

The Resilience of Chemically Modified Cottons. I. Reactions of Alkali Cellulose and of Sodium Cellulosates with Methylene Dibromide

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INTRODUCTION

The resilience of cotton, i.e., its recoverability from deformation, is important to many of its end uses. In particular, it is a primary factor in the crease-recovery performance of cotton fabrics, so important in present-day emphasis on wash-wear or minimum-care fabrics. The positive correlation between fiber or yarn elastic recovery and fabric crease recovery has been demonstrated in a series of papers from 1948 to 1950, in which Gruntfest and Gagliardi¹ reported on studies of the effects of formaldehyde and formaldehyde-containing resins on cotton and viscose rayon, and in the 1950 paper of Beste and Hoffman,² in which they reported on the extensional resilience of many different fibers, principally man-made ones.

The suggestion that urea-formaldehyde resins impart crease recovery to viscose rayon fabrics by crosslinking adjacent cellulose chains was made by Cameron and Morton in 1948.³ In 1954, Cooke, Dusenbury, Kienle, and Lineken⁴ confirmed earlier findings and showed that crease recovery is related to an increase in fiber elastic recovery, this increase being carried over into the yarns and fabrics constructed from the fibers. Their work indicated that urea- and melamine-formaldehyde resins are deposited primarily in the amorphous regions of the cellulose and that these resins crosslink adjacent cellulose chains in the fiber. They postulated that this crosslinking prevents irreversible slippage of adjacent cellulose chains past one another during fiber extension, thereby reducing permanent set and increasing elastic recovery. The results of the later 1955 study by Kärholm⁵ of the effects of formaldehyde treatments on the elastic-recovery behavior of rayon fibers were closely similar to those of Cooke et al.⁴

Other studies have been reported concerning the

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effects of crosslinking treatments on cellulosic fibers with different states of internal order, viz., cotton, Fortisan, and viscose rayon. Steele and Giddings considered the reactions of these fibers with dimethylol- and monomethylolureas in their 1956 paper,⁶ and in the same year, Woo, Dusenbury, and Dillon reported on their studies in which formaldehyde was involved.⁷ Bifunctional compounds other than aldehydes or aldehyde-containing resins have also been used to improve the crease recovery of cotton fabrics. Thus, for example, Schroeder and Condo⁸ have reported on the use of epoxy resins, Walter, Buxbaum, and Green⁹ have reported on diisocyanates, and Tesoro has reported on the uses of quaternary ammonium derivatives of bischloromethyl ethers¹⁰ and of derivatives of divinyl sulfone.¹¹

Most recently, studies have been reported in which consideration is given to whether all of the material reacted with the cellulose is in the form of interchain bonds or crosslinks and to the state of swelling of the cellulose at the time of reaction. Thus, Steele¹² has considered the roles of intra- and interchain bonds in causing wet and dry crease-recovery improvements, and has come to the view that crosslinking agents applied to fabrics in a wet, swollen state yield a larger proportion of intrachain bonds than the usual dry-state application. He has also expressed the view that the most effective agents for reducing interchain slippage during deformation are those which form covalent crosslinks between the cellulose chains. O'Brien and van Loo¹³ have developed a theoretical relationship 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. Sookne¹⁴ has described experiments in which diepoxide-treated fabrics were extracted with dimethyl-

formamide and has expressed the view that only a small amount of the reagent is involved in true crosslinking leading to improvement in dry crease recovery, with most of the reagent forming polymer that has contributed little or nothing to dry crease recovery. He has suggested, as have O'Brien and van Loo,¹³ that more economical treatments should be possible if better application procedures could be developed to utilize the treatment reagents more effectively. Finally, it is appropriate to mention that Reeves, Perkins, and Chance¹⁵ have studied the acid-catalyzed reaction of formaldehyde with cotton at various degrees of swelling, the swelling being regulated by using solutions containing varying amounts of water and acetic acid. It was found that fabrics crosslinked in the dry state (relatively small amounts of water) exhibited good crease recovery, both dry and wet, while fabrics crosslinked in the wet or more swollen state (relatively large amounts of water) exhibited good wet crease recovery but little or no increase in dry crease recovery.

The overall purpose of the work reported in this and the following paper¹⁶ has been to establish a sound quantitative picture of the chemistry and physical results of chemical reactions which improve the resilience of cotton. To do this, reactions have been employed in which the chemical complexity has been reduced hopefully to a minimum, for the purpose of producing chemical and physical changes whose interpretation will be as unambiguous as possible.

In this regard, studies have been carried out of the reactions of alkali celluloses and of sodium celluloses with methylene dibromide. The reactions in these cases have involved cotton cellulose in a swollen state and have resulted in the treated fabrics exhibiting improved wet crease recovery, but with unchanged or poorer dry crease recovery than that of untreated fabric. This is the work described in this paper. Studies have also been carried out of the reactions of cellulose with formaldehyde under acid conditions. Here, the 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. This work is covered in the second of these two papers.¹⁶

MATERIALS AND ANALYTICAL PROCEDURES

The cottons used in this study were an Acala 4-42 and a Pima S-1, used in the forms of card sliver

and fabric. They were two of the six cottons manufactured into a standard construction sheeting at the pilot plant of Dan River Mills and whose properties through processing have been reported by Rebenfeld.¹⁷ The fabrics prepared from the two cottons were of the same construction: a sheeting fabric of 65 × 64 construction, with the same 21/1 yarn at 4.75 twist multiplier used for both warp and filling. These fabrics were desized and subsequently alkali-scoured and bleached at the Cold Spring Bleachery. After this, the fabrics were given a purification procedure. Samples of card sliver from these same cottons were given the same purification as the fabrics, which consisted, first of all, of a chloroform extraction, followed by cold washes with acetone and distilled water. Then the cotton samples were treated 4-6 hr. with 2% NaOH solution at the boil with nitrogen bubbled through the treatment bath. This was followed by a distilled-water wash, a 15-min. treatment with 1% acetic acid solution at room temperature, and a final wash with distilled water until the samples were neutral.

Experiments were carried out to assess the reliability of various analytical procedures used to determine bound formaldehyde and bromine in treated samples. It was expected from information in the literature that, after proper washing of the treated product, the bound formaldehyde resulting from the reaction of the cotton with formaldehyde under acid conditions would exist in the acetal form or $ZOCH_2OZ'$, where Z, Z' represent cellulose chains. It was expected that the product resulting from the reactions of an alkali cellulose or of a sodium cellulose with methylene dibromide could be represented in the same way. In the case of these latter reactions, it was also thought that some of the product might exist in the form of bromomethyl sidechains, i.e., $ZOCH_2Br$.

The dimedone-precipitation procedure described by Yoe and Reid¹⁸ was used to standardize formaldehyde solutions with respect to their formaldehyde content. It was found that, when this precipitation was carried out in solutions buffered with acetate-acetic acid to give pH values of 4.55-4.57 as recommended by Yoe and Reid,¹⁸ the results were highly reproducible.

A more rapid procedure is that of Bricker and Johnson,¹⁹ which involves the spectrophotometric determination of the intensity of color developed when chromotropic acid reacts with formaldehyde in strongly acid solutions. The reproducibility of the chromotropic-acid procedure was evaluated by

measuring with a Beckman DU spectrophotometer the intensity of color development for a series of solutions of different known formaldehyde contents, these contents having been established by dimedone precipitation. In some instances, purified cotton cellulose was present, and it was established that the presence of the cotton prior to the removal of an aliquot and subsequent reaction of it with chromotropic acid caused no interference with the results. Over the range of concentrations of formaldehyde investigated, it was found that Beer's Law was well met, and the results of about 90 separate experiments were analyzed by the method of least squares to construct a calibration curve used in connection with determining the amounts of bound formaldehyde in various samples of treated cellulose. For all the determinations of bound formaldehyde reported here and in Part II,¹⁶ the optical densities measured were in the concentration range in which they were linearly related to concentration; in some instances, appropriate dilutions of aliquots were required to bring this about.

The bound formaldehyde was in all cases removed from the variously treated samples by hydrolysis with 12*N* H₂SO₄ at room temperature for ca. 16 hr. The hydrolyzate was then separated from the hydrolyzed cotton sample by filtration through a sintered-glass filter crucible. (It is important to remove all the fibrous material at this point, since any remaining in the hydrolyzate will be charred by the concentrated H₂SO₄ used during the subsequent chromotropic-acid determination of formaldehyde¹⁹ and will interfere with the determination.) The bromine in the treated samples was removed from the samples and converted to bromide ion by treatment with what was initially metallic sodium and ethanol (methanol is suitable also). It should be mentioned here that it is also possible to remove the bromine from treated samples with sodium hydroxide in the place of sodium. The results of some experiments in which NaOH was compared with Na in this regard, however, indicated that the bromide content was appreciably lower in the "blanks" where the sodium was involved. Since in some experiments the amounts of bromine in the treated samples may be very small, it is important to keep the size of the blanks to a minimum.

