron micrographs of residues of fiber cross-sections of form D' cotton following treatment with 0.5M cuene. Identification of samples is the same as that in Figure 1.

methacrylate swelling treatment of the expansion technique and the other half appearing indistinguishable from the sections illustrated for form D' samples in Figure 1. The fiber section shown in Figure 3, micrographs A, might represent an average state of the heterogeneity found in fibers of the form D series at 0.022  $\text{CH}_2\text{O}/\text{AGU}$  (0.4%). Residues remaining after treatment of thin cross-sections with cuene (Fig. 3, micrographs B and C) illustrate the preferential insolubilization of the peripheral regions of these form D fibers at 0.016 and 0.032  $\text{CH}_2\text{O}/\text{AGU}$ , respectively.

Gradients in density of crosslinks in the fiber cross-sections are less apparent for cottons crosslinked with formaldehyde by the other processes which have been examined in this study. In cottons treated by the forms W, C, and V processes to contain levels of formaldehyde below the amount required for complete development of network structure,<sup>6</sup> little or no evidence of heterogeneous distribution of crosslinks was found in electron micrographs of fiber cross-sections treated by the methacrylate expansion technique. For form W cotton, especially at 0.0027  $\text{CH}_2\text{O}/\text{AGU}$  (0.05%) but also at 0.0078  $\text{CH}_2\text{O}/\text{AGU}$  (0.15%), there is indication from the residues remaining after dissolution of cross-sections in cuene that a higher degree

