JOURNAL OF APPLIED POLYMER SCIENCE VOL. V, ISSUE NO. 18, PAGES 704-713 (1961)

The Resilience of Chemically Modified Cottons. II. Reactions of Cellulose with Formaldehyde under Acid Conditions

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INTRODUCTION

As indicated in the previous paper of this series,[1] the overall purpose of the work reported here has been to establish a sound quantitative picture of the chemistry and physical results of chemical reactions which improve the resilience of cotton. The study, in this regard, of the reactions of alkali celluloses and of sodium cellulosates with methylene dibromide has been described previously.[1] The work to be reported here has involved the reaction of cotton cellulose with formaldehyde under acid conditions and has resulted in the treated fabrics exhibiting improved crease recovery both dry and wet.

The reaction of cellulose with formaldehyde under acid conditions has been investigated by many researchers. In the case of the experiments to be reported here, the procedures described by Woo, Dusenbury, and Dillon[2] and by Wagner and Pacsu[3] have been used to apply the formaldehyde. The results of other studies in this field, as well as of these studies, have been summarized in the 1958 literature review by Roff.[4]

MATERIALS AND ANALYTICAL PROCEDURES

The cottons used in this study were the same Acala 4-42 and Pima S-1 described in Part I of this series.[1] Most of the analytical procedures used in connection with this study have also been described previously. Those not previously described will be mentioned later in this paper.

REACTIONS OF CELLULOSE WITH FORMALDEHYDE UNDER ACID CONDITIONS

Prior to reaction with formaldehyde, Acala and Pima cotton fabrics were purified as described earlier.[1] The procedure used to apply the formaldehyde was, again, closely similar to that described by Woo et al.[2] Fabric samples were padded to ca. 100% pickup with an aqueous solution containing 7.5% HCHO and maintained at pH 2 (0.01N HCl + 0.05M KCl); the fabrics were immersed in this solution 5 min. prior to the padding. After this, the fabric samples were placed on pinframes and treated 30 min. at 130°C. in the oven described by Woo et al.[2] After this baking, the samples were treated 30 min. in a boiling aqueous solution buffered at pH 7 (prepared from 0.2M Na_2HPO_4 and 0.1M citric acid, i.e., MacIlvaine's buffer mixtures), and washed with hot distilled water until free of unbound HCHO, as indicated by tests of the wash water with chromotropic acid.[5] The purpose of the treatments with the boiling pH 7 buffer solution and with hot distilled water was to remove any HCHO merely sorbed on the fabric and to remove hemiacetals. The efficacy of these treatments, as well as of similar treatments for card sliver samples reacted with formaldehyde by the method of Wagner and Pacsu,[3] for removing sorbed HCHO and hemiacetals will be discussed briefly later.

Effects of Boiling Dilute Acetic Acid on Formaldehyde Contents

After the formaldehyde treatment, some of the fabric samples were treated for various periods of time with aqueous 1% acetic acid at the boil under reflux conditions. The concentrations of the various acetic acid solutions used were checked before use by titration with NaOH, and after treatment with the acid, the fabric samples were rinsed with distilled water until neutral. The bound HCHO contents of the treated samples were then determined by the chromotropic acid procedure of Bricker and Johnson,[5] as described previously.[1]

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To assess the reproducibility of such formaldehyde treatments, both within a single treatment and between different treatments, fabric samples were given duplicate treatments, starting from the preparation of duplicate padding baths. For each fabric sample which had either no aftertreatment with boiling 1% acetic acid solution or some aftertreatment for a specified time, three separate samples were taken for HCHO analysis. These samples from the duplicate treatments were the same small rectangular strips whose dry crease recovery was measured prior to the HCHO analysis. The extents of reaction observed are listed in Table I and are expressed in terms of degree of substitution (D.S.), calculated on the assumption that only monomeric acetals result from the reaction of HCHO with the cellulose.

TABLE I

Extents of Reaction of Cotton Fabrics Treated with Formaldehyde under Acid Conditions According to Woo, Dusenbury and Dillon and Later Treated with Boiling 1% Acetic Acid Pima Solution

Time of treatment with boiling 1% acetic acid, hr.	D. S.[a]	
	Acala cotton	Pima cotton
0	0.321	0.311
2	0.298	0.293
5	0.242	0.240
10	0.218	0.210
20	0.196	0.189
50	0.174	0.161
100	0.119	0.124
200	0.117	0.107
Pooled 95% conference limit	±0.014	

[a] Each mean value is for 6 measurements.

The data for the results summarized in Table I were analyzed statistically, and the results of this analysis indicated first of all that the data for the two duplicate treatments are statistically indistinguishable. That is, for these treatments, the differences in extents of reaction observed between different treatments are no greater than the differences observed within a single treatment. (The same finding was also noted for the corresponding crease-recovery measurements.) For this reason, the mean values listed in Table I are for six measurements each; i.e., the two sets of three measurements each were pooled to give the values listed. The Acala cotton samples consistently exhibited greater extents of reaction than the Pima cotton samples, but not at a very high level of statistical significance (90% confidence level). This tendency for greater extents of reactions with the Acala cotton is consistent with the results given earlier for the reactions of the corresponding alkali cellulose samples treated with CH_2Br_2 (See Part I,[1] Tables VI and VII). The interactions in the statistical analysis were such that the rates of removal of bound HCHO from the two varieties of cotton fabric may be regarded as statistically indistinguishable.