Several procedures were considered for the determinations of bromine in treated samples. In all instances, the procedures involve the determination of bromine as bromide ion. One argentometric determination appeared to be quite promising and was

investigated in some detail; it was the Fajans adsorption-indicator method. This procedure was first described by Fajans and Hassel in 1923²⁰ and the mechanism of the color change with adsorption indicators was later elucidated by Kolthoff.²¹ Another procedure, involving the formation of nonionized mercuric bromide rather than insoluble silver bromide, was also investigated in some detail. The method used in these studies was closely similar to that described by Clarke in 1950,²² although the general procedure involved was reported on some years earlier by Dubsky and Trtilek²³ and by Roberts.²⁴

The utility of both the Fajans^{20,21} and Clarke²²⁻²⁴ methods were investigated over ranges of bromide concentrations apt to be encountered in the course of work. Aqueous solutions containing various known amounts of potassium bromide were prepared and analyzed by both methods. It was found that, for both methods, the reproducibility of the determinations was very good. When the necessary blank corrections were taken into account, however, it was found that the Clarke method could be used to determine amounts of bromide considerably smaller than those determinable by the Fajans method. For the purposes of this work, it was concluded that both the Fajans and Clarke procedures were suitable, with the Clarke procedure being used to determine very small amounts of bromine.

REACTION OF ALKALI CELLULOSES WITH METHYLENE DIBROMIDE

The results of some preliminary experiments indicated that an alkali cellulose prepared from NaOH solution and subsequently reacted with methylene dibromide could be converted into a product with appreciable amounts of the equivalent of bound formaldehyde. Following this work, a rather detailed study has been made of the reactions of alkali celluloses with methylene dibromide (a very few experiments have also involved methylene diiodide), and attempts have been made by various methods to characterize the structure of the reaction product. The results of this study are presented here, and suggestions are made concerning the chemical reactions involved.

The purification procedure (2% NaOH solution at the boil under N₂) used for the samples of card sliver and fabric studied has been described earlier in this paper. After this procedure, cotton samples were treated with solutions 5.9*N* in either NaOH or KOH to convert them to the corre-

sponding alkali celluloses. Unless otherwise stated here, all the treatments with alkalis to form the corresponding alkali celluloses were at room temperature for 26 min. After treatment with the alkaline solutions, the samples were blotted under pressure to definite weight increases, and the amounts of alkali present were determined by titration with sulfuric acid. To assure that all the alkali in the sample was thus titrated, the solution containing the alkali cellulose sample was boiled for 10 min. prior to the estimated endpoint, and the titration then resumed. It was found through separate experiments that this procedure gave satisfactory results with cellulose samples to which a known amount of NaOH or KOH solution had been added.

Some typical data for the results obtained are shown listed in Table I. Two characteristics of these results are apparent from inspection. The first is that the relative amounts of NaOH or KOH remaining on the samples after the alkali treatments are approximately the same on a molar basis; the second is that considerably more alkali remains on the card sliver than on the fabric samples, and this is consistent with the fact that the wet pickups of the card sliver were always greater than those of the fabric sample.

After the preparation of the alkali cellulose samples, they were added directly to anhydrous methylene dibromide, which had been previously heated to the desired temperature of reaction. The reactions with alkali-treated card sliver sam-

ples were carried out in large test tubes immersed in an oil-bath thermostat maintained at the desired temperature of reaction $\pm 0.2^\circ\text{C}$.; the corresponding reactions with fabric samples were carried out with the samples mounted on stainless steel frames in resin reaction kettles (glass) immersed in an oil-bath thermostat maintained at the desired temperature of reaction $\pm 1.0^\circ\text{C}$. Precautions were taken to maintain the reaction mixtures under conditions of reflux during a single experiment. The card sliver samples were loosely packed in the large test tubes during the reaction with methylene dibromide, as they were also during some after-treatments with 1% acetic acid and with 20% NaOH solutions, the results of which will be discussed later in this paper. These aftertreatments were also carried out on treated fabric samples in the resin reaction kettles. For all the aftertreatments, the temperature control of the NaOH solutions involved was to within $\pm 1.0^\circ\text{C}$.

The reaction with methylene dibromide was halted by removing the cotton samples from the reaction mixture. After this, the samples were air-dried, rinsed twice with distilled water, washed 15 min. with 1% acetic acid at room temperature, boiled ca. 6 hr. with distilled water (including several changes of distilled water during this period), and finally dried prior to analysis for their contents of formaldehyde equivalent and of bromine. The purposes of these washes with distilled water and with acetic acid were to remove any physically sorbed material, such as unreacted dibromide, alkali, or formaldehyde from the incidental hydrolysis of methylene dibromide, and to remove any reaction product existing as the hemiacetal of formaldehyde and cellulose.

The amounts of bromine present in the treated samples were found to be very small in comparison with the amounts of acetal (i.e., the product in the general form of $\text{ZOCH}_2\text{OZ}'$), and the methods used for determining the bromide have been given previously. In the case of a relatively large extent of reaction, such as indicated by a degree of substitution (D.S.) of 0.5 (on the assumption of monomeric acetal formation), the bromine contents found corresponded to a maximum D.S. of 0.004. In the case of a relatively small extent of reaction, such as indicated by a D.S. of 0.05, the bromine contents found corresponded to a maximum D.S. of about 0.002. In this latter instance, this amount of bromine present is of the same size as the blank for the determination. This indicates that, after the treatment with methylene dibromide

TABLE I
Amounts of Water and of Alkali that Remained on Cotton Samples before Reaction with CH_2Br_2

| Sample ^a | Increase of sample wt., % after treatment with | | Fraction of sample wt. increase due to alkali after treatment with | | Molar ratio (alkali/cellulose) after treatment with | |
|---------------------|--|-----------------|--|-------------------|---|-------------------|
| | NaOH (5.9N) | KOH (5.9N) | NaOH (5.9N) | KOH (5.9N) | NaOH (5.9N) | KOH (5.9N) |
| | Acala card sliver | 228 | 220 | 0.24 | 0.33 | 2.45 |
| Pima card sliver | 228 | 232 | 0.25 | 0.32 | 2.46 | 2.35 |
| Pima card sliver | 279 | 262 | 0.23 | 0.31 | 2.82 | 2.54 |
| Acala fabric | 116 | 116 | 0.31 | 0.40 | 1.59 | 1.46 |
| Pima fabric | 122 | 94 ^b | 0.28 | 0.38 ^b | 1.51 | 1.14 ^b |

^a Each sample weighed 0.50 g. before treatment.

^b 5.7N KOH solution was used in this case.

and the subsequent washes with distilled water and acetic acid, the amount of ZOCH_2Br present in the treated samples is quite small compared to the amount of $\text{ZOCH}_2\text{OZ}'$.

It is appropriate at this point to consider the amount of each ingredient in a typical reaction mixture for a reaction with a card sliver sample. In each instance, the methylene dihalide was present initially at an excess of ca. 53:1 (moles CH_2X_2 :moles cellulose). A typical reaction mixture is listed in Table II. For a treatment of fabric, the amounts of the various materials would be similar, except that the amounts of NaOH and of H_2O would be smaller due to the smaller wet pickups noted earlier. It should also be added that, for the wet pickup involved and for the amounts of cellulose and NaOH listed in Table II, the corresponding amount of water is closely similar to that to be expected from consideration of the data of Champetier for alkali cellulose.^{25,26}

As mentioned previously, some of the samples treated by the above procedure were given after-treatments with solutions of 1% acetic acid at the boil (Table III) and with solutions of 19% NaOH at 100°C. (Table IV). The results listed in Tables III and IV show clearly that the product of the reaction is readily removable by the 1% acetic

TABLE II
Typical Reaction Mixture for a Card Sliver Sample

| Material | Amount, g. | Amount, mmoles |
|---|------------------------------------|----------------|
| Cellulose | 0.50 | 3.1 |
| NaOH | 0.28 | 7.0 |
| H_2O | 0.86 | 48 |
| CH_2Br_2 or CH_2I_2 | 28.5 (11.4 ml.) 44.0 (13.2 ml.) | 164 |

TABLE III
Effect on Treated Cellulose Samples of 1% Acetic Acid Solution at the Boil

| Cotton sample | D.S. of samples after different times of treatment ^a | | | | |
|--------------------|---|-------|-------|--------|--------|
| | 0 hr. | 4 hr. | 8 hr. | 16 hr. | 44 hr. |
| Acala, card sliver | 0.239 | — | — | — | 0.030 |
| Pima card sliver | 0.238 | — | — | — | 0.039 |
| Acala fabric | 0.213 | 0.118 | 0.086 | 0.056 | — |
| Pima fabric | 0.213 | 0.115 | 0.077 | 0.054 | — |

^a Each mean value based on two or more measurements of bound formaldehyde equivalent.

TABLE IV
Effect on Treated Cellulose Samples of 19% NaOH Solution at 100°C.

| Cotton sample | D.S. of samples after different times of treatment ^a | | | |
|-------------------|---|-------|-------|--------|
| | 0 hr. | 4 hr. | 8 hr. | 42 hr. |
| Acala card sliver | 0.239 | — | — | 0.239 |
| Pima card sliver | 0.238 | 0.238 | 0.241 | 0.240 |
| Pima fabric | 0.092 | 0.092 | 0.090 | — |

^a Each mean value based on two or more measurements of bound formaldehyde equivalent.

acid, but is quite impervious to the 19% NaOH. These findings are consistent with the view that the product of the reaction between the alkali cellulose and the methylene dibromide exists primarily in the acetal rather than the hemiacetal form.

