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The Mechanism Involved in the Methylation of Cellulose  
Acetate and of Cellulose Dissolved in  
Trimethylbenzylammonium Hydroxide

by Gerald G. Johnston

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**THE MECHANISM INVOLVED IN THE METHYLATION OF CELLULOSE  
ACETATE AND OF CELLULOSE DISSOLVED IN  
TRIMETHYLAMMONIUM HYDROXIDE**

**A thesis submitted by**

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## INTRODUCTION

The conversion of cellulose into ethers is based--as are most of the cellulose reactions--upon the presence of hydroxyl groups. The modern conception of the molecular structure of cellulose calls for three reactive hydroxyl groups in the 2-, 3-, and 6-positions in each glucose anhydride of the chain which is composed of a great number of these units. Consequently, each glucose unit ought to form an ether in which all three hydroxyl groups have reacted with three molecules of the etherifying agent so that, on complete etherification, for instance, with the most commonly used etherifying agent, dimethyl sulfate, trimethylcellulose would result.

Although it is comparatively easy to obtain in a few operations a degree of substitution which approaches that of the tri-ether, it is very difficult actually to reach the theoretical value unless indirect or special methods, different from the one mentioned above, are employed.

One indirect method was suggested some years ago by Hoeser and Hiemer (1). It consisted of converting cellulose first into an acetate and then subjecting the acetate to alkylation. The method, which was applied also to cellulose which had been methylated to a certain extent, was based upon the idea that the acetyl groups would react with the alkylating agents more readily than the original hydroxyl groups. In other words, it was thought that acetylation would serve as a means of activating the otherwise tardily reacting

hydroxyl groups. Thus, the mechanism was thought to be this: Under the influence of the alkali in the alkylating mixture the acetyl groups would be saponified and the regenerated hydroxyls, quasi in statu nascendi, would simultaneously be alkylated. In this way Kauter and Hiemer obtained for cellulose regenerated from viscose a methoxyl content of 45.42 per cent, which is nearly the theoretical value of 45.5<sup>18</sup> per cent. The good results of this method seemed to justify, although they did not explain, the concept of the mechanism, and the principle of the method has been applied since by various investigators; for example, by Haworth and his school (2). In one case the latter reported that a methoxyl content of 45.6 per cent was reached. In a later publication (3), however, a maximum of only 45.0 per cent was reached. Several other workers have not been able to confirm the higher result.

Recently Harrow and Kecher (4) have postulated that the theoretical value for trimethylcellulose can be obtained only with cellulose degraded to a certain extent, no matter what method of methylation is used. They based their conclusion on experiments which involved repeated acetylation with acetic anhydride and sulfuric acid and subsequent methylation of the acetates; they eventually obtained products in which the methoxyl content had increased even above the theoretical value of a trimethyl product. Obviously, this increase is due to an increase of hydroxyl groups, which results from cleavage of glycosidic linkings of the cellulose chain under the influence of the acetylation mixture.

Kousser and Nicmer did not pay much attention to the possibility that the use of cellulose acetate as a starting material for methylation might involve a change in the physical state of the cellulosic constituent during the alkylation process and that this change might explain the improved results in a different way. Such a change in the physical state becomes obvious if methylation is carried out with the acetate dissolved in acetone, according to the modification used by Haworth, Hirst, and Thomas (2). In this case the solid phase is eliminated, at least for a part of the reaction, and a much more homogeneous and more complete reaction may be anticipated. Although the cellulosic material may precipitate as it is being regenerated and methylated, this precipitate represents a fine suspension which may be expected to be more accessible to the methylating agents than is cellulose in fibrous form.

From a consideration of these observations, it would appear objectionable to explain the higher rate of methylation and the almost theoretical methoxyl content as being due to chemical activation of hydroxyl groups as discussed above, provided that degradation of the cellulose during acetylation is avoided.

Thus, there are three possible explanations of the improved results obtained on methylating acetylated cellulose: (1) Acetylation activates the hydroxyl groups of the cellulose; (2) acetylation allows methylation to be carried out on cellulose in solution and subsequently on a finely divided precipitate; and (3)

acetylation is accompanied by degradation which opens up new hydroxyl groups, the latter being available for methylation.

The investigation reported below was concerned with an attempt to decide between these possibilities.



## HISTORICAL SURVEY

A more extensive historical survey is presented in order to establish a broader basis for discussion of the experimental results.

Exhaustive methylation of cellulose by use of dimethyl sulfate and sodium hydroxide was first carried out by Denham (5). After eighteen to twenty methylations a maximum value of 44.6 per cent methoxyl content was reached (the theoretical value is 45.57 per cent). Application of the same method by Houser and von Neumann (6) yielded a maximum methoxyl value of only 34.9 per cent, and by Irvine and Hirst (7) of 42 to 43 per cent.

Hess and co-workers (8) have made an extensive study of the factors involved in the methylation of fibrous cellulose directly with aqueous sodium hydroxide solution and dimethyl sulfate and have established more successful methods of producing highly methylated celluloses. Work by Hess, Abel, Schön, and Komarevsky (8) showed that the rate of methylation increased with the reaction temperature and the sodium hydroxide concentration. In attempts to produce completely methylated cellulose, three methylations of ramie resulted in a methoxyl content of 40 to 42 per cent. This material was triturated with ice water to give a partial solution. Addition of sodium hydroxide then formed a fine precipitate which could be methylated to 45.13 per cent methoxyl in three operations. It was reported that some methylated celluloses with 44 to 45 per cent

methoxyl showed a decrease in methoxyl content with further treatment.