The consensus of most studies of the reaction of cellulose with formaldehyde under acid conditions is that the reaction leads to the formation of acetal crosslinks, such as $ZOCH_2OZ'$, where Z and Z′ represent cellulose chains. The most extensive study of the structure of the reaction product appears to be that published in 1952 by Wagner and Pacsu.[3] They interpreted the results of their experiments to indicate that formaldehyde reacts only with the secondary hydroxyl groups of the cellulose and that the crosslinks are not polymeric. The results of infrared spectral studies of formaldehyde-treated films of cellulose reported later by Steele[6] are in general agreement with these interpretations of Wagner and Pacsu.

To gain further insight regarding the reaction of cellulose with formaldehyde, particularly with respect to the removal of acetals by treatment with boiling 1% acetic acid solution, it was decided to treat cotton samples by the method of Wagner and Pacsu.[3] This was done by treating 1 g. samples of purified Acala and Pima cotton card sliver 1 hr. at room temperature with an aqueous solution of 2.5% boric acid. Each sample was pressed to a weight increase of ca. 100%, dried in an oven at 55°C., and sealed in a glass tube containing 0.2 g. of paraformaldehyde. These tubes were then baked 24 hr. at 130°C. The tubes were subsequently broken open and the samples were removed and washed repeatedly with hot distilled water until free of unbound HCHO, as indicated by tests of the wash water with chromotropic acid.[5] After this formaldehyde treatment, some of the samples were treated further with boiling 1% acetic acid and subsequently rinsed with distilled water until neutral. The bound HCHO contents of the treated samples were then determined according to Bricker and Johnson.[5]

The extents of reaction observed for samples treated in this way are listed in Table II; each mean value, with the exception of the data for 150 hr. of acetic acid aftertreatment, is for two measurements on aliquot samples from a single treatment. In this case, the Pima cotton appeared to exhibit greater extents of reaction than the Acala, but the circumstances of these sealed-tube experiments are such that it is somewhat difficult to duplicate treatments, and the differences between the cottons indicated by the data of Table II are probably a reflection chiefly of this factor. As will be noted later, when relative extents of acetal removal by the boiling 1% acetic acid are considered, the relative rates of such acetal removal are closely similar for the two cottons listed in Table II. In fact, it may well be that attempts to duplicate experiments on the same cotton variety would lead to results similar to those noted in Table II for two different cottons.

TABLE II

Extents of Reaction of Cotton Card Slivers Treated with Formaldehyde under Acid Conditions According to Wagner and Pacsu and Later Treated with Boiling 1% Acetic Acid Solution

Time of treatment with boiling 1% acetic acid, hr.	D.S.[a]	
	Acala cotton	Pima cotton
0	0.328	0.420
2	0.203	0.314
5	0.190	0.274
10	0.184	0.225
20	0.160	0.211
50	0.118	0.144
100	0.090	0.119
150	0.084[b]	0.102[b]
200	0.068	0.090
Pooled 95% confidence limit	±0.035	

[a] Each mean value is for 2 measurements.
[b] Single measurement.

Before consideration of the kinetics of acetal removal and of the crease-recovery performance of the treated fabrics, it is important to attempt to establish that the washing procedures used after the formaldehyde treatments do indeed remove any sorbed HCHO and/or any hemiacetal remaining on the samples. Experiments to check this point were carried out on samples treated both by the method of Woo, Dusenbury, and Dillon[2] and by the method of Wagner and Pacsu.[3] The results obtained in both cases were closely similar, and those obtained where the cotton samples were treated by the method of Wagner and Pacsu[3] will be given here.

A sample of Acala cotton card sliver was treated with formaldehyde by the sealed-tube method of Wagner and Pacsu.[3] The sample after removal from the sealed tube was analyzed for its formaldehyde content; this corresponded to a D.S. of 0.229. A subsequent boiling for 2 hr. in distilled water caused no apparent reduction in D.S. (In the case of card sliver samples treated by the method of Woo, Dusenbury, and Dillon,[2] appreciable reductions in D.S. were caused by this boiling water aftertreatment, indicating these samples prior to washing to contain appreciable amounts of sorbed formaldehyde and/or hemiacetal. Otherwise, the results for these samples were closely similar to those for the samples treated by the method of Wagner and Pacsu.) After the boiling water treatment, aliquots of the sample of D.S. 0.229 were boiled for varying periods of time with pH 7 and pH 10 buffer solutions and the formaldehyde contents were determined. A MacIlvaine's buffer was used for pH 7 (0.1M citric acid + 0.2M Na_2HPO_4), and a Clark and Lubs buffer was used for pH 10 (0.1N NaOH + 0.1M H_3BO_3). In the cases of these treatments of card sliver samples (Table III), of their later treatments with boiling 1% acetic acid and with a urea–phosphoric acid mixture (Fig. 1), and of the treatments described earlier of formaldehyde-treated fabric samples (Table I) and card sliver samples (Table

TABLE IIIA

D.S. of Acala Cotton Card Sliver Samples Treated with HCHO According to Wagner and Pacsu and Later Treated with Boiling H_2O

Time in boiling H_2O, hr.	D.S.[a]
0	0.229
2.0	0.229
Pooled 95% confidence limit	±0.002

[a] Each mean value is for 2 measurements.