Reaction Rate and Mechanism

After these experiments were carried out, other and more extensive measurements were made to examine the kinetics of the reaction. The overall purpose of this study was to gain an idea of the mechanism of the reaction(s) involved in the alkali cellulose-methylene dihalide system. One of the first factors investigated was that of the extent of blotting the alkali cellulose sample with respect to its effect on the rate of reaction with methylene dibromide. As may be seen from inspection of Figure 1, the effect is fairly pronounced as far as extent of reaction is concerned and appears insignificant as far as the rate is concerned. It is likely that the greater D.S. values at 278% weight increase are associated with correspondingly greater amounts of alkali present in the samples during reaction. Each point shown plotted in Figure 1 is the mean of two measurements, and the slopes of the least-squares lines drawn through the points, together with their corresponding standard deviations, are thus each based on eight measurements. The reaction was carried out at the relatively high temperature of 91.3°C. to accentuate the effect of the difference in the initial weight increases when the alkali celluloses were prepared.

As will be noted from inspection of Figure 1, there appears to be a linear relationship between D.S. (calculated on the assumption of forming monomeric acetals) and the time of reaction with CH_2Br_2 . This linear relationship has been found to hold throughout the course of this study, is consistent with zero-order reaction kinetics, and will be discussed in more detail later.

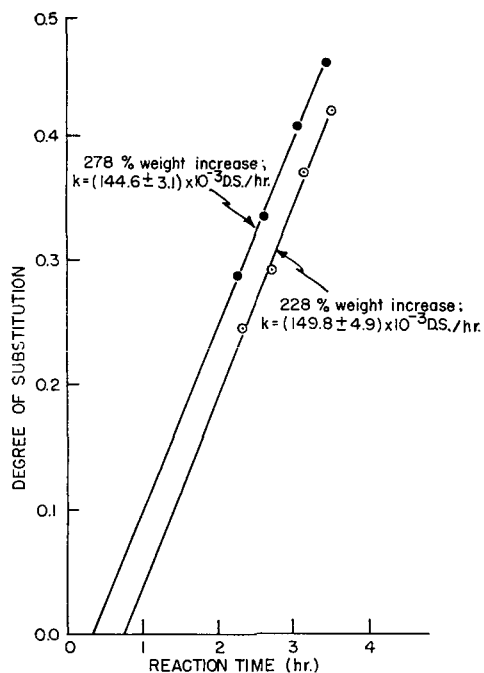


Fig. 1. Effect of the extent of blotting alkali cellulose sample (NaOH-treated Pima cotton, card sliver) on the rate of reaction with CH_2Br_2 at 91.3°C .

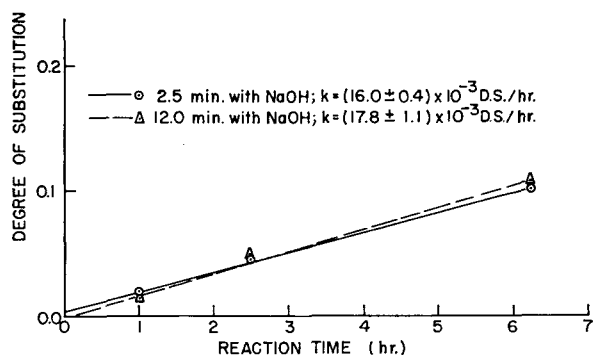


Fig. 2. Effect of time of treating cellulose (Acala cotton fabric) with 5.9*N* NaOH on the rate of reaction with CH_2Br_2 at 77°C .

Another set of experiments involved a study of the effect of varying the time of treatment with NaOH to form the alkali cellulose on its subsequent reaction rate with CH_2Br_2 . The results of these experiments are summarized in the data of Table V and are plotted in Figure 2; the limits indicated are 95% confidence limits. The $(\text{D.S.})_0$ values listed in Table V are for the intercepts of the least-squares lines on the ordinate shown in Figure 2. Two characteristics of the data are apparent from inspection: the intercepts have values indistinguishable from zero, and the rate of reaction of the alkali cellulose sample resulting from 12.0

TABLE V
Effect of Time of Treating Acala Cotton Fabric with 5.9*N* NaOH Solution on the Rate of Reaction with CH_2Br_2 at 77°C .

| Measure of reaction ^a | Time of treatment with NaOH | |
|--|-----------------------------|----------------|
| | 2.5 min. | 12.0 min. |
| Rate constant, k , D.S./hr. $\times 10^3$ | 16.0 ± 0.4 | 17.8 ± 1.1 |
| $(\text{D.S.})_0 \times 10^3$ | 3.3 ± 3.9 | -1.8 ± 4.2 |

^a Each mean value based on 6 measurements; limits shown are 95% confidence limits.

min. treatment with NaOH is somewhat greater than the corresponding rate for the sample resulting from 2.5 min. treatment. As mentioned earlier, the time of treatment with NaOH (or with KOH) used throughout this study—with the exception just noted—was 26 min. The results with varying the time of treatment with NaOH suggest that this time of treatment is more than adequate for the purpose of reaction with methylene dibromide and that although the rate after 12.0 min. of NaOH treatment is significantly greater than that after 2.5 min., the difference is small enough to indicate that most of the alkali cellulose has been formed within the shorter time of treatment.

Experiments were also carried out to compare the effects of using NaOH and KOH to prepare the alkali cellulose samples; some typical results are shown plotted in Figure 3. In this figure, as well as in Figure 4, the limits shown are standard deviations. Each point shown in Figure 3 is the mean value for two measurements, and thus the value indicated for each rate constant is based on eight measurements. It is clear that the least-squares lines shown drawn through the data intersect the ordinate at values close to zero and, more importantly, that the rate of reaction with the alkali

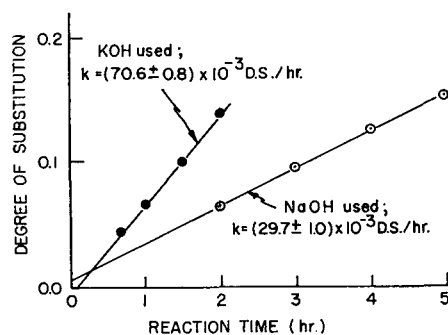


Fig. 3. Effect of alkali used (KOH or NaOH) in preparing alkali cellulose (from Pima cotton, card sliver) on the rate of reaction with CH_2Br_2 at 82.4°C .

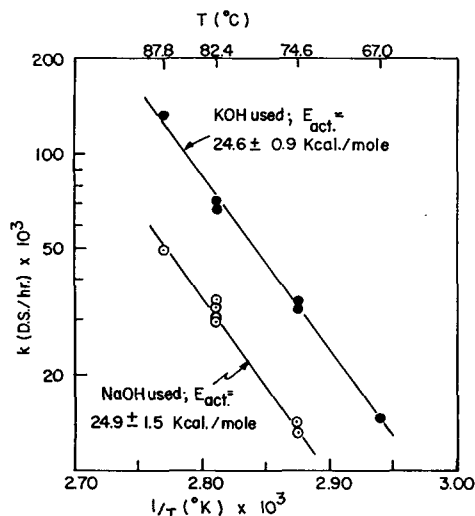


Fig. 4. Effects of temperature on the rates of reaction of Pima cotton alkali celluloses (prepared from card sliver) with CH_2Br_2 .

cellulose prepared from KOH is more than twice that for the samples prepared from NaOH.

The effects of temperature on the rates of reaction with CH_2Br_2 were measured for alkali cellulose samples prepared both from NaOH (Table VI) and from KOH (Table VII). As noted in Table VI, the data obtained for the NaOH-treated samples at 91.3°C . were not included in the calculation of the corresponding activation energies. The temperature control was not particularly good during these experiments and, furthermore, the rate observed compared with that at the next lower temperature studied is too large to allow the values to fit well on a plot of the logarithm of reaction rate versus reciprocal of absolute temperature. At present it is not clear whether this "abnormal" increase in rate with increasing tempera-

TABLE VI

Effect of Temperature on the Rate of Reaction of Alkali Cellulose (Prepared from NaOH) with CH_2Br_2

| Reaction temp., $^\circ\text{C}$. | k , D.S./hr. $\times 10^{3a}$ | |
|------------------------------------|---------------------------------|-----------------|
| | Acala cotton | Pima cotton |
| 74.6 | 16.2 ± 0.4 | 14.6 ± 0.6 |
| 82.4 | 32.5 ± 0.5 | 29.4 ± 1.0 |
| | | 29.7 ± 1.0 |
| 87.8 | 53.5 ± 1.2 | 49.2 ± 1.9 |
| 91.3 ^b | 121.8 ± 3.4 | 149.8 ± 4.9 |

^a Each mean value based on 8-10 measurements on purified card sliver; limits shown are standard deviations.

^b Data not included in calculation of activation energies.

TABLE VII

Effect of Temperature on the Rate of Reaction of Alkali Cellulose (Prepared from KOH) with CH_2Br_2

| Reaction temp., $^\circ\text{C}$. | k , D.S./hr. $\times 10^{3a}$ | |
|------------------------------------|---------------------------------|-----------------|
| | Acala cotton | Pima cotton |
| 67.0 | 15.7 ± 0.6 | 14.8 ± 0.4 |
| 74.6 | 33.6 ± 0.3 | 32.4 ± 0.9 |
| 82.4 | 71.2 ± 1.1 | 70.6 ± 0.8 |
| | | 67.0 ± 1.9 |
| 87.8 | 136.7 ± 3.8 | 134.0 ± 1.3 |

^a Each mean value based on 8-10 measurements on purified card sliver; limits shown are standard deviations.

ture is to be associated with a change in the nature of the reaction.