A modification by Urban (9), whereby the dimethyl sulfate was used in conjunction with 45 per cent potassium hydroxide solution at 20° C., resulted in a maximum methoxyl value of 44.7 per cent after two methylations of cotton cellulose.

Lawerth, Hirst, and Thomas (2) designed a method whereby the aqueous 30 per cent sodium hydroxide solution and the dimethyl sulfate were added simultaneously to the cellulose suspended in acetone. The temperature was 56° C., the boiling point of acetone. Methylation of finely ground cellulose (filter paper) resulted in a methoxyl content of 37 per cent. One further methylation increased this to a maximum value of 45 per cent methoxyl. When this method was applied to wood pulp (not ground) by Barsha and Hibbert (10), a maximum value of 41.32 per cent methoxyl was reached after three methylations. This value could be increased to 44.63 per cent by remethylation after the product had been precipitated from chloroform. ?

A unique method of methylation, which evidently has not been applied to the preparation of highly methylated celluloses, is that described by Beak (11). The cellulose is dispersed in a quaternary ammonium base--for example, trimethylbenzylammonium hydroxide--and methylated with dimethyl sulfate in this solution. The outstanding property of methylated celluloses thus prepared is that they exhibit water solubility at a lower methoxyl content (about 13

per cent), water solubility usually being found at 23 to 30 per cent methoxyl when the cellulosic material is in fibrous form. Similar products have been prepared by Traube, Piwenka, and Funk (12) from thallium and sodium cupricelluloses. Products showing 15 per cent methoxyl were found to be soluble in hot and cold water. Both Bosk and Traube suggested that by their methods the methoxyl groups are more evenly distributed along the cellulose chains than when cellulose is used in fibrous form, such distribution facilitating uniform access of water to the intramolecular (unmethoxylated) hydroxyl groups. Therefore, a relatively low degree of substitution should suffice for making the reaction product soluble in water.

More complete methylation of cellulose (both cotton and ramie), permethylated to 42 to 43 per cent methoxyl by the usual methods, was secured by Freudenberg and Boppel (13). The material was suspended in liquid ammonia and treated with metallic sodium and methyl iodide. A fibrous product was obtained which yielded methoxyl values ranging from 44 to 46 per cent. This treatment, however, was associated with a considerable decrease in the viscosity of solutions of the material. Very similar results were reported by Hess and Lung (14) when the same general method was applied to highly methylated starch dissolved in anisole. Freudenberg, Boppel, and Meyer-Delius (15) further investigated the drop in viscosity in chloroform solution. Before treatment with sodium and methyl iodide the highly methylated ramie (44 per cent methoxyl), still having a high viscosity in solution, yielded, on hydrolysis 0.05 per cent tetra-

methylglucose. After the second methylation step, a low viscosity product of 45 per cent methoxyl content was obtained, which yielded about four times more tetramethylglucose (0.2 per cent). This result was in accord with the observation that on methylation with methyl iodide the degree of polymerization had dropped from 2000 to 500.

Houser and Hiemer (1) studied the possibilities of preparing trimethylcellulose from a number of modified celluloses, such as cellulose regenerated from cuprammonium solution, from viscose, from cellulose acetate, as well as cuprammonium and viscose silk, cellulose dextrin, etc. These authors showed that the number of methylations required to reach a certain methoxyl content decreases with the degree of polymerization. But even with these modified cellulose preparations, it was difficult to reach the theoretical value required for the tri-ether. For example, one methylation of cuprammonium cellulose resulted in a methoxyl content of 10.66 per cent, sixteen methylations gave 47.1 per cent, and twenty-two methylations gave 44.95 per cent. Further methylation resulted in decomposition of the product and decrease in methoxyl content in a similar manner as reported by Hess (14).

*Handwritten notes:*  
 45.42%  
 16 methylations  
 47.1%  
 22 methylations  
 44.95%  
 Hess (14)  
 p. 122

As mentioned above, Houser and Hiemer have advanced the theory that the tardily reacting groups would be activated if they were first converted into acetyl groups. Under the influence of the alkali in the alkylating mixture the acetyl groups would be saponified

and the regenerated hydroxyls, quasi in statu nascendi, would simultaneously be alkylated.\*

This principle was applied to two types of compounds. Dimethylcellulose of 32.12 per cent methoxyl, prepared by five methylations of viscose cellulose (50 per cent sodium hydroxide at 60 to 70° C.), was acetylated according to a procedure adapted from Hess and others (17) by Houser and van Heusenstein (6). This involves acetylation with sulfuric acid as a catalyst and precipitation of the acetylated product from the acetylation mixture by way of neutralization. Such a product corresponded approximately to the theoretical acetyl and methoxyl contents of dimethylcellulose monoacetate after two methylations with 50 per cent sodium hydroxide solution and two methylations with powdered sodium hydroxide, it yielded a product of  $45.4\frac{2}{4}$  per cent methoxyl--i.e., practically the theoretical value. Cotton linters also were acetylated in the usual manner to give a triacetate--i.e., with a combined acetic acid content of 63.36 per cent (the theoretical being 62.55 per cent). This product upon a two-step methylation in 50 per cent sodium hydroxide solution yielded a product with a methoxyl content of 35.71 per cent.