TABLE IIIB

D.S. of Acala Cotton Card Sliver Samples Treated with HCHO According to Wagner and Pacsu and Later Treated with Boiling Buffer Solutions

Time in boiling buffer, hr.	D.S.[a]	
	pH 7	pH 10
0.5	0.224	0.224
2.0	0.226	0.222
5.0	0.217	0.213
Pooled 95% confidence limit	±0.011	±0.004

[a] Each mean value is for 2 measurements.

II), the liquor-to-sample ratio was 667 ml./g. Consideration of the molar quantities involved demonstrated that in all cases the treating liquor was in great excess with respect to the amount of cellulose.

The effect of the boiling water treatment is illustrated by the data of Table IIIA, and the effects of the subsequent treatments with boiling buffer solution are illustrated by the data of Table IIIB. It is apparent that nearly all of the sorbed formaldehyde and/or hemiacetal present was gone prior to any aftertreatment and that very little additional such material is present for removal by the prolonged boilings in the pH 7 and pH 10 buffer solutions.

After boiling in the two buffer solutions for 5 hr., samples were removed and subsequently treated for varying periods of time in boiling 1% acetic acid[1] and in a boiling mixture of 1.5% phosphoric acid and 5% urea.[7] The results obtained are shown plotted in Figure 1, where each point is the mean value for two measurements. The reproducibility of these measurements was quite good; i.e., the pooled 95% confidence limits for each of the four sets of data indicated in Figure 1 were, in terms of D.S., ±0.007 or less, values similar to those indicated previously in Table III.

These data indicate quite clearly that both types of treatments with acid remove acetals from a starting product (product after 5 hr. in either pH 7 or pH 10 buffer at the boil) containing no sorbed formaldehyde or hemiacetal. In the case of the boiling 1% acetic acid, it is apparent that nearly all the acetal initially present has been removed after 200 hr. of aftertreatment. In the case of the urea–phosphoric acid mixture, it is apparent that the system reaches a state of equilibrium after about 2 hr. of aftertreatment and that at this point 32–40% of the initial acetal content has been removed. A brief explanation is appropriate here for the selection of the urea–phosphoric acid mixture as an aftertreatment. Cooke et al.[7] reported in 1954 that this mixture of 1.5% phosphoric acid and 5% urea applied for 1.5 hr. at 85°C. removed little or no formaldehyde from formaldehyde-treated cotton fabric, but did completely remove the resin from fabric treated with either urea formaldehyde or melamine formaldehyde. It appeared puzzling that boiling 1% acetic acid (pH 2.8 at room temperature) would remove acetals, but that the urea–phosphoric acid solution at 85°C. (pH 1.9 at room temperature) would not. (The formaldehyde in the study of Cooke et al.[7] was applied differently than was the case in this study, but this difference should have little bearing on the problem of removing formaldehyde by acid aftertreatment.) For this reason, it was decided to examine the effect of treatments with urea and phosphoric acid, but at the boil, in order to have a more direct comparison with the 1% acetic acid at the boil. First of all, the results of the present study would appear to be in general accord with those of the study by Cooke et al.,[7] since they found little formaldehyde removal after 1.5 hr. at 85°C., and in the present work little formaldehyde removal is noticeable after 0.5 hr. at the boil, a comparable time considering the temperature difference. The surprising attainment of an apparent equilibrium for the experiments with urea–phosphoric acid solutions, in contrast with the nonattainment of an equilibrium and a greater loss of formaldehyde content for the experiments with 1% acetic acid solutions, requires further comment.

As will be discussed later here, it is known that

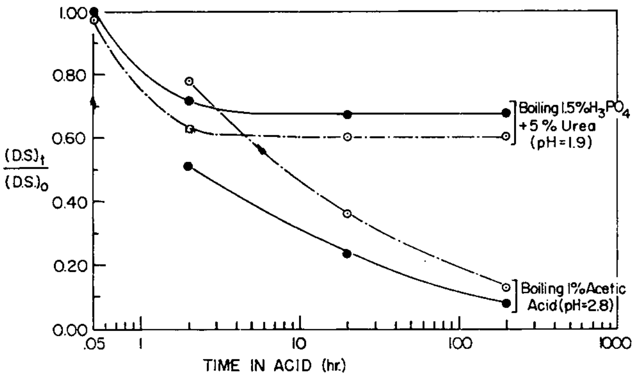

Fig. 1. Effects of boiling solutions of 1% acetic acid and of 1.5% phosphoric acid + 5% urea on formaldehyde contents of treated Acala cotton card sliver samples previously treated 5 hr. with boiling buffer solutions: (●) pH 7 buffer; (⊙) pH 10 buffer.