Two general characteristics of the data listed in Tables VI and VII are that (1) at the same temperature, the reaction rates with the KOH-alkali celluloses are more than double those with the NaOH-alkali celluloses, and (2) the Acala cotton samples react consistently at a somewhat faster rate than the Pima cotton samples. (This does not hold for the NaOH-alkali celluloses at 91.3°C ., but the difficulties with these measurements have been mentioned previously.) The reproducibility of the rate measurements listed in Tables VI and VII was checked by making the duplicate runs indicated in both tables for Pima cotton samples at 82.4°C . The results of statistical analysis of these data show that for both the cases of the NaOH-treated samples (Table VI) and the KOH-treated samples (Table VII) these duplicate rates of reaction are indistinguishable from one another.

All the reaction-rate data obtained were plotted to determine the activation energies involved; i.e., the rate constants were plotted on a logarithmic scale as ordinate versus the reciprocal of absolute temperature as abscissa. The method of least squares was then used to obtain the activation energies from the slopes of the straight lines involved. The data thus plotted for the samples

TABLE VIII

Activation Energies for the Reaction of Alkali Cellulose with CH_2Br_2

| Cotton ^a | Alkali used | Activation energy, kcal./mole ^b |
|---------------------|-------------|--|
| Pima | NaOH | 24.9 ± 1.5 |
| Pima | KOH | 24.6 ± 0.9 |
| Acala | NaOH | 22.1 ± 3.6 |
| Acala | KOH | 24.9 ± 0.8 |

^a Purified card sliver.

^b Limits shown are standard deviations.

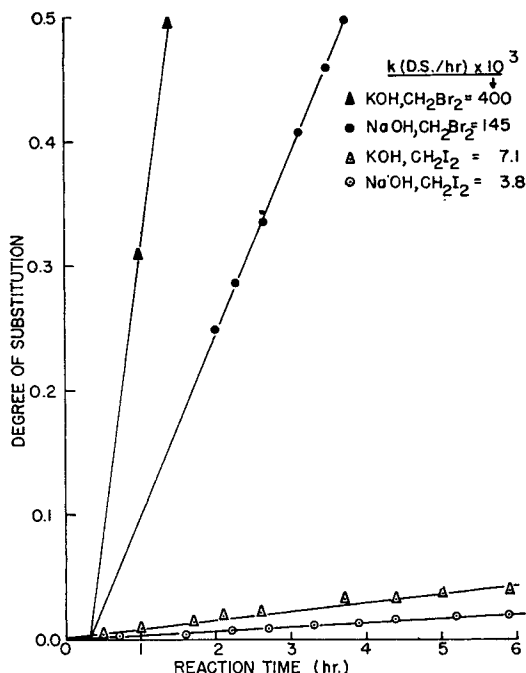


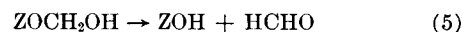
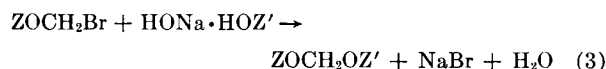
Fig. 5. Effects of alkali used and of dihalogen compound used on the rates of reaction of alkali celluloses (prepared from Pima cotton, card sliver) with CH_2X_2 at 91.3°C .

prepared from Pima cotton are shown in Figure 4; the corresponding data for the Acala cotton samples appear closely similar. The activation energies thus obtained are shown summarized in Table VIII.

As indicated in Table VIII, the four different activation energies involved are statistically indistinguishable and consistent with the energy to be associated with the formation of a covalent bond. Whatever the process involved is, and this matter will be discussed shortly, the identity of the activation energies listed in Table VIII argues strongly for the same process being involved in each case.

It was also observed in another series of experiments that the rates of reaction of the NaOH- and KOH-alkali celluloses were much smaller with methylene diiodide than with methylene dibromide. The results obtained in this case, where the reaction was carried out at the relatively high temperature of 91.3°C . to facilitate obtaining a measurable rate with the CH_2I_2 , are shown plotted in Figure 5. It may also be noted from Figure 5 that the KOH-treated samples react more rapidly than the NaOH-treated samples with the CH_2I_2 , a behavior consistent with that previously observed for the reactions with CH_2Br_2 .

It is appropriate to consider at this point possible reaction mechanisms for the results observed. In these considerations, Z and Z' written in the reactions represent cellulosic chains. The reactions likely or possible to take place in an alkaline medium are as follows:



Reaction (1) represents the formation of alkali cellulose, reaction (2) represents the reaction of the alkali cellulose with methylene dibromide to form the bromomethyl sidechain derivative, and reaction (3) represents the formation of the acetal by reaction of the bromomethyl derivative with another "molecule" of alkali cellulose. Possible side reactions are indicated by the next three reactions: reaction (4) represents the alkaline hydrolysis of a bromomethyl sidechain to the hemiacetal form, reaction (5) represents the subsequent reversible decomposition of the hemiacetal to cellulose and formaldehyde, and reaction (6) represents the incidental alkaline decomposition of methylene dibromide to form formaldehyde as indicated.

It will be noted for this set of reactions that the alkali cellulose prepared from NaOH is represented as $\text{ZOH} \cdot \text{NaOH}$, a formula consistent with the conditions used to form the material in this study. It is important to point out, however, that the actual structure of alkali cellulose has not been definitely established—if it indeed exists in a form expressible as a definite stoichiometric relationship—and that it appears extremely unlikely that any appreciable portion of it exists in form of a true cellulosate, e.g., as ZONa .²⁷

The fact that the same activation energies were observed for the reactions of methylene dibromide with the alkali celluloses prepared from both types of alkali (NaOH and KOH), and—less importantly—for both types of cotton, suggests strongly that the same reaction is involved in both cases. Furthermore, the size of the activation energy (Table VIII) is consistent with the formation of a covalently bonded product. It appears unlikely that the reaction is diffusion-controlled, because of the magnitude of the activation energy. At this stage,

it is not possible to say whether reaction (2) or (3) is rate-determining in the formation of the acetal. The apparent zero-order kinetics of the process appear to warrant further consideration. It is likely that the reaction system is effectively "flooded" with respect to methylene dibromide, and this would eliminate changes in this reactant during the reaction and thus lead to first-order kinetics. If, in addition, the "intermediate" $ZOH \cdot NaOH$ could be regarded as being at an effectively constant, albeit small, concentration (a steady-state concentration), it would be possible to explain the apparent zero-order kinetics. Another possibility is that the plots of D.S. versus reaction time with CH_2Br_2 appear to be linear simply because the reaction has not proceeded very far, and that all such plots are effectively linear for the first part of the reaction. In some instances, however, the extents of reaction were relatively large (Figs. 1 and 5) and the reaction still appeared to be of zero order.

The greater reaction rates observed with the KOH-alkali celluloses suggest either that there is relatively more alkali cellulose ($ZOH \cdot KOH$) formed in this case or that the potassium alkali cellulose is more reactive towards methylene dibromide than the sodium alkali cellulose. The much slower reaction rates observed for the reactions with methylene diiodide suggest that this material is either much more subject to alkaline hydrolysis than is methylene dibromide or is much less reactive towards the alkali celluloses formed from sodium and potassium hydroxides.

At this point it is important to mention that this

reasoning, although speculative in character, does have the virtue of providing at least a qualitative explanation for the results observed. Another possibility not yet mentioned is that, during the course of the reaction, all the alkali is destroyed, the solution becomes acid, and what in fact is being measured is the acid-catalyzed (HBr) reaction of formaldehyde (from the hydrolysis of CH_2Br_2) with cellulose. The observation that the product of the reaction after removal from the methylene dibromide is still strongly alkaline argues against this possibility. Some experiments were carried out, however, to examine quantitatively the amounts of alkali remaining on the samples after reaction and the amounts of bromide ion formed during reaction.

Although some of these experiments involved the reaction of NaOH-treated cotton with CH_2Br_2 , the most extensive ones involved the similar reaction with KOH-treated cotton, since in this latter case the extents of reaction with CH_2Br_2 are relatively greater as noted earlier. A procedure was worked out whereby it was possible to determine the amounts of acetal formation (based on HCHO analysis), of alkali remaining on the treated sample (titration with HNO_3), and of bromide ion produced (titration with $0.00513N$ $Hg(NO_3)_2$ according to Clarke²²) all on the same sample. The results for a series of experiments, in which 200 mg. samples of purified Pima cotton card sliver were treated with CH_2Br_2 for varying times at 83.9°C. after formation of the KOH-alkali cellulose, are listed in Table IX. In each case, the cotton samples were treated 26 min. at room temperature

TABLE IX

Production of Br^- and Consumption of OH^- during Reaction of Alkali Cellulose (KOH Treatment of Pima Cotton Card Sliver) with CH_2Br_2 at 83.9°C.; 200-mg. Cotton Samples Used in Each Experiment

| Time of reaction with CH_2Br_2 , hr. | Amount of acetal formed (based on HCHO analysis) | | Cellulosic—OH groups substituted, mmoles | Amount of $[OH^-]$ remaining on sample, mmoles | Calculated amount of $[OH^-]$ consumed, mmoles | Amount of $[Br^-]$ produced, mmoles |
|--|--|-------|--|--|--|-------------------------------------|
| | D.S. | | | | | |
| 0 | 0 | 0 | 0 | 2.71 | 0 | 0 |
| 1 | 0.069 | 0.085 | 0.085 | 2.04 | 0.67 | 0.48 |
| 1 | 0.064 | 0.079 | 0.079 | 2.11 | 0.60 | 0.55 |
| 3 | 0.246 | 0.304 | 0.304 | 1.74 | 0.97 | 1.16 |
| 3 | 0.257 | 0.317 | 0.317 | 1.64 | 1.07 | 1.35 |
| 4 | 0.317 | 0.391 | 0.391 | 1.26 | 1.45 | 1.37 |
| 4 | 0.271 | 0.334 | 0.334 | 1.58 | 1.13 | 1.31 |
| 5 | 0.394 | 0.487 | 0.487 | 0.99 | 1.72 | 1.49 |
| 5 | 0.370 | 0.457 | 0.457 | 0.82 | 1.89 | 1.53 |
| 6 | 0.450 | 0.555 | 0.555 | 0.81 | 1.90 | 1.74 |
| 6 | 0.441 | 0.545 | 0.545 | 0.92 | 1.79 | 1.79 |

with 5.82*N* KOH, blotted to a weight of 700 mg. (500 mg. weight increase from the KOH treatment), and immersed in 108 g. (43.3 ml.) of CH₂Br₂.