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\* It is interesting to note in this connection the work by Freudenberg and Gohn (16) concerning the methylation of phenolic compounds. Methylation of phenolic compounds does not give good yields of fully methylated products, possibly because of keto forms. In the acetyl derivative, the enol form is stabilized and is thus available for methylation. It could not be determined whether methylation was preceded by saponification or if the acetate group was directly replaced by the methoxyl group.

which on two further such treatments, using powdered sodium hydroxide, could be increased to 44.98 per cent. This product was quite soluble in cold water whereas other highly methylated products, prepared by Hensen and Hiemer (1) were insoluble in water. The authors therefore suggested that the behavior to water may indicate that the cellulose had become degraded during acetylation, since highly methylated cellulose (methoxyl content of 45 per cent) prepared by Hess and Voltrien (15) from cellulose A (cellulose regenerated from cellulose acetate, considered to be an extensively degraded cellulose) was also soluble in water.

It has been mentioned above that cellulose acetate was also used as a starting material for the preparation of a highly methylated cellulose by Haworth, Hirst, and Thomas (2). Their methylation method differed from that used by Hensen and Hiemer (1) in that an acetate was used which could be dissolved in acetone, which was methylated by the simultaneous addition of 30 per cent sodium hydroxide solution and dimethyl sulfate. Only one operation yielded a product which showed practically the theoretical value--namely, 45.6 per cent methoxyl. The acetate was prepared from cotton linters, but the method of acetylation was not specified. It is very probable that it had a rather low degree of polymerization.

Application of the same method by Haworth and Macosker (3) resulted in only 45 per cent methoxyl, a value which was not increased by further operations. The acetate was prepared according

to a modification of Barnett's method (19) in which chlorine and sulfur dioxide are used as acetylation catalysts. The acetone-soluble acetate was prepared from the primary triacetate by partial saponification with sulfuric acid. Although temperatures were kept at a minimum to lessen degradation effects, and although preparations showing appreciable reduction toward Fehling solution were rejected, it is likely that the preparations used had a low degree of polymerization.

Other investigators have reported somewhat lower results by the use of this method. Hess and co-workers (5) made the following statement:

"It may be mentioned that, on the basis of repeated experiments . . . we could not confirm the statement by Haworth and co-workers that completely methylated cellulose could be prepared from cellulose acetate in one operation by the action of dimethyl sulfate and alkali in the presence of acetone. Such products exhibited about 42 per cent methoxyl. Therefore, the method given by Haworth possesses no advantage over other known procedures."

Application of the same method to a commercial acetone-soluble acetate by Welfren, Sowden, and Lassettre (20) resulted in products varying from 43 to 44 per cent methoxyl in one methylation.

Methylation of acetone-soluble acetates at lower temperatures were carried out by Staudinger and Scholz (21). The triacetate, prepared from cotton with zinc chloride as a catalyst, was deacetylated to an acetone-soluble product with a 95 per cent acetic acid

content--i.e., without the use of sulfuric acid. Such acetates upon methylation, according to Haworth's procedure, but in a nitrogen atmosphere at 20° C. (in place of 50° to 55° C. as used by Haworth), yielded products ranging from 34 to 41 per cent methoxyl. This was in agreement with work of Haworth which showed that in no case could complete methylation be effected in the cold. Besides, it is likely that the acetates used by Standinger and Schels were, due to the procedure of partial saponification, somewhat less degraded than those used by Haworth and co-workers.

Sperka (22) applied Haworth's acetylation and methylation procedures to high alpha wood pulp. Clear acetone solutions of the acetate, as were reported by Haworth and co-workers (3), were not obtained, but methylation of the acetate resulted in a methoxyl content of 43.6 per cent. Apart from the lower degree of polymerization of the source material, it is probable that this result was due to degradation during acetylation and partial saponification.

Karrer and Mosher (4) made the following comment: "Haworth and Mosher have been able to convert their slightly degraded cellulose acetate into methylcellulose of 45.0 per cent methoxyl in one operation. Under accurate control of the given methylation conditions we obtained from such a cellulose acetate of rather low copper number, the following methylated products:

After 1 methylation - 41.76 per cent  $\text{OCH}_3$

After 2 methylations - 41.76 per cent  $\text{OCH}_3$

After 3 methylations - 42.20 per cent  $\text{OCH}_3$ "



These authors then prepared a series of acetates of increasing copper numbers; these were methylated and it was found that the maximum possible methoxyl content had increased with the copper number. Indeed, from an acetate of a copper number of as high as 27.93, a methylcellulose with a methoxyl content of 45.93 per cent (which is above the theoretical value) was prepared. These results indicate that a stage of methylation corresponding to three hydroxyls per glucose unit can only be reached if new hydroxyls are generated by hydrolytic processes.