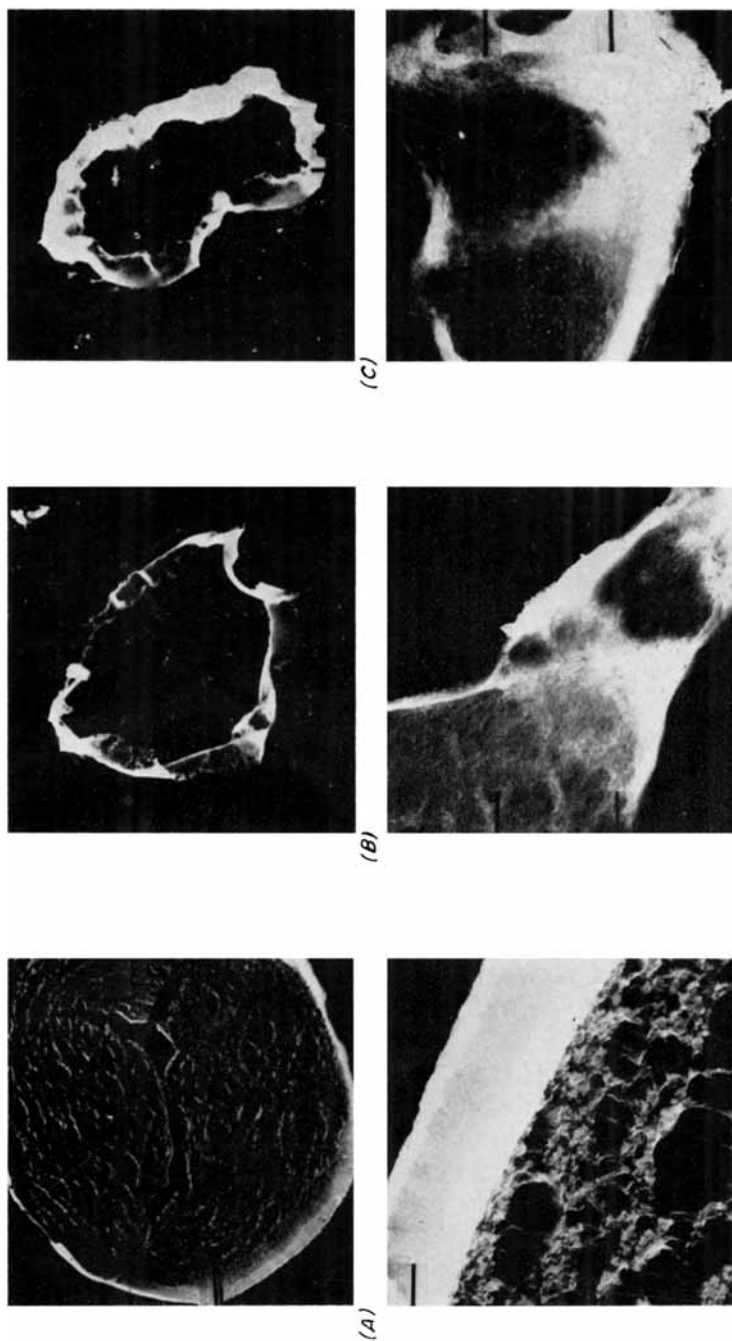


Fig. 3. Electron micrographs at low and high magnifications of cross-sections of form D fibers: (A) expansion pattern, 0.4%  $\text{CH}_2\text{O}$  or 0.022 moles  $\text{CH}_2\text{O}/\text{AGU}$ ; (B), (C) residues from 0.5M cuene treatments of specimen containing 0.016 (0.30%) and 0.032 (0.59%)  $\text{CH}_2\text{O}/\text{AGU}$ , respectively.