The data listed in Table IX indicate clearly that, even after 6 hr. at 83.9°C., 30–34% of the alkali initially present still remains on the samples, and accordingly, that the danger of the system going acid during the course of the reactions discussed here is negligible. There should be a balance between the consumption of hydroxide and the production of bromide ions, and the data listed in the last two columns on the right of Table IX indicate that this balance obtains. The data for calculated amount of [OH⁻] consumed in Table IX are based on the assumption that all of the alkali cellulose samples initially contained 2.71 mmoles of KOH; the results of replicate titrations indicated that this number is reproducible to within ±0.05 mmoles for these experiments.

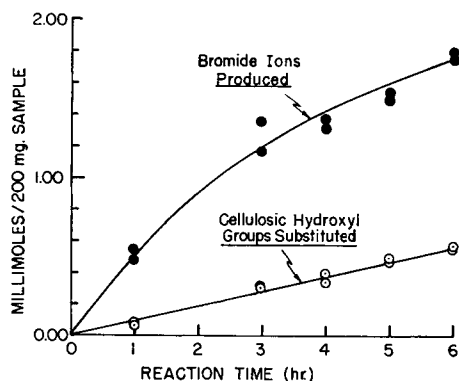


Fig. 6. Reaction of alkali cellulose (KOH-treated Pima cotton, card sliver) with CH₂Br₂ at 83.9°C.

The data for bromide-ion production and cellulosic hydroxyl-group substitution are shown plotted in Figure 6. The rate constant derived from the slope of the straight line through the cellulosic hydroxyl groups substituted points in Figure 6 is consistent with the rate constants observed and noted previously in the other experiments involving KOH-treated samples (Tables VII and VIII and Fig. 4). That is, it is 0.0742 D.S./hr. at 83.9°C., compared with the values of 0.0706 and 0.0670 D.S./hr. listed in Table VII for the reaction at 82.4°C. The differences indicated between the two sets of data plotted in Figure 6 (Br⁻ production versus ZOH substitution) indicate the extent of the side reaction of the alkaline hydrolysis of CH₂Br₂ to form HCHO; as may be noted, it is appreciable.

Measurements of Cupriethylenediamine Viscosity and Crease Recovery

As indicated previously, the products of the reactions of the alkali celluloses with methylene dibromide appear to exist in the acetal rather than the hemiacetal form. The observations that the products resulting from such reactions are reduced in acetal content by boiling 1% acetic acid (Table III), but are unaffected by 19% NaOH at 100°C. (Table IV) are consistent with this view. Two additional methods have been used to characterize the products of such reactions: measurement of viscosity in cupriethylenediamine and measurement of both dry and wet fabric crease recovery.

TABLE X
Viscosity at 25.00 ± 0.05°C. of Variously Treated Acala Cotton Card Sliver Samples in 0.5*M* Cupriethylenediamine

| D.S. of sample | Amount of sample taken for, dissolution, mg. | Time of contact with solvent before measurement | Time of flow of solution, sec. ^a |
|----------------|--|---|---|
| 0 | 11.8 | 45 min. | 178.8 |
| 0.035 | 42.3 | 4 days | 103.0 |
| 0.038 | 12.2 | 4 days | 101.7 |
| 0.075 | 12.2 | 4 days | 101.7 |
| 0.166 | 12.2 | 4 hr. | 101.6 |
| — | Solvent | — | 100.9 |

^a Each value based on three measurements; 95% confidence level = ±0.1 sec.

The measurements of viscosity in cupriethylenediamine were carried out on variously treated samples of Acala cotton card sliver. In all cases, the reaction with methylene dibromide was carried out on purified samples previously treated with NaOH to form the alkali cellulose. The times of flow of the various solutions tested were measured with a Cannon-Fenske viscometer immersed in an oil-bath thermostat maintained at 25.00 ± 0.05°C. The results of these measurements are summarized in Table X. Although it is apparent that small portions of the variously treated samples have dissolved in the 0.5*M* reagent, the extent of this dissolution is obviously far less than that for an untreated sample of cotton (D.S. = 0), where the sample was observed to dissolve completely. In the case of most of the treated samples, it may be estimated that no more than 1% of the material was soluble in the cupriethylenediamine. The results of these experiments suggest that at least some of the methylene dibromide has reacted with the alkali cellulose to form a crosslinked product.

The crease recoveries of variously treated samples were measured both dry and wet with the Monsanto Wrinkle Recovery Tester.²⁸ The dry tests were carried out on samples conditioned to and tested at 65% R.H. and 70°F.; the wet tests were carried out at 70°F. on samples immersed 5 min. in an aqueous 0.1% solution of Tween 80 (nonionic surface-active agent) and then blotted quickly with filter paper before measurement of the crease-recovery angle. A procedure similar to this for making wet crease-recovery measurements has been described by Lawrence and Phillips.²⁹

It was generally found that the treatments of the sort described previously have resulted in the treated fabrics exhibiting improved wet crease recovery and unchanged or poorer dry crease recovery than that of untreated fabric. Some of the earliest crease-recovery measurements were carried out simply to gain an idea of the effects produced. Later measurements were made under more carefully controlled conditions, and the results of these will be given here.

Samples of cotton fabric, purified as described previously, were treated 20 min. at room temperature with 5.9*N* KOH, and some of these samples were later treated 3 hr. at 87°C. with CH₂Br₂. After these treatments, the samples were after-washed in the way described previously for the card sliver samples. An attempt was also made in these experiments to estimate the possible effects of tension on the fabrics during the treatments. Strained treated samples were prepared by fixing the fabric samples on stainless steel pinframes in an initially flat and essentially tensionless condition. They were then treated with the KOH and CH₂Br₂ while maintained at the original dimensions. Slack treated samples were prepared by carrying out the same treatments on samples not mounted on pinframes. In the case of these latter treatments, it was observed that the fabric samples exhibited, on the average, warp shrinkages of ca. 13% and filling shrinkages of ca. 9% as a result of the KOH treatments and that the fabric dimensions were only slightly affected by the later CH₂Br₂ treatments. The extents of reaction observed for the variously treated fabric samples are listed in Table XI, and the warp-crease-recovery values observed are listed in Table XII. (The crease recoveries expressed in per cent in Table XII are based on 180° = 100% recovery.)

The two sets of results listed in Tables XI and XII were analyzed statistically, and it was found that they were consistent with one another and

TABLE XI
Extents of Reaction of Cotton Fabrics Treated with 5.9*N* KOH, 20 Min. at Room Temperature, and with CH₂Br₂, 3 Hr. at 87°C.

| Treatment | D.S. ^a | |
|-----------------------------|-------------------|-------------|
| | Acala cotton | Pima cotton |
| Strained | 0.375 | 0.365 |
| Slack | 0.394 | 0.368 |
| Pooled 95% confidence limit | ±0.050 | ±0.050 |

^a Each mean value is for 3 measurements.

TABLE XII
Crease Recoveries (Warp Direction) of Cotton Fabrics Treated with KOH and with KOH + CH₂Br₂

| Treatment | Dry crease recovery after 5 min., % ^a | | Wet crease recovery after 5 min., % ^a | |
|--|--|-------------|--|-------------|
| | Acala cotton | Pima cotton | Acala cotton | Pima cotton |
| Untreated | 39.7 | 41.0 | 33.0 | 30.7 |
| KOH, strained | 34.3 | 25.3 | 32.3 | 37.3 |
| KOH, slack | 33.0 | 25.7 | 41.7 | 37.3 |
| KOH + CH ₂ Br ₂ , strained | 40.0 | 36.3 | 80.0 | 81.0 |
| KOH + CH ₂ Br ₂ , slack | 43.0 | 39.0 | 80.7 | 79.7 |
| Pooled 95% confidence limit | | | ±6.3 | |

^a Each mean value is for 3 measurements.

with data reported previously. It may be noted from Table XI that larger extents of reaction are obtained with the Acala cotton (95% confidence level); this difference between the cottons was also noted earlier for the card-sliver experiments, and the extents of reaction obtained with these fabric samples are somewhat smaller than would be expected for the corresponding card sliver samples (Table VII). For the data in both Tables XI and XII, there was found to be no statistically significant difference between the "strained" and "slack" samples. As may be noted from Table XII, the effects of the CH₂Br₂ are to cause marked increases in wet crease recovery and little or no change in dry crease recovery. The dry crease recoveries of the CH₂Br₂-treated fabrics are somewhat greater than those of the corresponding KOH-treated "controls," but about the same as those of the original untreated fabrics. (The KOH treatments alone appear to cause appreciable but small reductions in dry crease recovery.) These results appear consistent with the view that at least some crosslinking has

occurred and that this crosslinking has occurred while the cellulose is in a swollen state.^{12,13,15} Sookne¹⁴ has also reported minimal effects of stretching on the crease recovery of cotton fabrics treated with a diepoxide, vinylcyclohexene dioxide, but has also shown that important gains in strength retention obtained in the direction of the stretch, the filling direction in the case of Sookne's experiments.