The work on the methylation of starch offers an interesting and instructive parallelism with that of cellulose. As in the case of cellulose, the usual direct methylation of starch with sodium hydroxide and dimethyl sulfate was found to be difficult. To facilitate methylation, Hawerth, Hirst, and Webb (23) prepared first the starch triacetate according to Barnett's method (19). This was then dissolved in acetone, in which solution it could be methylated to a methoxyl content of 36 per cent in an operation quite similar to that described above for acetone-soluble cellulose acetate. A comparative methylation, in which the same starch triacetate was not dissolved in acetone, resulted in a somewhat lower methoxyl content--namely, 32.7 per cent. There was no advantage in reacetylation after the first methylation, and the authors concluded that, inasmuch as such acetylated methyl products were insoluble in acetone, the solubility of the starch acetate apparently was the decisive factor.

A similar method was applied by Staudinger and Husemann (24).

who prepared acetone-soluble starch triacetate in pyridine without using an acid catalyst, thus greatly decreasing the possibilities of degradation. One methylation by the method of Haverth yielded a methoxyl content of only 25.7 per cent. Freudenberg and Rapp (25) obtained not more than 35 to 39 per cent methoxyl after four treatments by the same general method.

The above discussion also illustrates how most of the reactions leading to methylated cellulose take place in heterogeneous systems. In some cases, as pointed out by Hess (8) the system may have three phases: two liquid phases, sodium hydroxide and dimethyl sulfate; and one solid phase, cellulose. Methylation, like all reactions taking place upon solid cellulose, is topochemical in character--i.e., the degree of methylation will depend upon the extent to which the reagents are capable of penetrating the outer layer of the cellulose as well as those which already have reached a certain degree.

Summing up the conclusions which may be drawn from this review, it appears very likely that the theoretical value required for trimethyl cellulose can only be reached in cases where the cellulose, either as such or in the form of its acetate, has a low degree of polymerization. In cases where the acetate is used, it cannot be said with certainty that it is the activation of hydroxyl groups of cellulose which facilitates methylation. In the cases where the acetate is dissolved in acetone, the probability exists

that the reaction is largely accelerated under these conditions, at least as long as a solution is maintained.

The investigation reported in the following sections is concerned with an attempt to throw more light on the mechanism of the reaction.

TABLE I

## SUMMARY OF SUCCESS OF VARIOUS PROCEDURES FOR THE PREPARATION OF TRIMETHYL CELLULOSE

Investigator	Starting Material	Methoxyl Content	Type of Base	Concentration of Base %	Temperature of Reaction °C.	Number of Methylations	Remarks, Type of Reaction, etc.
Denham	fibrous cotton	44.6	NaOH	20-30	up to 70	18-20	Reagents added at beginning.
Irvine and Hirst	fibrous cotton	42-43.8	NaOH	30	up to 70	12	Four methylations in same manner as used by Denham. Subsequent treatments in presence of ether and methyl alcoholic NaOH.
Hess, Abel, Schön, and Komarevsky	ramie	45.13	NaOH	30	20	6	Fibers suspended in alkali solution, dimethyl sulfate gradually added. After three methylations, reaction proceeded upon fine material precipitated from a water solution of the methyl cellulose.
Urban	cotton	44.7	KOH	45	20	2	Fibers suspended in alkali solution, dimethyl sulfate gradually added.

TABLE I (Continued)

Investigator	Starting Material	Methoxyl Content	Type of Base	Concentration of Base %	Temperature of Reaction °C.	Number of Methylations	Remarks, Type of Reaction, etc.
Heuser and Hiemer	cotton cellulose from cuprammonium solution	44.98	NaOH	18-60	60	22	Fibers mixed with the alkali and dimethyl sulfate added dropwise.
Heuser and Hiemer	dimethyl cellulose acetate and viscose cellulose	44.42	NaOH	50 and powdered	60	2-4	Dimethyl product resulting from five methylations of viscose cellulose was acetylated and then remethylated.
Heuser and Hiemer	cellulose triacetate from cotton linters	45.0	NaOH	50 powdered	60	1-6	Carried out in same manner as with cuprammonium solution.
Haworth, Hirst, and Thomas	filter paper, finely ground	45.0	NaOH	30	56	2	Cellulose was suspended in acetone and the reagents were added simultaneously.
Baraba and Hibbert	wood pulp	44.63	NaOH	30	56	8	Same as above except that material was precipitated from chloroform solution after three methylations.

TABLE I (Continued)

Investigator	Starting Material	Methoxyl Content	Type of Base	Concentration of Base %	Temperature of Reaction °C.	Number of Methylations	Remarks, Type of Reaction, etc.
Freudenbergs and Boppel	cotton and ramie pre-methylated to 42 to 43 per cent	44-46	liquid $\text{NH}_3$ and methyl iodide			1	Viscosity of solution of material decreased.
Haworth, Hirst, and Thomas	acetone-soluble acetate from cotton linters	45.6	$\text{NaOH}$	30	56	1	Acetate was dissolved in acetone and treated simultaneously with the methylating agents.
Haworth and Machamer	acetone-soluble acetate from good specimen of cellulose	45.0	$\text{NaOH}$	30	56	2	Same procedure as Haworth, Hirst, and Thomas.
Hess and co-workers	commercial acetone-soluble cellulose acetate (Cellite)	42.0	$\text{NaOH}$	30	56	-	Same procedure as Haworth, Hirst, and Thomas.