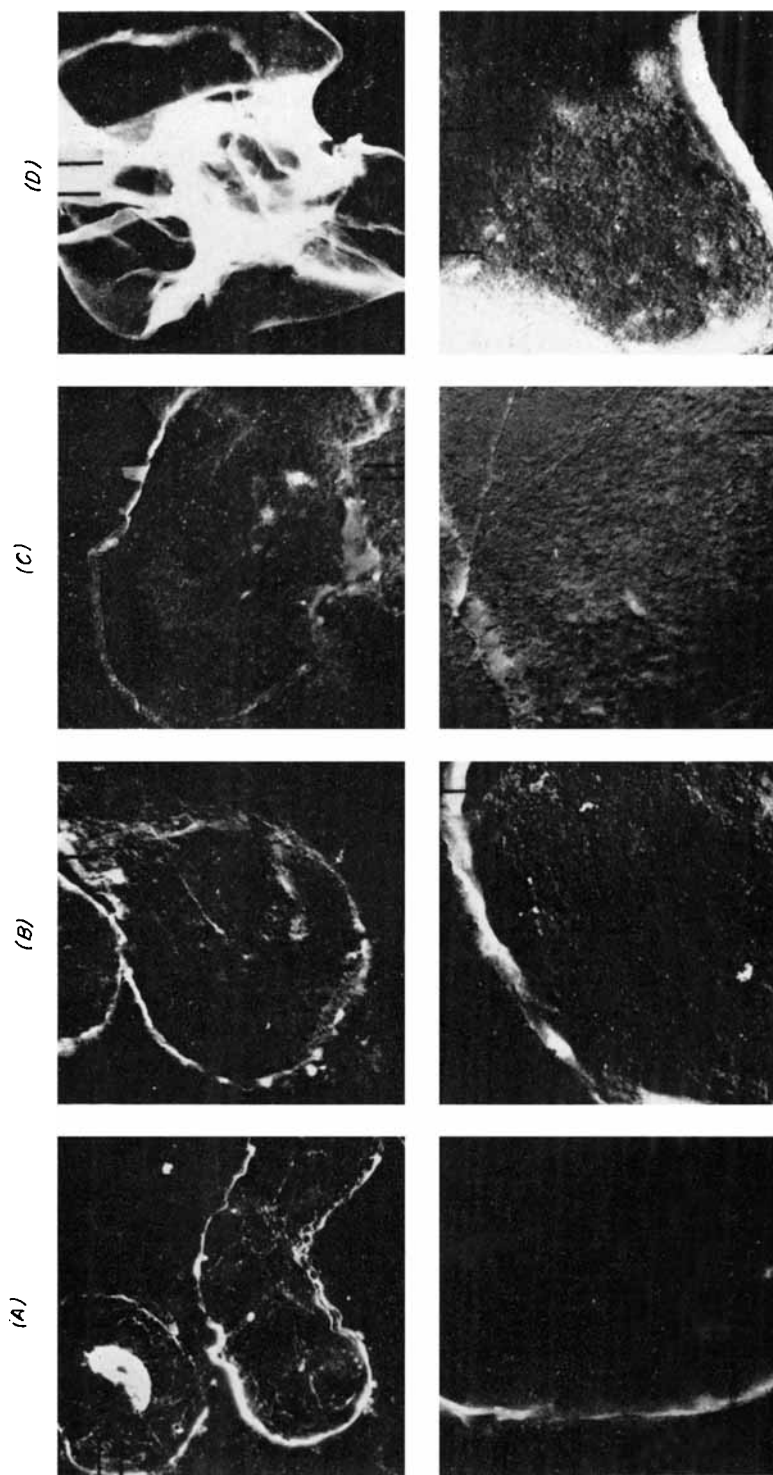


Fig. 4. Electron micrographs at low and high magnifications of cross-sections of fibers following treatments with 0.5M cuene: (A) form W, 0.0027 CH<sub>2</sub>O or 0.0049 CH<sub>2</sub>O/AGU; (B) form W, 0.05% CH<sub>2</sub>O or 0.0078 CH<sub>2</sub>O/AGU; (C) form V, 0.09% CH<sub>2</sub>O or 0.0049 CH<sub>2</sub>O/AGU; (D) form C, 0.09% CH<sub>2</sub>O or 0.0049 CH<sub>2</sub>O/AGU.

of insolubilization occurs at the periphery of the fiber than in the interior portion (Fig. 4, micrographs *A* and *B*); however, the insoluble band formed is thin compared to that obtained for form *D* cotton (compare to Fig. 3, micrographs *C*). Form *V* cotton at 0.0027 CH<sub>2</sub>O/AGU (micrographs *C* of Figure 4) shows high insolubilization in an even thinner surface layer accompanied by more insoluble residue within the fiber than observed for the corresponding form *W* sample. Cross-sections of forms *V* and *C* cottons at ca. 0.0050 CH<sub>2</sub>O/AGU left similar and substantial residues upon treatment with 0.5*M* cuene (micrographs *D* for form *C* cotton) without evidence of nonrandom distribution of crosslinks. The pattern and texture of insoluble residue left from the bulk of the fiber are quite different for form *W* cotton (micrographs *A* and *B*) compared to form *V* cotton (micrographs *C*). While the residue of the latter appears uniform, that of the former is distributed in a manner suggestive of channels.

It appears, therefore, that forms *D'* and *D* cottons exhibit heterogeneity of distribution of crosslinks which is indicative of a reaction progressing from the surface of the fiber to the interior. Progressive reaction in the case of form *W* cotton appears to start on the surface and in pores or channels of the fiber structure. While there is an indication of a thin surface skin for form *V* cotton in the initial stage of crosslinking (Fig. 4, micrograph *C*), there is no evidence for nonuniform distribution of crosslinks in this case (or in the case of form *C* cotton: Fig. 4, micrograph *D*). It is apparent, also, that only major differences in distribution of crosslinks can be identified by electron microscopic observations and that these are generally limited to the early stage of a crosslinking process when gross differences are being detected between regions which are extensively crosslinked, on the one hand, and those which are essentially unmodified, on the other hand.

The foregoing observations on distribution of crosslinks in cotton fibers are indicative of diffusion-controlled processes of crosslinking superimposed upon rapid initial reactions involving readily available sites, including surfaces. Although, as summarized by Timell,<sup>7</sup> little success has been realized in a general kinetic analysis of heterogeneous reactions of cellulose, Woo et al.<sup>12</sup> found evidence for rapid and slow phases of reaction of formaldehyde with cotton under baking conditions at low pH. In this case the rapid reaction was characterized by an energy of activation of approximately 16 kcal./mole and the slow reaction by approximately 6 kcal./mole, results which are consistent with phases which are controlled by rates of chemical reaction and by diffusion, respectively. Subsequently, Datye<sup>13</sup> and Mack in the appendix of a paper by Roff<sup>14</sup> analyzed the kinetics of formaldehyde-cotton reactions in aqueous systems in terms of rapid and slow phases with good agreement between the calculated and actual results. In other cases an expression derived by Sakurada,<sup>15</sup> eq. (1),