REACTIONS OF SODIUM CELLULOSATES WITH METHYLENE DIBROMIDE

The utility of alkali celluloses as intermediates for subsequent reaction with CH_2Br_2 to form a product probably containing acetal crosslinks has been considered previously here, and it has been pointed out that the structures of these intermediates are in considerable doubt. To reduce the ambiguity associated with these intermediates, it would appear to be desirable to study the reactions of true sodium celluloses with difunctional alkyl halides such as CH_2Br_2 . In such reactions one would expect the reaction path with the sodium cellulose, ZONa , to be as follows:



where Z and Z' as previously, represent cellulose chains. Here eq. (7) represents the formation of a bromomethyl sidechain derivative, and eq. (8) represents the subsequent reaction of this derivative with a second "molecule" of sodium cellulose to form the acetal product. Another difficulty associated with the use of alkali celluloses, rather than sodium celluloses, is that alkali usually may not be used for regenerated cellulose fibers in connection with their chemical modification. It is also fairly obvious that the presence of water in alkali cellulose would eliminate or greatly reduce the possibility of using $-\text{OH}$ group-sensitive reagents for subsequent chemical modification.

For all these reasons, the use of a true sodium cellulose would appear to offer many advantages for the chemical modification of cellulose, but the preparation of such intermediates appears to have received little attention for such purpose. The preparation of sodium and potassium alcoholates of carbohydrates by using solutions of sodium and potassium in liquid ammonia was described as early as 1925 by Schmid and his co-workers,^{30,31} and later work in this area was reported in 1934 by Muskat.³² The first use of sodium dissolved in liquid ammonia to prepare sodium cellulose

appears to be that described in 1931 by Scherer and Hussey³³ for the modification of cotton linters. In 1940, Harris and Purves³⁴ described the preparation of thallium cellulose by reaction of cellulose with thallous ethylate in benzene. Later in 1949, Sugihara and Wolfrom³⁵ used an amorphous form of regenerated cotton cellulose to prepare what they called sodium-2-cellulosate; in this case, the cellulose was refluxed with a mixture of concentrated NaOH and butanol-1. More recently in 1958, Derevitskaya, Prokofieva, and Rogovin³⁶ prepared sodium celluloses from cotton fibers by reaction with sodium isoamylate in dry xylene. In 1960, Lenz³⁷ used the procedure of Sugihara and Wolfrom³⁵ to prepare a product from regenerated wood cellulose which was subsequently methylated and the distribution of methoxyl groups studied to assess the relative reactivities of the cellulosic hydroxyl groups. Most recently, Schwenker, Kinoshita, Beurling, and Pacsu³⁸ have described the preparation of sodium celluloses from cotton and viscose-rayon celluloses by reactions with anhydrous systems of sodium methoxide in methanol and of sodium *n*-butoxide in *n*-butanol. In this work, as well as in that of Derevitskaya et al.,³⁶ the sodium celluloses result from exchange reactions between cellulose and the sodium alkoxides.

In the work to be described here, sodium celluloses have been reacted with CH_2Br_2 , with the sodium celluloses being formed by reaction with sodium in liquid ammonia³⁰⁻³³ and by reaction with sodium isoamylate in xylene.³⁶

Reactions Involving Sodium in Liquid Ammonia

A vacuum system was designed and constructed to facilitate the preparation of sodium cellulose and its subsequent reaction with CH_2Br_2 . Several different procedures were investigated for preparing the sodium cellulose, and as a result of these preliminary studies, the following general procedure was developed. (1) A 30-300 mg. portion of cellulosic material is dried on the vacuum system at room temperature for a definite period of time (up to several hours). Either a Dry Ice-Cellosolve ($-78^\circ\text{C}.$) or a liquid nitrogen ($-195.8^\circ\text{C}.$) cooling trap is used for trapping the water. (2) A piece of specially cleaned metallic sodium (5-125 mg.) in petroleum ether is introduced into the reaction chamber with the cellulose, and the mixture is then dried for an additional period of time to remove the petroleum ether and additional water present. (3) When the petroleum ether and

water have been removed from the reaction chamber, ammonia is distilled over into it. Liquid nitrogen is used as a coolant and the ammonia is solidified. The initial source of the ammonia is from a tank (anhydrous ammonia, Matheson), and prior to distillation into the reaction chamber, the ammonia is distilled once to remove traces of water in a cold-finger trap ($-195.8^{\circ}\text{C}.$) separated from the reaction chamber. (4) The liquid nitrogen coolant is removed from around the reaction chamber, and the reaction mixture warms to about $-34^{\circ}\text{C}.$ and is kept at approximately this temperature until the end of the reaction, which is manifested by disappearance of the dark-blue color of the solution of sodium in liquid ammonia. The temperature of the reaction is determined by the pressure in the system, and this is regulated by controlling the rate of evaporation of ammonia from the reaction chamber, this rate being governed by control of the speed of condensation of the ammonia in a cold-finger trap.

After the sodium cellulose is formed (disappearance of the dark-blue color), the remaining ammonia is distilled over into the cold-finger trap and discarded. The cellulose product remaining in the reaction chamber is then dried for 5–15 min. by vacuum pumping in the absence of any coolant to remove most of the ammonia still present. (Note: actually, to prevent collapse of the cellulose structure at this point and a corresponding decrease in the reactivity of the product, a small portion of the adsorbed ammonia should be left with the product;^{39,40} attempts were made to do this in these experiments.) An amount of methylene dibromide, sufficient to cover all the cellulosic material in the reaction chamber, is then added to the reaction chamber. The reaction of this CH_2Br_2 with the sodium cellulose is then allowed to proceed at room temperature for 24 hr. or more.

When the reaction with CH_2Br_2 is believed to be completed or advanced to a reasonable extent, the cellulosic product is removed from the CH_2Br_2 and rinsed with dioxane at room temperature and three times with dioxane at the boil ($101.5^{\circ}\text{C}.$). In each case, the dioxane is anhydrous, having been previously distilled both from NaOH and from metallic sodium. The product is then treated with three portions of boiling, aqueous phosphate buffer solution (pH 7.0, 0.1M) and finally rinsed several times with distilled water. The products obtained in this way appear to be free of bromine, as indicated by negative copper-wire flame tests for halogen.

A typical set of experiments, involving the preparation of a crosslinked sample will be considered next; descriptions of the treatments used are summarized in Table XIII. The cotton cellulose used was prepared from Acala cotton card sliver. Treatment 1 (Table XIII) is the "purification" procedure described earlier in this report. Treatment 2 involved the preparation of a blank sample treated with liquid NH_3 and with CH_2Br_2 , and Treatment 3 involved the preparation of a different blank sample treated with Na dissolved in liquid NH_3 . Treatment 4 involved the preparation of a crosslinked product. About 200 mg. of the cotton from Treatment 1 were treated with 60 mg. of Na in liquid NH_3 at $-33^{\circ}\text{C}.$ (789 mm. Hg pressure); the treatment was carried out for 22 min., at which time the dark-blue color was observed to disappear, and the NH_3 was pumped away for about 5 min. Some foaming was noticed on the addition of 10 ml. of CH_2Br_2 . An additional 10 ml. were added, the reaction was allowed to proceed for a total of 64 hr., and no formation of sodium amide was observed while the reaction mixture was on the vacuum line. The reaction with CH_2Br_2 took place almost entirely at room temperature, and the amount of CH_2Br_2 used, about 287 mmoles, was in large excess compared to the amounts of cellulose, about 1.23 mmoles (calculated on the basis of the molecular weight of glucose), and of sodium, about 2.61 mmoles, involved. The washing procedure used also for Treatments 2 and 3 was then applied to this sample. This washing procedure involved boiling, aqueous phosphate buffer solution, as previously described and indicated in Table XIII.

The mechanical behavior of the fibers, taken from the samples whose treatments are described in Table XIII, was also examined. The fibers were mounted on small brass tabs at a gage length of ca. 0.5 in., vibroscoped to determine their mass per unit length, and stretched to the break in a manner similar to that described by Wakeham, Virgin, and Spicer;⁴¹ all tests were carried out on conditioned fibers at 65% R.H. and $70^{\circ}\text{F}.$ Two major differences between the present tests and those described previously are that the vibroscoping was carried out in a separate prior operation according to the method of Montgomery and Milloway,⁴² and the rate of extension was 0.2 in./min. for the tests reported here.