the acid hydrolysis of acetals is free of general acid catalysis effects,[8,9] and it is thus difficult to attribute the different rates of acetal removal shown in Figure 1 to differences in the specific natures as acids of acetic and phosphoric acids. What seems more likely is that the treatments with urea–phosphoric acid solutions may be sufficiently more acid than the treatments with acetic acid to cause appreciable amounts of back reaction to occur. That is, it is known that acid hydrolysis of acetals is a reversible reaction (it would necessarily be thus, since acetal formation occurs through acid catalysis), and it may be that the experiments with urea–phosphoric acid solutions involve sufficient amounts of acid and formaldehyde present to cause acetal re-formation and the apparent attainment of equilibrium indicated by the data of Figure 1. Experiments to check this point are currently underway in these laboratories.

From all the data collected, about one-half of them being shown in Table III and Figure 1, it may be safely concluded that the washing procedures used after the formaldehyde treatments have indeed removed sorbed formaldehyde and/or hemiacetals. It may also be assumed that any subsequent reductions in formaldehyde content caused by treatments with boiling 1% acetic acid solution represent reductions in the amounts of acetal present.

It is also important to consider briefly what is known about the kinetics of the acid hydrolysis of acetals. The data obtained by several groups of workers are consistent with the view that the rate expression is:

$$-d[\mathrm{ROCH_2OR}]/dt = k[\mathrm{ROCH_2OR}][\mathrm{H^+}] \quad (1)$$

where [ROCH$_2$OR] represents the concentration of acetal—the acetal of formaldehyde and cellulose or the formal in this case—and [H$^+$] represents the concentration of hydrogen ion. The validity of this rate expression and the absence of any general acid catalysis effects in acetal hydrolysis were demonstrated in 1930 by Brønsted and Grove.[8] Their work has since been confirmed by several workers, notably by McIntyre and Long in 1954.[9] In 1926, Skrabal and Eger[10] showed that the acetals of formaldehyde exhibit a wide range of hydrolysis rates, depending on the alcohol involved, with the acetal involving isopropanol hydrolyzing 47.2 times faster at 25°C. than the acetal involving methanol. When the acid concentration during an experiment may be considered effectively constant, as is the case in the experiments reported here for treatments with boiling 1% acetic acid under reflux, the hydrolysis kinetics become pseudo-unimolecular. This has been demonstrated for the HCl hydrolysis of formaldehyde acetals by Löbering and Fleischmann.[11] Discussions of the reaction mechanism in detail are to be found in papers by Taft[12] and by McIntyre and Long.[9]

At first glance, it might appear surprising that formaldehyde acetals are removable from treated cellulose by 1% acetic acid, since 12N H$_2$SO$_4$ at room temperature for 16 hr. is used for their quantitative removal for analytical purposes, as noted previously in Part I.[1] It must be borne in mind, however, that the acetic acid is applied at the boil. When account is taken of the ionization constant of acetic acid at 100°C.,[13] of the kinetics of the acid hydrolysis of formaldehyde acetals[8–12] and of a likely value for the activation energy for the reaction, it is possible to estimate the equivalent hydrogen-ion concentration at 25°C. (as room temperature) of 1% acetic acid solution at 100°C. That is, to achieve the same rate of reaction at 25°C. as at 100°C., one can estimate the larger [H$^+$] required at 25°C. to compensate for the much smaller rate constant at this lower temperature. Thus, for an activation energy of 20 kcal./mole, the equivalent [H$^+$] at 25°C. would be 1.2N; for 25 kcal./mole, it would be 6.4N; and for 30 kcal./mole, it would be 35.1N. These values, taken together with known effects of temperature on the rates of acetal hydrolysis,[11] suggest that the activation energies for the hydrolysis of the acetals of cellulose and formaldehyde are probably in the range of 20–25 kcal./mole.

The data listed in Tables I and II were plotted, first of all, to check whether simple first-order kinetics might be involved, due to the existence of a single pseudo-unimolecular process as mentioned earlier. The results of such plots are shown in Figure 2, where $(\mathrm{D.S.})_t/(\mathrm{D.S.})_0$, i.e., the extent of reaction at time t relative to the initial extent of reaction at zero time (before any exposure to the boiling 1% acetic acid), is plotted as ordinate on a logarithmic scale versus time in the boiling 1% acetic acid as abscissa. As is apparent from inspection, the data are not to be fitted by a single first-order reaction rate constant, and at least several such constants must be involved. It is also apparent from Figure 2 that the data for the two different cotton varieties, when plotted in this way, fall on a single curve for each of the two different types of treatment.