TABLE I (Continued)

Investigator	Starting Material	Methoxyl Content	Type of Base	Concentration of Base %	Temperature of Reaction °C.	Number of Methy-lations	Remarks, Type of Reaction, etc.
Sperka	acetone-soluble cellulose acetate from wood pulp	45.6	NaOH	30	56	1	Same procedure as Haverth, Hirst, and Thomas.
Karrer and Eicher	acetone-soluble acetate from cotton linters	42.2	NaOH	30	56	3	Same procedure as Haverth, Hirst, and Thomas.
Welfron, Swiden, and Lassette	commercial acetone-soluble acetate	43.44	NaOH	30	56	1	Same procedure as Haverth, Hirst, and Thomas.
Standing and Scholz	acetone-soluble cellulose acetate from cotton	44.41	NaOH	30	20	1	Same procedure as Haverth, Hirst, and Thomas.

## MATERIALS USED FOR INVESTIGATION

1. Cotton linters. Bleached linters were supplied by Hercules Powder Company, Hopewell, Virginia. Low copper number (0.07), low pentosan content (0.50 per cent), and high alpha-cellulose content (99.05 per cent) indicated that this material was quite suitable for the investigation. Before use, the linters were disintegrated in the Gösta-Hall disintegrator.

2. Acetone-soluble acetate. This material was prepared from the above cotton linters according to the method of Barnett (19), as applied by Haworth and Wachsmeyer (3). Inasmuch as it was found advantageous to make several minor alterations in the application of the method to the material at hand, the method will be described in full.

The air-dry equivalent of 50 grams of oven-dry shredded cotton linters was agitated in water with a "Lightnin'" mixer for four hours and allowed to soak overnight. This completely disintegrated the small balls which had been formed in the shredder, however, in case they are not removed, they dissolve slowly in the acetylation mixture. The fibers were then filtered off and washed with alcohol to displace the water and allowed to air dry. They were placed in a two-quart Mason jar with 360 cc. of glacial acetic acid into which a slow stream of chlorine had been passed for two and three-fourths minutes. After thirty minutes at room temperature the jar was placed in an ice-salt mixture and cooled to 5° C. over a period of



two to three hours. The mixture was stirred until the acetic acid had crystallized. (This could be done conveniently with a straight, heavy glass rod which had been sharpened at one end to facilitate scraping the sides of the jar.) If stirring is neglected during this early stage of the cooling, the entire material will freeze to a stone-like mass, and later it is impossible to mix it uniformly with acetic anhydride. If stirred properly, the material becomes similar to finely crushed ice. One hundred and eighty cubic centimeters of acetic anhydride (into which sulfur dioxide had been bubbled for six minutes at approximately the same rate as was used for the chlorine), also at a temperature of  $5^{\circ}\text{C}$ ., was added to the cellulose-acetic acid mixture over a period of thirty minutes under constant manual stirring. The reaction mixture was maintained at this temperature and stirred frequently for one hour, after which time the cellulose was still fibrous. The jar was placed on a rotating wheel for one-half hour and then for fifteen hours in a water bath maintained at  $20^{\circ}\text{C}$ . At the end of this time the material was slightly soluble in chloroform. After one and one-half hours at a temperature of  $35^{\circ}\text{C}$ . it was almost completely soluble, indicating that acetylation was practically complete.

To accomplish partial deacetylation to form an acetone-soluble product, the acetylation mixture was cooled to  $5^{\circ}\text{C}$ . and into it was gradually stirred a cold solution of 75 cc. acetic acid, 70 cc. water, and 7.5 cc. concentrated sulfuric acid. After remaining at this temperature for one hour, the reaction mixture was rotated

for one-half hour on the wheel and then placed in a bath maintained at 20° C. After thirty to forty hours the material became nearly soluble in acetone. A longer period of time did not appear to increase this solubility. After it was diluted with an equal volume of acetic acid, the acetylation mixture was filtered through a 03, 7-cm. fritted glass filter and atomized into cold water, whereby a fine precipitate of cellulose acetate was formed. This was accomplished by directing a jet of air toward the end of a capillary out of which flowed a fine stream of the acetylation solution. The material was washed with cold water until free of acid and allowed to air dry.

The dry powdered material was then treated with 1 liter of acetone in order to dissolve the acetone-soluble fraction. Most of the insoluble portion was removed by centrifuging. Filter aid ("High-flo" obtained from the Johns-Manville Company) was then added to the still turbid solution, and filtration through a Büchner funnel, fitted with a paper covered with about 1/8 inch of the same filter aid, yielded a clear solution. Ordinary methods of filtration were unsuccessful because gummy residues clogged the filtering medium. This solution was allowed to flow in a fine stream into ice water. The fiberlike precipitate (cellulose acetate) was collected on a Büchner funnel with the aid of suction, washed with cold and hot water, alcohol, and ether, and allowed to dry. The yield of acetone-soluble product was 65 to 75 per cent of the theoretical. The characteristics of the two products prepared--i.e., 2a and 2b--are re-

ceded in connection with the methylation experiments.

3. Commercial acetone-soluble acetate (Sample I). This material (supplied by E. I. du Pont de Nemours & Company) was used for studies on the mechanism of the methylation of acetone-soluble acetates. A combined acetic acid content of 56.0 per cent, a copper number of 3.5, and a degree of polymerization of 160 corresponding to a molecular weight of 26,200 (according to Staudinger's viscosity method) are characteristics of the acetate.