$$x = kt^m \quad (1)$$



(where  $x$  is extent of reaction,  $t$  is time, and  $k$  and  $m$  are constants) has been employed by many investigators in analyzing diffusion-controlled reactions of cellulose for linear relationship of  $\log x$  versus  $\log t$ .<sup>14-17</sup> Two phases of reaction appear to be indicated in many cases. Equation (1) is closely related to eq. (2), which states the relationship between sorption  $Q$  and time which is associated with Fickian diffusion.<sup>18-21</sup>

$$Q \cong k't^{1/2} \quad (2)$$

The diffusion of water vapor in a regenerated cellulose fiber has been shown by Denton<sup>22</sup> to occur also in primary and secondary transport processes. The former progresses rapidly from periphery to center and is estimated to require 7 sec. for a textile fiber of 10  $\mu$  diameter at 80% R.H., whereas the latter continues over an extended period (beyond 500,000 sec.). Although these processes are undoubtedly faster for fibers immersed in water, the effect of instantaneous reaction occurring during a diffusion process is to slow down diffusion<sup>23a</sup> to the point that it is reasonable to expect a diffusion-controlled process to occur over the several-hour intervals that characterize the formaldehyde-cotton reactions at room temperature.

It is pertinent, then, to examine this series of formaldehyde-modified cottons for evidence of rapid and slow components of reaction, since the rates, extents, and durations of these phases will provide information relative to heterogeneity of distribution of crosslinks. It is readily apparent that the initial rapid stage of reaction might best be treated as a pseudo first-order reaction when the reagent bath is employed in large excess so that it is essentially constant throughout the reaction. Then the amount of agent,  $M_t'$ , which has reacted with the cellulose in time  $t$  when concentrations at the surface are constant may be expressed as

$$M_t' = C_{0a}(1 - e^{-k_1t}) \quad (3)$$

$C_{0a}$  is related to the initial concentration of readily available reactive groups in the cellulose, and  $k_1$  is proportional to the velocity coefficient for a specific composition of reagent. The later phase of reaction, assuming it to be diffusion-controlled with constant concentration of reagents at the surface of the fibers, may be expressed as

$$M_t'' = C_{0d}k_2't^{1/2} = k_2t^{1/2}$$

$C_{0d}$  is the initial concentration of reactive groups which are available for reaction through the process of diffusion, and  $k_2'$  and  $k_2$  are proportional to the velocity coefficient for this phase of reaction for a specific reagent system. This expression is limited in applicability to the relatively early portion (ca. 60% of  $M_\infty$ ) of the diffusion reaction.<sup>22, 23b</sup> The sum of eqs. (3) and (4) will describe the actual reaction, provided the conditions noted above are satisfied.

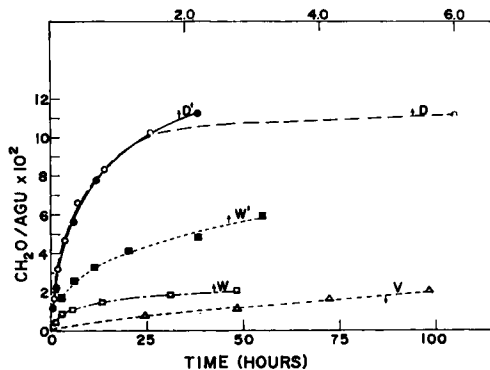


Fig. 5. Rates of incorporation of formaldehyde into cotton under various conditions of reaction: (●) form D'; (○) form D; (■) form W'; (□) form W; (△) form V. Lower time scale applies to form V process only.