Another way to test the data of Tables I and II is to plot $(\mathrm{D.S.})_t/(\mathrm{D.S.})_0$ as ordinate versus time in

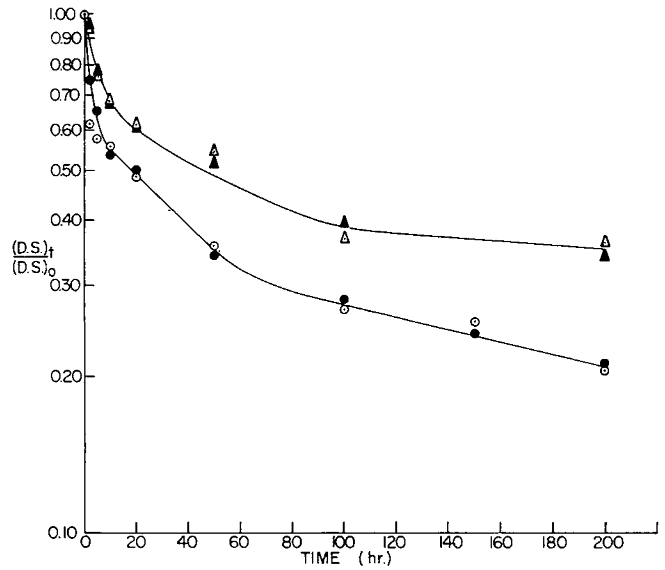

Fig. 2. Formaldehyde contents of variously treated cotton samples vs. time in boiling 1% acetic acid solution: Wagner and Pacsu treatments on (⊙) Acala cotton card sliver, (●) Pima cotton card sliver; Woo, Dusenbury, and Dillon HCHO treatments on (◬) Acala cotton fabric, (▲) Pima cotton fabric. (Data plotted to test for first-order reaction kinetics.)

the boiling acetic acid as abscissa on a logarithmic scale; this has been done in Figure 3. This procedure, suggested by Powell and reported by Frost and Pearson,[14] enables the overall kinetics of a reaction system to be evaluated according to its overall order. In the case of a single type of overall kinetic order (first, second, etc.), the fit of the data to one of a series of sigmoidal curves establishes the overall kinetic order of the reaction. It will be noted from inspection of Figure 3 that the data for the two cotton varieties again follow the same pattern for each of the two different types of treatment. More importantly, no simple overall kinetic order appears from the analysis.

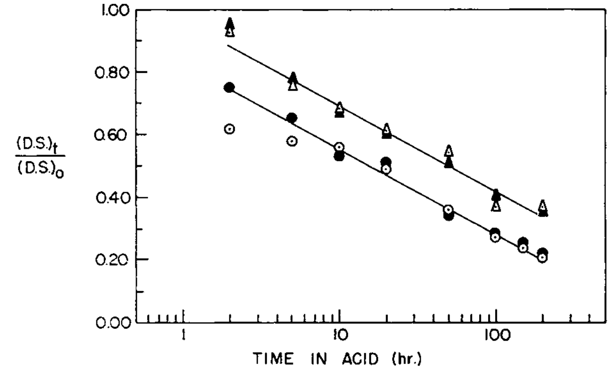

Fig. 3. Formaldehyde contents of variously treated cotton samples vs. time in boiling 1% acetic acid solution: Wagner and Pacsu treatments on (⊙) Acala cotton card sliver, (●) Pima cotton card sliver; Woo, Dusenbury, and Dillon treatments on (◬) Acala cotton fabric, (▲) Pima cotton fabric. (Data plotted to examine overall reaction kinetics.)

It would appear reasonable, in view of the probable complexity of the reaction system, to assume the existence of a fairly large number of concurrent first-order reactions. As indicated by the fit in Figure 3 of the data for both types of formaldehyde treatment to straight lines of the same negative slope, the same type of complex reaction system undoubtedly obtains in both cases. Furthermore the approximate linear fit of the data to time on a logarithmic scale indicates the existence of a distribution of first-order reaction rates, with all first-order rate constants over at least a 100-fold range being of equal probability of occurrence in terms of these experiments. (It is appropriate to mention again that Skrabal and Eger[10] found a 47-fold range of rates for the formaldehyde acetals they studied.) This method of analysis, it should be pointed out, is analogous to that used for estimating distributions of relaxation times in connection with the stress-relaxation behavior of high polymeric systems. A good discussion of the method is to be found in the book by Mark and Tobolsky.[15] The type of distribution indicated by the fit of the data in Figure 3 to the straight lines is called a box distribution, reflecting the equal probability of all first-order reaction rates over the range of time encompassed by the data. This is not to say that the actual distributions may not be somewhat different, but to a first approximation the box distribution would appear to offer the best general fit of a reaction model to the data obtained.

Effects of Boiling Dilute Acetic Acid on Dry and Wet Crease Recoveries

Both dry and wet crease recoveries were measured for the fabric samples whose extents of reaction are listed in Table I. The methods for making these measurements have been described previously,[1] and the number of samples tested was the same for these measurements as for the measurements of extents of reaction (Table I). As indicated earlier, the measurements of dry crease recovery were made on the same fabric samples whose formaldehyde contents were determined later and are indicated in Table I; the measurements of wet crease recovery were made on different subsamples from the same treated fabrics. The crease recoveries measured for some blank treatments are listed in Table IV; the crease recoveries for the samples after various times of treatment with boiling 1% acetic acid are listed in Table V.