4. Commercial acetone-soluble acetate (Sample II). This material (obtained from the source mentioned above) was used in the preparation of highly methylated celluloses which were reacetylated and remethylated. The copper number was 2.0 and the combined acetic acid content was 54.2 per cent; the degree of polymerization was 140.

5. Nonfibrous cellulose triacetate. This was prepared from the above-mentioned cotton linters using chlorine and sulfur dioxide as a catalyst according to the method of Barnett (19). Since it was desired to keep degradation at a minimum, the temperatures were kept as low as possible according to the following procedure.

Fifty grams of the air-dry, disintegrated cotton linters were allowed to soak one hour in a two-liter jar containing 200 cc. of acetic acid and 3.2 grams of chlorine. The mixture was then cooled at 5° C. and 200 cc. of acetic anhydride containing 2.6 grams of sulfur dioxide were added slowly with stirring. During cooling, the same precautions as described under preparation of the acetone-

soluble acetate were followed. After one hour at 5° C. the flask was placed on a rotating wheel for fifteen hours. The material had by then acquired the appearance of a white paste and was heated to 65° C. for one-half hour, whereby it changed into a transparent gel. After dilution with an equal volume of glacial acetic acid, the viscous solution was sprayed into water which was stirred constantly. The finely precipitated triacetate was filtered and washed with water on a Büchner funnel until it was free of acid. After washing thoroughly with 95 per cent ethyl alcohol and ether, it was allowed to air-dry. The yield was 95 per cent of the theoretical. The combined acetic acid content was 62.4 per cent (the calculated value for cellulose triacetate is 62.55 per cent). The degree of polymerization was 234, which corresponds to a molecular weight of 38,000.

6. Fibrous triacetate. The cotton linters were used to prepare this product according to the method of Boehringer and Seehne (26) as described by Dorée and Healey (27). The acetylating mixture consisted of acetic anhydride as the acetylating agent, toluene as a nonsolvent, and perchloric acid and sulfur dioxide as catalysts. After a ten-hour treatment, a 96 per cent yield of a chloroform-soluble but acetone-insoluble material of 61.5 per cent combined acetic acid content was obtained. The product was washed with alcohol and acetone. It was allowed to remain moist with acetone until methylated. The degree of polymerization of this product was 666 corresponding to a molecular weight of 108,000.

7. Fibrous diacetate. This product was prepared according to the method of Hess and Ljubitsch (28) in which acetic anhydride acts upon cellulose in the presence of pyridine as a nonsolvent. Such a procedure was shown by Standinger and Filers (29) not to degrade cellulose. After twenty-five days at room temperature, the fibers were filtered off, washed with alcohol and acetone, and stored while moist with acetone for methylation. This product contained 45 per cent combined acetic acid, and, in accord with the results of Standinger and Filers, it was found that it was insoluble in the solvents generally used for viscosity measurements.

8. Wood cellulose dispersed in Triton B (40 per cent solution of trimethylbenzylammonium hydroxide). This solution was supplied by Rohm and Haas and had been prepared from a finely ground chemical wood pulp with a copper number of 1.57 and a cuprammonium viscosity (Institute Method 420) of 9.0 centipoises. To check the concentration of cellulose (about 4 per cent), the latter was precipitated by neutralization of the Triton B with hydrochloric acid. The cellulose was washed thoroughly with water and then with acetone on a Büchner funnel. It was air-dried to a fine white powder; 3.9 per cent was found. The precipitated cellulose showed a copper number of 0.64 and a cuprammonium viscosity of 3.2 centipoises. Its degree of polymerization was 164.

## STANDARD METHODS, PROCEDURES, AND EQUIPMENT

1. Methylation of cellulosic materials. The procedure used by Haworth, Hirst, and Thomas (2) for the methylation of acetone-soluble acetates was applied as follows: A quantity of the cellulosic material corresponding to 6.06 grams of oven-dry cellulose (10 grams of acetone-soluble cellulose acetate) was suspended, or dissolved, in 250 cc. of acetone in a triple-necked one-liter round-bottomed flask. This flask was partially immersed in a bath maintained at 54 to 56° C., and its contents were agitated with the standard stirrer. The apparatus is shown in Figure 1. The stirrer used was designed to give adequate agitation of the cellulosic materials without the use of high speeds, but it possessed considerable power and was capable, if necessary, of developing high speeds without vibration. Such requirements were satisfied by a "Lightnin'" mixer, Model A, which is driven by an electric motor and is capable of speeds as high as 2800 r.p.m. without excessive vibration. A rheostat allowed the speed to be controlled. Since the neck of an ordinary triple-necked flask is small in comparison with the size of the propeller required, the following type of propeller was satisfactory. It functions like a single-blade type propeller, but the blade, cut in two parts, is placed on a pivot in the center so that it will fold downward as the propeller is introduced into the flask. As the shaft is rotated, the blades are thrown out by centrifugal force, thus offering a large agitating surface. In the case of fibrous cellulose it was found necessary to increase somewhat the