For meaningful comparative purposes our kinetic analysis is limited to those formaldehyde-cotton reactions which were conducted at room temperature by the forms W, W', D, D', and V processes. Gross differences in the courses of these reactions are illustrated in the curves of Figure 5, for which the form V data require a special time scale. The latter portion of each of these reactions yields a linear relationship for  $\log M_t$  (where  $M_t$  denotes moles of  $\text{CH}_2\text{O}/\text{AGU}$ ) versus  $\log t$  or for  $M_t$  versus  $t^{1/2}$ . The  $M_t$  versus  $t^{1/2}$  relationship provides the basis for calculating  $k_2$  of eq. (4), for isolating the apparent extent of reaction due to the initial rapid phase, and subsequently, for obtaining a value for  $k_1$  from eq. (3). The kinetic data are quite amenable to this analysis without major scatter from the relationships of eqs. (3) and (4). Pertinent results are summarized in Table I.

Pronounced similarity is apparent among the velocity factors ( $k_1$ ) for the initial rapid components of the formaldehyde-cotton reactions. It is likely that small, but real, differences are masked in these analyses. The

TABLE I  
Estimated Velocity Factors for Formaldehyde-Cotton Reactions

Process	$k_1$ , min. <sup>-1</sup> <sup>a</sup>	$C_{0a}$ , $\text{CH}_2\text{O}/\text{AGU}$ <sup>a,b</sup>	$k_2$ , moles $\text{AGU}^{-1} \text{min.}^{-1/2}$ <sup>c</sup>
Form D'	0.06	0.038	0.006
Form D	0.09	0.031	0.007
Form W'	0.08	0.012	0.003
Form V	d	-0.003	0.0003
Form W	0.09	0.009	0.001

<sup>a</sup> From eq. (3).

<sup>b</sup> From intercept of ordinate in plot of  $M_t$  vs.  $t^{1/2}$  in terms of moles of  $\text{CH}_2\text{O}/\text{AGU}$ .

<sup>c</sup> From eq. (4).

<sup>d</sup> Little or no evidence for a rapid phase of reaction.

general similarity in order of magnitude provides a confirmation of the identities of the chemical reactions. The extents of reaction  $C_{0a}$  during the initial phases are significantly different for the various processes. Such results are the consequence of dissimilar fractions of readily accessible hydroxyl groups and/or different states of equilibria in the reactions among the accessible hydroxyl groups. The increase in  $C_{0a}$  in proceeding from the form W to the form W' process appears due to a state of equilibrium which is displaced farther toward products (Fig. 6) for form W' cotton since fractions of readily available hydroxyl groups are expected to be very similar in these cases. Likewise, the higher value of  $C_{0a}$  for the form D versus the form W process is understood in terms of a displacement of equilibrium farther toward the products in the case of the form D process even though a lower fraction of readily available hydroxyl groups (i.e.,  $C_{0a}$ ) would be expected for the nonaqueous system solely on the basis of swelling

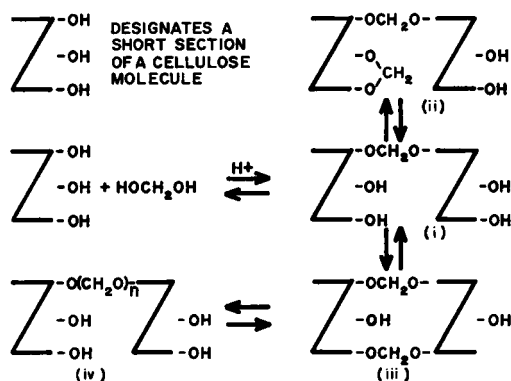


Fig. 6. Simplified depiction of reactions of formaldehyde with a short segment of the cellulose chain.

data.<sup>24</sup> The velocity factors  $k_2$  for the slow components of the various reactions, which fall in the same general order as the values of  $C_{0a}$ , are interpreted as reflections of different extents of reaction of agent or of accumulation of bound formaldehyde per available hydroxyl group (e.g., structures i-iv of Fig. 6) in addition to different rates of diffusion of reagents into the cellulosic structure.