In connection with the blank treatments for which data are listed in Table IV, it is important to point out that the effects of the various treatments listed on crease recovery may be considered negligible. In effect, this means that the changes noted later in crease recovery as consequences of formaldehyde treatment and subsequent treatment with boiling 1% acetic acid (Table V) may be ascribed solely to the introduction and removal of formaldehyde from the samples.

TABLE IV
Crease Recoveries (Warp Direction) of Cotton Fabrics Treated under Various Acid Conditions in Absence of Formaldehyde

Treatment of various blanks	Dry crease recovery after 5 min., %[a]		Wet crease recovery after 5 min., %[a]	
	Acala cotton	Pima cotton	Acala cotton	Pima cotton
Untreated	35.0	31.5	32.2	29.2
Boiling 1% acetic acid, 10 hr.	35.0	—	32.2	—
Boiling 1% acetic acid, 200 hr.	33.7	—	32.1	—
Padded with pH 2 buffer and baked 30 min. at 130° C.	30.6	29.2	33.1	30.2
Pooled 95% confidence limit	±3.1		±1.9	

[a] Each mean value is for 3 measurements.

TABLE V
Crease Recoveries (Warp Direction) of Cotton Fabrics Treated with Formaldehyde under Acid Conditions and Later Treated with Boiling 1% Acetic Acid Solution

Time of treatment with boiling 1% acetic acid, hr.	Dry crease recovery after 5 min., %[a]		Wet crease recovery after 5 min., %[a]	
	Acala cotton	Pima cotton	Acala cotton	Pima cotton
Untreated[b]	35.0	31.5	32.2	29.2
0	80.4	71.8	88.3	83.7
2	75.6	67.8	82.0	78.6
5	70.1	64.3	79.6	76.9
10	67.5	62.6	77.1	72.9
20	64.8	60.0	74.3	70.5
50	62.4	58.1	70.3	67.7
100	57.1	55.2	66.8	63.8
200	50.8	48.0	62.4	60.1
Pooled 95% confidence limit	±1.7		±1.6	

[a] Each mean value is for 6 measurements.

[b] Each mean value is for 3 measurements; data not included in calculation of pooled 95% confidence limits.

The data for the results summarized in Table V were also analyzed statistically. The results of this analysis indicated that the data for the two duplicate treatments are statistically indistinguishable for both dry and wet crease recovery. (The same finding was noted earlier for the data for extents of reaction in Table I.) For this reason, as was done in Table I, the mean values listed in Table V are for six measurements each; i.e., the two sets of three measurements each were pooled to give the values indicated. It will also be noted from Table V that the Acala cotton samples consistently exhibit greater crease recoveries—both wet and dry—than the Pima cotton samples (99% confidence level). These greater crease recoveries may be due to the correspondingly greater extents of formaldehyde incorporation (Table I), but it should also be borne in mind that the crease recoveries of the untreated Acala cotton samples are greater than those of the untreated Pima cotton samples (Tables IV and V).

More importantly, the data of Table V indicate that the reaction of the cotton fabrics with formaldehyde is highly reproducible with respect to the crease-recovery improvements observed, as was noted previously also for the extents of reaction (Table I) and that there is good correlation for both dry and wet crease recovery with the extents

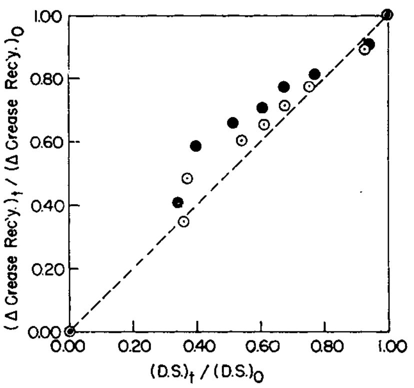

Fig. 4. Crease-recovery improvement vs. formaldehyde content for (⊙) Acala cotton and (●) Pima cotton fabrics treated with formaldehyde under acid conditions and later treated with boiling 1% acetic acid solution. (Crease recovery tests at 65% R.H. and 70°F.)

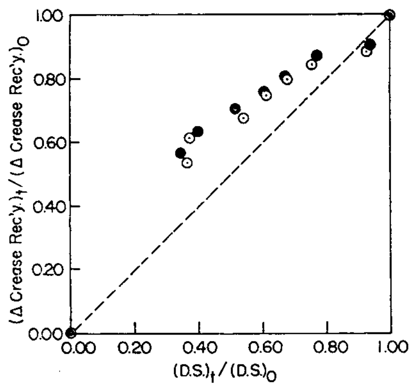

Fig. 5. Crease-recovery improvement vs. formaldehyde content for (⊙) Acala cotton and (●) Pima cotton fabrics treated with formaldehyde under acid conditions and later treated with boiling 1% acetic acid solution. (Wet crease-recovery tests at 70°F.)

of reaction involved. Most importantly, it may also be noted that the effects of the formaldehyde treatments are to cause marked increases in both dry and wet crease recovery, and that treatments such as those described here provide a good means of preparing samples of highly reproducible crease recovery and formaldehyde content over appreciable ranges of crease recovery and formaldehyde content.