From the vibroscopic data and the load-extension curves obtained with the Instron tester, the following properties were determined: elastic mod-

TABLE XIII
Descriptions of Treatments Used for Cotton Fibers (Acala Cotton, Card Sliver)

| Treatment no. | Description |
|---------------|---|
| 1 | Card sliver, purified by chloroform extraction and alkali scouring (2% NaOH under N ₂), followed by washing with distilled water, acetic acid, and several distilled water washes. |
| 2 | Sample from Treatment 1, treated with liquid ammonia and with methylene dibromide, and washed with dioxane, methanol, phosphate buffer solution (pH 7.0, 0.1M), and distilled water. |
| 3 | Sample from Treatment 1, treated with sodium in liquid ammonia, and washed as in Treatment 2. |
| 4 | Sample from Treatment 1, treated with sodium in liquid ammonia and with methylene dibromide, and washed as in Treatment 2. This sample contained the equivalent of 1.60% bound formaldehyde (D.S. = 0.174). |

ulus, k/g , in g./grex; breaking stress, F_B/g , in g./grex; breaking extension, e_B , in per cent of the initial fiber length, l_0 ; and breaking energy per unit length and grex, E_B/l_0g , in g.-cm./cm. grex. Since the mass per unit length is involved here rather than the actual cross-sectional area, it is not strictly correct, of course, to refer to these properties in such terms as "modulus" and "stress." For purposes of convenience, however, these terms are used here, with the reservation mentioned being borne in mind. The results of the tests are shown summarized in Table XIV; for comparison purposes, data calculated from the results of Rebenfeld for bale fibers¹⁷ are also included.

TABLE XIV
Mechanical Properties of Fibers Tested at 65% R.H. and 70°F.

| Treatment used | Number tested | k/g , g./grex | F_B/g , g./grex | e_B , % | E_B/l_0g , g.-cm./ cm. grex |
|----------------------------|---------------|--------------------|----------------------|-----------|-------------------------------------|
| 1 | 13 | 52.5 | 3.40 | 7.4 | 0.116 |
| 2 | 13 | 40.0 | 2.32 | 8.7 | 0.097 |
| 3 | 10 | 23.4 | 1.55 | 12.1 | 0.079 |
| 4 | 4 | 28.6 | 0.74 | 6.5 | 0.029 |
| Previous work ^a | | 33.6 | 2.76 | 7.9 | 0.104 |

^a Calculated and/or obtained from Rebenfeld's data¹⁷ for fibers from bale; each mean value is for 144 fibers.

As may be noted from inspection of Table XIV, only 4 of the 15 fibers selected from Treatment 4 survived the total testing procedure. This is probably another, indirect manifestation of the relatively severe effects of the treatment. The coefficients of variation for the measurements listed in Table XIV were found to be similar from treatment to treatment and in general correspondence with those which have been reported in the literature. The values observed for grex, but not reported in Table XIV, were found to be closely similar to those reported for the same Acala cotton by Rebenfeld¹⁷ and indicative of the possibility that some fiber swelling may have occurred in the cases of Treatments 3 and 4, wherein the fibers were exposed to Na in liquid NH₃. The values observed for the properties of the essentially untreated fibers (Treatment 1) are closely similar to those reported previously by Rebenfeld for the corresponding bale fibers.¹⁷ The larger values observed for elastic modulus and breaking stress in the case of the present work are probably associated with the present tests being carried out at a fourfold greater rate of extension, i.e., 0.2 in./min. vs. 0.05 in./min. for the earlier work.¹⁷

As may be noted from inspection of Table XIV, there are appreciable effects caused by exposure to liquid NH₃ and CH₂Br₂ (Treatment 2), but these are relatively smaller than the effects caused by sodium in liquid ammonia (Treatment 3) and by this latter combination plus a subsequent reaction with CH₂Br₂ (Treatment 4). The increase in breaking elongation caused by the Na in liquid NH₃ is very high and similar to the values which have been reported for slack-mercerized fibers by Rebenfeld⁴³ and by Orr et al.⁴⁴ Although there is no present information to indicate whether fiber longitudinal shrinkage also occurred in this situation of essentially tensionless treatment with Na in liquid NH₃, as it did in the case of slack mercerization,^{43,44} it is not unlikely that such shrinkage did occur. It is also to be noted that, in this case, Treatment 3 resulted in marked decreases in both elastic modulus and breaking stress; this behavior may indicate the existence of some degradation caused by the treatment.

The effects caused by treatment with CH₂Br₂ following treatment with Na in liquid NH₃ are striking. Although large reductions in breaking stress, breaking extension, and breaking energy are observed (Treatment 3 vs. Treatment 4), the elastic modulus remains essentially unchanged. It may also be noted that the breaking extension, al-

though reduced, for Treatment 4 is not very much lower than that of the "untreated" fiber, Treatment 1. These changes are qualitatively similar to those reported by Woo, Dillon, and Dusenbury⁷ for cotton fibers taken from fabrics treated with formaldehyde; in this earlier work HCl was the acid catalyst used and the resulting bound formaldehyde content was 0.7%. One interesting aspect of the present results—as well as of the earlier ones⁷—is that there is no increase in the elastic modulus as a result of crosslinking. This suggests that this property, which undergoes considerable increase in the cases of Fortisan and viscose rayon,⁷ may not be particularly useful for measuring the effects of crosslinking cotton fibers.

These measurements of mechanical behavior are limited in their present scope, but they are reported here for the purpose of providing some insight into the modification of fiber properties likely to be encountered in the course of treatments such as those described here.

Further studies were also made of the reaction system described here. From experiments carried out under a variety of conditions, it was found that three conclusions could be drawn from the results obtained: (1) greater removal of water from the cellulose prior to the reaction with Na in liquid NH₃ results in a greater extent of reaction with CH₂Br₂; (2) greater removal of NH₃ after formation of sodium cellulose results in a lower extent of reaction with CH₂Br₂, probably because the removal of NH₃ causes a "collapse" of the swollen cellulose structure; and (3) the amounts of bromine in the reaction product correspond to only a small fraction of the total amount of CH₂Br₂ reacted with the sodium cellulose.

What this indicates, in effect, is that the formation and reaction with CH₂Br₂ of sodium celluloses formed by reaction of cotton with sodium in liquid ammonia appears to be interesting but essentially difficult to control. This difficulty of control appears to be associated principally with the collapse-of-structure problem indicated previously, and it may be taken as indicative that this approach to the problem is apt to be an unproductive one.

Reactions Involving Sodium Isoamylate in Xylene

The formation of sodium celluloses by reaction of cotton fibers with sodium isoamylate in xylene was carried out in a way closely similar to that described by Derevitskaya, Prokofieva, and Rogo-

vin.³⁶ This procedure, as well as that of Schwenker, Kinoshita, Beurling, and Paesu,³⁸ involves the use of an alcohol-exchange reaction with the cellulose functioning as one of the alcohols:



where Z represents a cellulose chain and R represents the alkyl group of the particular sodium alkoxide used, e.g., an isoamyl group in the case of sodium isoamylate.

In the preparation of sodium isoamylate, as well as in its subsequent reaction with cellulose, care was taken to exclude all water from the reaction system, and the reagents involved were carefully dried and freshly distilled before use. In a typical case, 2.39 g. of sodium were introduced into 150 ml. of *p*-xylene, and the mixture with stirring was brought to the boil and kept there until a suspension of Na in xylene was formed. After cooling the mixture to 70°C., a small excess of isoamyl alcohol (with respect to the sodium) was added, and the formation of sodium isoamylate began, accompanied by the evolution of hydrogen. When the H₂ evolution ceased, the reaction was considered complete, and in some cases, the reaction was speeded up by raising the temperature to 80 or 90°C.

Before reaction with the sodium isoamylate in xylene, a 1.2-g. sample of purified cellulose (prepared from Pima cotton, card sliver, as described previously) was placed for 20 min. in 60 ml. of 10% NaOH solution at 5°C. Then 60 ml. of 2% NaOH solution were added, and the mixture was kept at 5°C. for an additional 20 min. The purpose of this NaOH treatment was to swell or otherwise affect the cotton to facilitate subsequent reaction. After removal from the alkali, the sample was washed with distilled water, with 1% acetic acid, and finally with distilled water until the wash liquor exhibited a neutral pH value. After this, the cellulose sample was treated twice, 30 min. each time, with methyl alcohol, and treated similarly twice with isoamyl alcohol. When this treatment procedure was completed, the cellulose was placed in the reaction mixture of sodium isoamylate in xylene.

Most of the reactions were carried out at 70°C. for varying periods of time up to 4 hr.; temperature control during these times was achieved by carrying out these reactions in vessels immersed in an oil-bath thermostat. At various times, samples were removed, carefully washed several times with boiling benzene and/or xylene, and analyzed for

their Na content by titration with H_2SO_4 . Additional aliquots of these same samples were reacted with methyl iodide, and the resulting products were analyzed for their methoxyl contents according to the method of Vieböck and Schwappach,⁴⁵ as later modified by Clark⁴⁶ and by Steele and Pacsu.⁴⁷ This method involves the formation of methyl iodide by reaction of the methoxyl derivative with hydroiodic acid. A typical set of results obtained for experiments such as these is given in Table XV, wherein the $D.S._{Na}$ values are indicated for duplicate experiments, together with the corresponding $D.S._{OCH_3}$ values for duplicate experiments carried out on each of the two samples whose $D.S._{Na}$ values are indicated. The results listed in Table XV are closely similar to those reported by Derevitskaya, Prokofieva, and Rogovin³⁶ and are generally consistent with those reported by Schwenker, Kinoshita, Beurling, and Pacsu,³⁸ where as noted earlier a different procedure was used for the alcohol-exchange reaction. The results listed in Table XV indicate that quite high $D.S._{Na}$ values may be achieved, that the extents of conversion of the sodium cellullosate to the corresponding methyl derivative by reaction with CH_3I are relatively high (71–83% for the data in Table XV), and that the reproducibilities of the reactions involved are fairly good. It is not possible to state at this time whether the $D.S._{Na}$ and the $D.S._{OCH_3}$ values of Table XV indicate incomplete conversion of sodium cellullosates to their methyl derivatives or whether the $D.S._{Na}$ values may be too high due to incomplete removal of sodium isoamylate from the treated samples prior to titration with H_2SO_4 . It may be that both possibilities are involved.