It is evident, therefore, that kinetic analyses are consistent with the preceding observations of heterogeneity obtained from electron micrographs. The form V process shows little or no evidence for more than a single phase of reaction, and exhibits one of the most homogeneous distributions of crosslinks observed via electron micrographs. Among the other processes, high heterogeneity of distribution of linkages is anticipated in proportion to values of  $C_{0a}$ . Thus, the decreasing order of heterogeneity from kinetic analysis is indicated to be form D', form D, form W', form W, and form V.

## CONCLUSIONS

The distribution of formaldehyde crosslinks within the cotton fiber varies considerably with the process of introduction. The heterogeneity of distribution of linkages can be followed in electron micrographs in the relatively early stages of reaction; kinetic analysis provides a confirmation of the presence or absence of heterogeneity throughout the remaining course of the reaction. Nonuniform distribution of crosslinks in this series of formaldehyde-modified cottons was most pronounced for reactions conducted in nonaqueous systems (forms D and D'), in which cases the density of crosslinks decreased from the surface to the interior of the fiber. In the very early stage of reaction of formaldehyde with cotton in an aqueous system (form W), crosslinked regions were limited to the periphery and isolated interior portions, the latter suggesting diffusion through pores or channels. Although there is evidence for preferential insolubilization of a thin surface layer (perhaps the outer winding) in the early stage of reaction via the vapor process (form V), both micrographs and kinetics point to a high degree of homogeneity in distribution of crosslinkages in this case. Form W' and C cottons, for which data are less definitive, appear most closely related and generally similar in heterogeneity of distribution of crosslinks to form W and form V cottons, respectively.

A general pattern becomes apparent from the above observations on specific compositions. The development of crosslinks in cotton fiber during immersion in a reagent proceeds by reaction at readily available sites on or in the fiber simultaneously with penetration into, and reaction with, regions which are reached through swelling and diffusion processes. The distribution of total reactive sites between "readily available" and "available-by-diffusion" sites depends on swelling capacity of the medium. Nonuniform distribution of crosslinks throughout the fiber is accentuated, the greater the difference in rates of the two phases of reaction; i.e., the more rapid and the more complete the chemical reaction and the slower the diffusion process.

Relatively low heterogeneity of distribution of crosslinks is the result of the pad-dry-cure process (form C) which allows opportunity for diffusion of reagent prior to reaction.

In addition to differences in heterogeneity of distribution of crosslinks throughout the fiber structure, there are indicated to be substantial differences among the various processes in extent of reaction of agent or in accumulation of bound formaldehyde per accessible hydroxyl group. The "excessive" accumulation of agent beyond that essential for insolubilization may be present in structures such as illustrated in ii, iii, and iv of Figure 6. This latter type of heterogeneity is superimposed on top of that from physical distribution of crosslinks.

It is most interesting that these considerable variations in distribution of crosslinks and in accumulation of agent per accessible hydroxyl group have been observed for an agent which, in its monomeric form, is among the

smallest in molecular dimensions. Accentuation of heterogeneity is anticipated for agents of larger dimensions.