The data listed in Tables I and V were examined to determine the relationships between crease-recovery improvement and formaldehyde content. It was decided, first of all, to examine whether linear relationships existed. For this purpose, the data for dry crease recovery were plotted versus formaldehyde content in Figure 4; the corresponding plot for the wet-crease-recovery data is shown in Figure 5. If linear relationships exist, the data should fall on the straight dashed lines of unit slope in both Figures 4 and 5. It is apparent from inspection that the relationships involved are nonlinear. The method of plotting the data indicated in Figures 4 and 5 provides a particularly severe test for linearity, and the results indicate clearly that crease-recovery improvement is not directly proportional to formaldehyde content.

Another method for the analysis of such data is that recently presented by O'Brien and van Loo.[16] In their approach, a theoretical relationship is developed between crease-recovery improvement and amount of crosslinking agent bound to the fabric, in which it is postulated that there is a linear relationship between crease-recovery improvement and true interchain bonding, but that nearly all of the agent bound to the fabric exists in the form of intrachain rather than interchain bonds. A consequence of their analysis is that a plot of $R_0/\Delta W$ (extent of reaction/crease-recovery improvement) versus R_0 should be a straight line with a positive intercept on the $R_0/\Delta W$ axis. The data listed in Tables I and V were treated in this way, and it was found that the fit of the data for dry crease recovery to such a straight line was rather poor. In the case of the results for

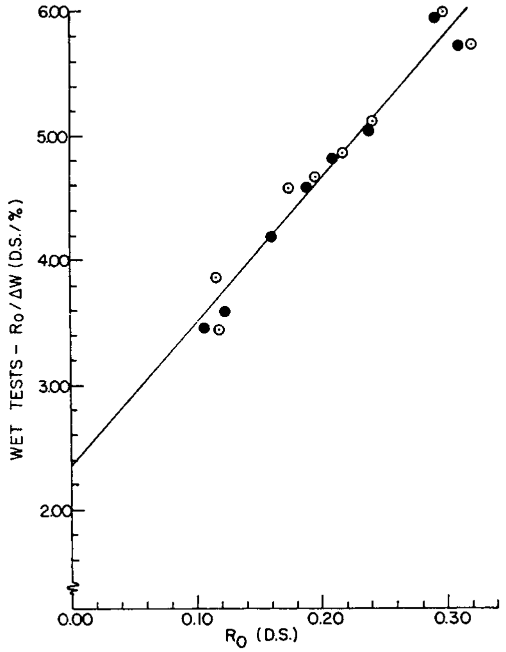

Fig. 6. Data for wet crease recovery tests plotted according to O'Brien and van Loo: (⊙) Acala cotton; (●) Pima cotton.

wet crease recovery, however, the fit turned out to be excellent and is illustrated in Figure 6.

Although the results for wet crease recovery appear consistent with the theoretical relationship of O'Brien and van Loo,[16] it is not clear why the corresponding data for dry crease recovery are not equally consistent with the theory, since O'Brien and van Loo find that their equation will fit data for both dry and wet crease recovery. There would appear to be little point at this stage in speculation beyond the facts as indicated. The procedure used for analysis of such data by O'Brien and van Loo would, however, appear to have merit, in that it provides an explanation for the fact that the changes observed in mechanical properties for the amounts of formaldehyde introduced as reported in this and other studies[2,7,16] would appear to be remarkable for being as relatively small as they are. That is, if the probable amounts of the cotton or other cellulosic fiber volume inaccessible to reaction with the treating agents are taken into account, the changes in mechanical behavior observed are quite small for a situation wherein all the treating agent has reacted to form true intermolecular crosslinks. On the other hand, it would appear unlikely that, in the case of formaldehyde treatments, much intramolecular acetal formation could occur.[3] In his literature review, Roff[4] has speculated on the formation of 2–3 formals on the same anhydroglucose unit and has suggested on the basis of studies with slightly flexible molecular models that these 2–3 formals might be readily formed. There are considerable arguments against this type of bonding, however. They involve the evidence that the cellulose chain molecules are actually quite stiff, that the anhydroglucose units in cellulose exist in the chair form, and that the corresponding 2–3 formals have never been reported for the analogous simple sugars.

SUMMARY

When cotton fabrics are treated with formaldehyde under acid conditions and subsequently baked at elevated temperature, the result is a product exhibiting improved crease recovery both dry and wet. It has been found that appropriate aftertreatments remove any sorbed formaldehyde and/or hemiacetal and that, after this, it is possible to remove the acetals reproducibly by boiling solutions of 1% acetic acid. This reduction of acetal content is reflected in corresponding reductions in both dry and wet crease-recovery improvement. It has also been found that samples of cotton card sliver treated with boric acid and later heated with paraformaldehyde in a sealed tube may have their acetal contents reduced by treatment with boiling 1% acetic acid. The kinetics of acetal removal for both the treated fabric and the treated card sliver samples indicate a fairly complex kinetic scheme, in which there is a wide variety of rates of acetal removal, probably reflecting various types and availabilities of acetals in the formaldehyde-treated cellulose.