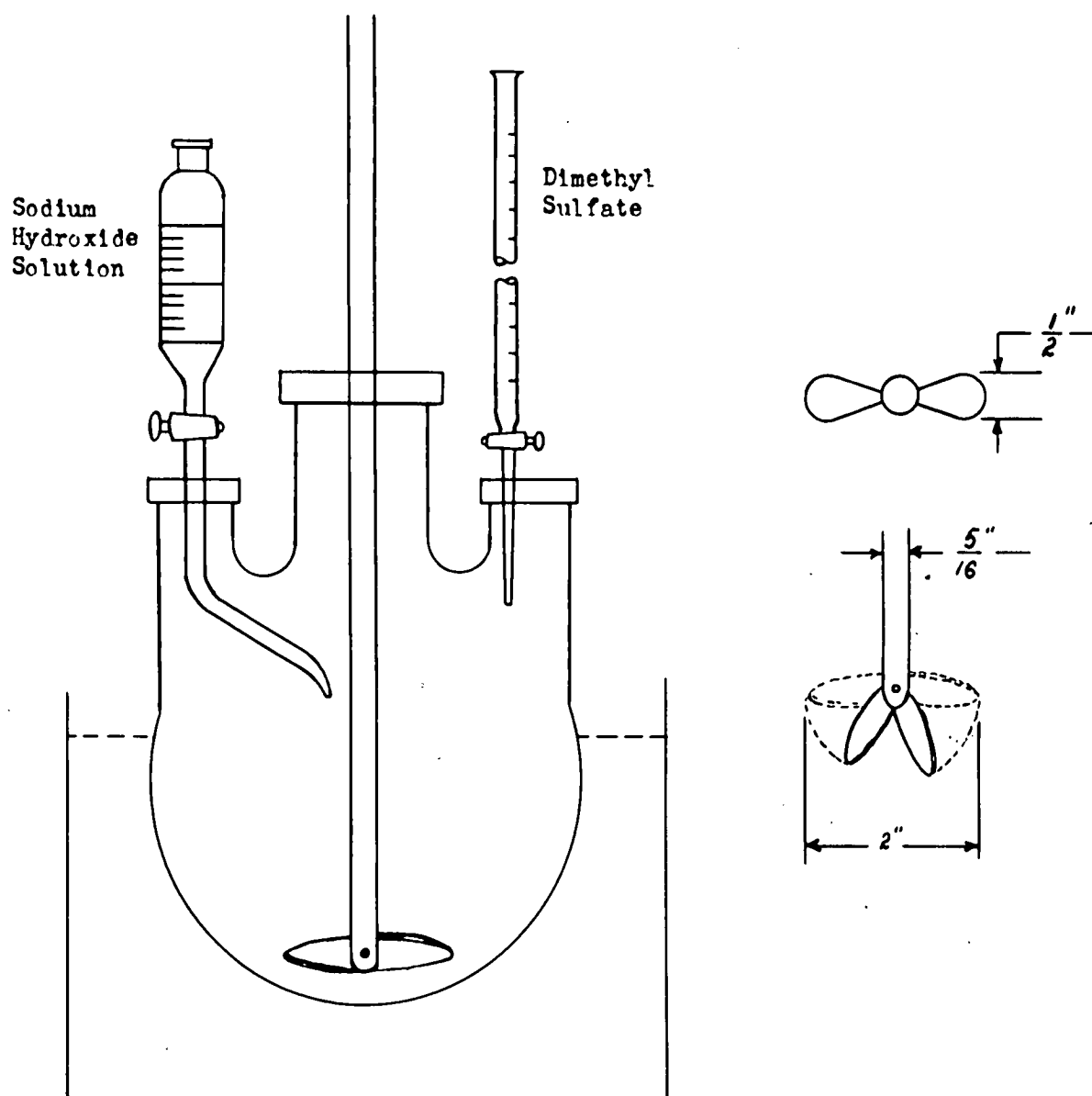


FIGURE 1

APPARATUS FOR METHYLATION OF CELLULOSIC MATERIALS

speed of stirring. In all other cases this was maintained fairly constant at 1000 r.p.m. With constant stirring, 120 cc. of dimethyl sulfate and 120 cc. of 30 per cent sodium hydroxide solution were allowed to drop in at the rate of 0.1 of the total volume every ten minutes. After the one hundred minutes of addition, the bath was brought up to and maintained at 70° C. until the acetone had distilled off. Care was taken not to heat for a longer time as this would cause a hardening of the surface of the product. The methylated product was then collected on a 9-cm. Büchner funnel fitted with J. Green, Grade 904 filter paper (which appeared to be especially adapted to filtering alkaline solutions) and washed until free of sulfate with nearly boiling water. In case of nonfibrous products the material was triturated in a mortar several times with hot water. The material was then freed of water by washing with acetone and air-dried. If it were to be remethylated, it was not dried but worked up in acetone for the subsequent treatment.

2. Methoxyl content of cellulosic materials. This was determined according to the method of Viebeck and Schwappach which is a modification of the Zeisel method as described in Institute Method 15.

3. Combined acetic acid content of cellulose acetates. A modification of Eberstadt's method as applied by the Eastman Kodak Company was used (11). This method was selected by them as being most adequate after an extensive review and study of the known procedures. It involves saponification by 0.5 N sodium hydroxide



solution in the presence of ethyl alcohol at moderate temperatures.