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### References

1. J. G. Frick, Jr., L. C. Weiss, B. A. Andrews, A. B. Cooper, J. N. Grant, W. F. McSherry, A. R. Markezich, A. T. Moore, R. T. O'Connor, A. G. Pierce, Jr., W. A. Reeves, M. L. Rollins, and R. H. Tsoi, *Am. Dyestuff Repr.*, **52**, 952 (1963).
2. W. A. Reeves, R. M. H. Kullman, J. G. Frick, Jr., and R. M. Reinhardt, *Textile Res. J.*, **33**, 169 (1963).
3. W. A. Reeves, R. M. Perkins, and L. H. Chance, *Textile Res. J.*, **30**, 179 (1960).
4. J. G. Frick, Jr., A. G. Pierce, Jr., and V. W. Tripp, *Textile Res. J.*, **32**, 425 (1962).
5. S. P. Rowland, E. R. Cousins, and D. Mitcham, *J. Appl. Polymer Sci.*, **9**, 3869 (1965).
6. S. P. Rowland and A. W. Post, *J. Appl. Polymer Sci.*, **4**, 1751 (1966).
7. T. Timell, *Studies in Cellulose Reactions*, Esselte A/B, Stockholm, Royal Inst. of Technology, 1950, p. 68.
8. V. W. Tripp, A. T. Moore, and M. L. Rollins, *Textile Res. J.*, **31**, 295 (1961).
9. M. L. Rollins, A. T. Moore, W. R. Goynes, J. H. Carra, and I. V. deGruy, *Am. Dyestuff Repr.*, **54**, 512 (1965).
10. M. L. Rollins, J. H. Carra, E. J. Gonzales, and R. J. Berni, *Textile Res. J.*, **36**, 185 (1966).
11. J. Dlugosz, *Polymer*, **6**, 427 (1965).
12. H. K. Woo, J. H. Dusenbury, and J. H. Dillon, *Textile Res. J.*, **26**, 745 (1956).
13. K. Datye, *Textile Res. J.*, **32**, 825 (1962).
14. W. J. Roff, *J. Textile Inst.*, **54**, T281 (1963).
15. I. Sakurada, *Cellulose Chemie*, **15**, 3 (1934).
16. P. K. Chatterjee and C. M. Conrad, *J. Polymer Sci. A-1*, **4**, 459 (1966).
17. C. M. Conrad, P. Harbrink, and A. L. Murphy, *Textile Res. J.*, **33**, 784 (1963).
18. T. Alfrey, *Chem. Eng. News*, **43**, No. 41, 64 (Oct. 11, 1965).
19. H. Fujita and A. Kishimoto, *Textile Res. J.*, **22**, 94 (1952).
20. R. M. Barrier and D. W. Brook, *Trans. Faraday Soc.*, **49**, 1049 (1953).
21. H. Fujita, *Fortschr. Hochpolymer. Forsch.*, **3**, 1 (1961).
22. P. Denton, *J. Textile Inst.*, **47**, T570 (1956).
23. J. Crank, *Mathematics of Diffusion*, Oxford Univ. Press, London, 1957, (a) p. 122, (b) p. 247.
24. B. R. Porter and R. S. Orr, *Textile Res. J.*, **35**, 159 (1965).

### Résumé

La distribution de ponts formaldéhydiques dans la cellulose de coton a été suivie par analyse électronique micrographique de sections transversales des fibres, et par analyse cinétique des vitesses de réaction du formaldéhyde avec le coton. L'importance des phases rapides et lentes des réactions de pontage varient suivant le processus spécifique de la réaction. On trouve un vaste domaine d'hétérogénéité de distribution des ponts dans les diverses compositions étudiées, la distribution la plus hétérogène apparaissant à une concentration élevée de ponts dans les régions périphériques de la fibre. Il est évident que d'autres différences substantielles entre les cotons pontés au formaldéhyde sont dues au degré d'avancement différent de la réaction suivant l'accessibilité du groupe hydroxyle.

### **Zusammenfassung**

Die Verteilung der Formaldehydvernetzungsstellen in Baumwollcellulose wurde anhand von elektronenmikroskopischen Aufnahmen von Faserquerschnitten und durch die kinetische Analyse der Reaktion von Formaldehyd mit Baumwolle verfolgt. Rasche und langsame Phasen der Vernetzungsreaktion werden in Abhängigkeit von den spezifischen Reaktionsvorgängen festgestellt. Bei den untersuchten Zusammensetzungen wird ein weiter Heterogenitätsbereich der Vernetzungsverteilung erhalten, wobei die am stärksten heterogene Verteilung in einer hohen Vernetzungskonzentration im peripheren Teil der Faser auftritt. Offenbar werden weitere wesentliche Unterschiede zwischen den formaldehyd-vernetzten Baumwollen durch ein verschiedenes Ausmass der Formaldehydreaktion pro zugängliche Hydroxylgruppe bedingt.

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