The authors are indebted to Mrs. Agnes I. Revesz for assistance with some of the experiments reported here and to Mrs. Clare Michalowski and Miss Marna Garwood for some of the statistical calculations. Valuable advice concerning some of the statistical analyses has been given by Professor John C. Whitwell. The research reported here has been carried out in connection with a project at Textile Research Institute sponsored by a group of T.R.I. Member Firms and the Foundation for Cotton Research and Education.

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Synopsis

A study has been made of the reactions of cellulose with formaldehyde under acid conditions, where the fabrics are baked at elevated temperature. These treatments have

involved cotton cellulose in a "dry" or relatively unswollen state and have resulted in the treated fabrics exhibiting improved crease recovery both dry and wet. It has been found that boiling 1% acetic acid solution reduces the acetal contents of the treated fabrics and causes corresponding decreases in both dry and wet crease-recovery improvement. The reproducibility of these treatments, with respect both to extents of formaldehyde incorporation and to dry and wet crease recovery, is found to be very good within a single treatment and, more importantly, between different treatments carried out under the same conditions. The rates of acetal removal by the boiling 1% acetic acid and the relationships between acetal content and crease-recovery improvement have been found to be fairly complex. A study has also been made of the rates of acetal removal by boiling 1% acetic acid for samples of cotton card sliver treated with acid and subsequently heated in sealed tubes with paraformaldehyde. The rates of acetal removal in this case have been observed to be qualitatively similar to those observed for treated fabrics. The implications of these findings are discussed.

Résumé

On a étudié les réactions de la cellulose avec le formaldéhyde en milieu acide pour des échantillons "cuits" à température élevée. Ces traitements ont été effectués sur la cellulose de coton à l'état sec ou relativement non-gonflé, et ont fourni des produits montrant une meilleure récupération du froissement à l'état sec et humide. On a trouvé qu'une solution bouillante d'acide acétique à 1% diminue la teneur en acétal des échantillons traités, et cause une diminution correspondante de l'amélioration de la récupération au froissement à l'état sec et humide. On a trouvé que la reproductibilité de ces traitements, par rapport au taux d'incorporation du formaldéhyde, et à la récupération au froissement sec et humide était très bonne lors d'un traitement simple et meilleur suite à différents traitements menés dans des conditions identiques. On a trouvé que les vitesses d'élimination de l'acétal par l'acide acétique bouillant à 1% et que les relations entre la teneur en acétal et l'accroissement de la récupération après froissement sont assez complexes. On a également effectué une étude sur les vitesses d'élimination de l'acétal par de l'acide acétique à 1% bouillant sur des échantillons de coton cardé traités par l'acide et chauffés ensuite dans des tubes scellés avec du paraformaldéhyde. Dans ce cas, on a observé que les vitesses d'élimination de l'acétal sont qualitativement semblables à celles observées pour les échantillons traités. On discute la valeur de ces découvertes.

Zusammenfassung

Eine Untersuchung der Reaktion von Cellulose mit Formaldehyd unter sauren Bedingungen und Einwirkung auf die Gewebe bei erhöhter Temperatur wurde durchgeführt. Die Versuche wurden an Baumwollcellulose in einem "trockenen" oder verhältnismässig ungequollenen Zustand ausgeführt und als Ergebnis zeigten die behandelten Gewebe eine verbesserte Trocken- und Nassknitterfestigkeit. Es zeigte sich, dass siedende 1% Essigsäure-lösung den Acetalgehalt der behandelten Gewebe herabsetzt und eine entsprechende Abnahme der Verbesserung der Trocken- und Nassknitterfestigkeit verursacht. Die Reproduzierbarkeit dieser Behandlung sowohl was das Ausmass des Formaldehydeinbaus als auch die Trocken- und Nassknitterfestigkeit betrifft, erwies sich bei einer einzelnen Behandlung, und was noch wichtiger ist, bei verschiedenen, unter den gleichen Bedingungen ausgeführten Behandlungen als sehr gut. Die Geschwindigkeit der Verminderung des Acetalgehaltes durch siedende 1% Essigsäure und die Beziehung zwischen Acetalgehalt und Verbesserung der Knitterfestigkeit erwies sich als ziemlich komplex. Weiters wurde die Geschwindigkeit der Acetalentfernung durch siedende 1% Essigsäure an säurebehandelter und dann im zugeschmolzenen Rohr mit Paraformaldehyd erhitzter Baumwolle untersucht. Es zeigte sich, dass die Geschwindigkeit der Acetalentfernung in diesem Fall qualitativ der an behandelten Geweben beobachteten entspricht. Die Folgerungen aus diesen Befunden werden diskutiert.

Received June 23, 1961