For the reactions with CH_2Br_2 , the sodium cellullosate samples were prepared similarly to the procedure indicated previously (Table XV) and were subsequently reacted with CH_2Br_2 similarly to

the procedure described earlier for the experiments involving alkali cellulose. An important difference, of course, is that for the reactions with sodium cellullosates attempts were made to rigorously exclude water. After reaction with the CH_2Br_2 , the samples were washed and analyzed for their acetal contents (HCHO analysis).

The results of some typical experiments carried out at 70°C. are shown plotted in Figure 7, where the data for duplicate experiments are indicated for both dry and wet experimental conditions. In the set of experiments labeled Dry Na^- alcoholate, great care was taken to exclude all water; in the experiments labelled Wet Na^- alcoholate, less care was taken, and relatively small amounts of water are known to have been present during the reaction.

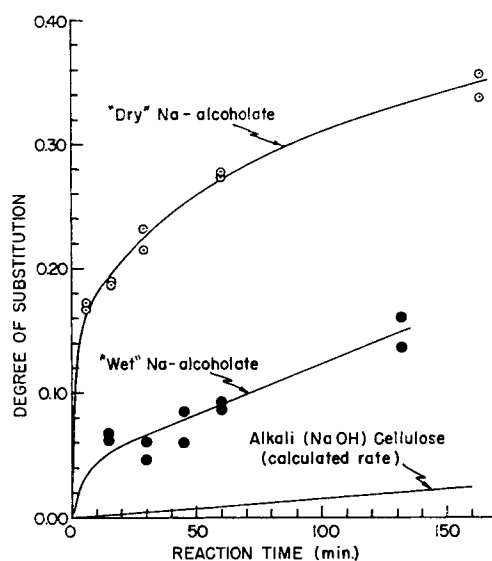


Fig. 7. Rates of reaction with CH_2Br_2 at 70°C. for Pima cotton, card sliver samples treated with either Na or NaOH.

The large adverse effect of this water on the extents of reaction observed is apparent from inspection of Figure 7. Also shown in Figure 7 is the corresponding rate to be expected for the reaction of NaOH-alkali cellulose with CH_2Br_2 at 70°C.; this rate was obtained from suitable extrapolation of data obtained at higher temperatures for this reaction (Table VI and Figure 4). It is apparent that the sodium cellullosate reacts at a much greater rate than the corresponding alkali cellulose with CH_2Br_2 . In the case of the experiments where water was rigorously excluded, it is also apparent from Figure 7 that the reproducibility of the experiments is quite good.

TABLE XV

Extents of Reaction for Formation of Sodium Cellulosate^a and Subsequent Reaction with Methyl Iodide^b

| Expt. no. | Extent of reaction | |
|-----------|--------------------|----------------|
| | $D.S._{Na}$ | $D.S._{OCH_3}$ |
| 1 | 1.72 | 1.43 1.31 |
| 2 | 1.64 | 1.24 1.17 |

^a Na^- isoamylate reacted with cellulose, 112 min. at 70°C.

^b Na^- cellulose reacted with CH_3I , 195 min. at 108°C.

SUMMARY

It has been shown that both alkali celluloses and sodium celluloses react readily with methylene dibromide to give products containing appreciable amounts of acetal (the equivalent of the formaldehyde acetal of cellulose) and that, after washing, very little of the reaction product exists in the form of hemiacetals or of bromomethyl side-chains. In the case of the reactions of alkali cellulose, the treated fabrics exhibit improved wet crease recovery but little or no improvement in dry crease recovery. In the case of the sodium cellulose reactions, when the celluloses are formed by reaction of cotton with sodium in liquid ammonia, the reaction leads to appreciable acetal formation, but is essentially difficult to control. When the sodium celluloses are formed by reaction of the cotton with sodium isoamylate in xylene and when proper care is taken to exclude water from the reaction system, it is found that appreciable acetal formation takes place, that the reproducibility of duplicate experiments is good, and that the rate of reaction of the sodium cellulose with methylene dibromide is much greater than that found for the corresponding alkali cellulose.

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Synopsis

A study has been made of the reactions of alkali cellulose with methylene dihalides, particularly methylene dibromide. These reactions have involved cotton cellulose in a swollen state, and the treated fabrics have been found to exhibit improved wet crease recovery, with little or no effect on dry crease recovery. The rates of reaction of methylene dibromide with alkali celluloses prepared from potassium hydroxide have been found to be more than double those with alkali celluloses prepared from sodium hydroxide. The energies of activation in both cases are about 25 kcal./mole, statistically indistinguishable for the two types of alkali, and consistent with the view that covalent bonds are being formed in the course of reaction. The implications and limitations of these results are discussed. Studies have also been made of the reactions of sodium celluloses with methylene dibromide. In one case, the sodium celluloses were prepared by reaction of the cellulose with sodium dissolved in liquid ammonia. Here, the reactions appear interesting, but essentially difficult to control. Sodium celluloses were also prepared by reaction of the cellulose with sodium isoamylate in xylene. When proper care is taken to exclude water from the reaction system, it is found that the reproducibility of duplicate experiments is quite good and that the rate of reaction of the sodium cellulose with methylene dibromide is much greater than that found for an alkali cellulose prepared from sodium hydroxide.

Résumé

On a étudié les réactions de l'alcali-cellulose avec les dihalométhanes, en particulier avec le bromure de méthylène. Ces réactions ont été effectuées avec la cellulose de coton à l'état gonflé, et on a trouvé que les produits traités montrent une amélioration dans la récupération du froissement à l'état humide avec peu ou pas d'effet sur la récupération du froissement à l'état sec. On a trouvé que les vitesses de réaction du bromure de méthylène avec les alcalicelluloses, préparées à partir de l'hydroxyde de potassium sont plus

du double des vitesses obtenues avec les alcali-celluloses préparées à partir de l'hydroxyde de soude. Les énergies d'activation sont d'environ 25 kcal/mole dans les deux cas, et ne peuvent statistiquement pas être distinguées pour les deux types d'alcali. Elles sont compatibles avec l'idée que des liaisons covalentes se sont formées au cours de la réaction. On discute de la valeur et des limitations de ces résultats. On a également effectué des études sur les réactions des celluloses de soude avec le bromure de méthylène. Dans un cas, les celluloses de soude ont été préparés par réaction de la cellulose avec le sodium dissous dans l'ammoniac liquide. Dans ce cas, les réactions semblent intéressantes, mais particulièrement difficiles à contrôler. Les celluloses de soude ont également été préparés par réaction de la cellulose avec l'isoamylate de soude dans le xylène. Lorsqu'on prend soin d'éliminer l'eau du système réactionnel, on trouve que la reproductibilité des expériences est très bonne, et que les vitesses de réaction du cellulose de soude avec le bromure de méthylène sont beaucoup plus élevées que celles trouvées pour l'alcali-cellulose préparée à partir de l'hydroxyde de soude.

Zusammenfassung

Eine Untersuchung der Reaktionen zwischen Alkalicellulose und Methylendihaliden, besonders Methylendibromid, wurde durchgeführt. Diese Reaktionen erfolgten an Baumwollcellulose im gequollenen Zustand und es wurde gefunden dass die behandelten Gewebe eine verbesserte Nassknitterfestigkeit aufweisen, bei kleinem oder fehlendem Einfluss auf die Trockenknitterfestigkeit. Die mit Kaliumhydroxyd hergestellte Alkalicellulose reagiert mit Methylendibromid mehr als doppelt so rasch als mit Natriumhydroxyd hergestellte Alkalicellulose. Die Aktivierungsenergie beträgt in beiden Fällen etwa 25 kcal/Mol; es besteht hierin kein merklicher Unterschied zwischen den beiden Alkalitypen, was mit dem Gesichtspunkt der Bildung kovalenter Bindungen während der Reaktion vereinbar ist. Die Folgerung aus den Ergebnissen und ihre Beschränkungen werden diskutiert. Auch die Reaktionen von Natriumcellulosen mit Methylendibromid wurden untersucht. In einem Falle wurden die Natriumcellulose durch Reaktion von Cellulose mit in flüssigem Ammoniak gelöstem Natrium dargestellt; die Reaktion scheint hier einen interessanten Verlauf zu nehmen, ist aber schwierig unter Kontrolle zu halten. Dann wurden Natriumcellulose durch Reaktion von Cellulose mit Natriumisoamylat in Xylol dargestellt; bei genügend sorgfältigem Ausschluss von Wasser vom Reaktionssystem, ist die Reproduzierbarkeit der Ergebnisse recht gut und die Reaktionsgeschwindigkeit des Natriumcelluloses mit Methylendibromid viel grösser als die einer mit Natriumhydroxyd hergestellten Alkalicellulose.

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