4. Copper number. This was determined by Institute Method 609. According to Krüger (32) such a procedure is satisfactory for partially saponified acetone-soluble cellulose acetates but would be questionable for completely acetylated cellulose. Here the reducing group, as in glucose-penta acetate, would be combined with acetic acid and under the conditions of the copper number determination might not be completely removed. Thus, it would not show true reductivity. During the preparation of the acetone-soluble acetates by partial saponification of the triacetate this reducing group is freed, for such acetyl groups are more easily split off than those existing in the main body of the glucose molecule. This free reducing group then enables a true copper number of the acetone-soluble cellulose acetate to be determined. Therefore, the determination was applied only to partially saponified acetone-soluble acetates and not to cellulose triacetates.

5. Determination of degree of polymerization through viscosity measurements. In the case of cellulose acetates and highly methylated cellulose the degree of polymerization or molecular weight was calculated from the specific viscosity of the material dissolved in m-cresol by Staudinger's equation (30):

$$\eta_{sp}/c = K_{\eta} M \quad ; \quad M/162 = \text{degree of polymerization}.$$

$K_{\eta}$  is a constant characteristic for each polymeric series. For highly methylated cellulose Staudinger and Reinecke (30) have determined

the value of  $\underline{K}_m$  to be  $12.5 \times 10^{-4}$ , and for cellulose to be  $8 \times 10^{-4}$ .  
 $\underline{c}$  is the concentration of the solution in unit moles per liter, i. e.,  
 (grams per liter)/ $0.6 \times 10^5$ . Specific viscosity represents the increase  
 in viscosity which the dissolved substance produces in the solvent,  
 or  $\eta_{sp} = (\underline{T}_1 - \underline{T}_0)/\underline{T}_1$ , where  $\underline{T}_0$  is the time required for the flow of  
 the solvent through the capillary, and  $\underline{T}_1$  is the time required for  
 the same quantity of the solution to pass through the capillary.  
 The viscosities were determined in an Ostwald type viscosimeter.

Whether or not these values represent the true molecular  
 weight, they do provide a basis for comparing the degree of degradation,  
 which occurs during the various processes.

## EXPERIMENTAL WORK

## PREPARATION OF HIGHLY METHYLATED CELLULOSES

Application of the Method of Haworth, Hirst, and Thomas  
to Cotton Linters

Cotton linters were acetylated to form an acetone-soluble acetate (Material 2a) (57.2 per cent combined acetic acid, degree of polymerization, 171, corresponding to a molecular weight of 21,200) as described above. Methylation of this according to the standard procedure as described by Haworth, Hirst, and Thomas (2) yielded the following results.

In the first experiment a methoxyl content of 44.65 was obtained after one methylation. This was increased to 44.75 by a further methylation. The product was then dissolved in chloroform, filtered, and precipitated into petroleum ether. The precipitate was washed with petroleum ether and acetone. The milky suspension of the material in acetone was then again subjected to methylation, but the methoxyl content was the same as before--namely, 44.75 per cent. The degree of polymerization was 120, corresponding to a molecular weight of 19,350.

A second experiment, starting with cellulose acetate (Material 2b) prepared from cotton linters resulted in a methoxyl content of 43.3 per cent after one methylation, 44.0 per cent after two methylations, and 44.5 per cent after the third and fourth methylations. The degree of polymerization of the acetate was 141

(molecular weight, 23,100); that of the final methylated product was 130 (molecular weight, 21,000).

The methoxyl values fall below those reported by Haworth, Hirst, and Thomas (2), Haworth and Wachemer (3), and Sperka (22), but they compare with those obtained by Hess and his co-workers (8), by Karrer and Moscher (4), and by Wolfrom, Sowden and Lassettre (20).

Application of the Method of Haworth, Hirst, and Thomas  
to a Commercial Acetone-Soluble Acetate (Material 3)

The maximum value obtained from this acetate by application of the standard procedure was 44.7 per cent methoxyl after one methylation and 44.8 per cent after two methylations; other values ranged down to about 43.0 per cent. The highest value remained constant with further treatment.

With regard to details of experiments, the following observations were made: The stirring should be downward and such that a vortex action of the solution is just obtained. More vigorous agitation gives no better results, and there is the possibility of throwing the material upon the side of the flask and out of the reaction. The use of a reflux condenser to prevent evaporation of acetone is of no advantage. In two experiments where a reflux was used, methoxyl values of only 41 per cent and 42 per cent were reached. Further, the use of a reflux makes it difficult to remove gelatinous material which sometimes forms and may adhere to the sides of the flask. Thus, it may happen that the reaction is retarded because

of the inaccessibility of such material to the methylating agents. When the flask is left open, such material may be continuously scraped from the sides (conveniently with a wire upon which is placed a "rubber policeman") while stirring is in progress; very little material need be held in this way for any length of time. This possibility of gelatinous material adhering to the sides of the flask exists only for a short time between the thirty- and forty-minute intervals of the reaction and is not critical if the first portions are removed before greater quantities are accumulated. Indeed, if correct stirring is used, no difficulty exists at all. The propeller should be large so that good agitation may be obtained without excessive speed. If a high speed is used, the gelatinous material is thrown against the sides of the flask and cling to it. In experiments where an excessive stirring speed was used, no advantage was gained in methoxyl content. The phenomenon of globulation of the alkali is discussed later.

When the methylation time, accompanied by a proportional increase in amounts of methylating agents, was extended, no higher values were reached. Such an experiment resulted in a methoxyl content of 44.6 per cent.

A methylation, when the quantity of methylating agents was increased by 40 per cent, with the same time of addition, resulted in a methoxyl content of 43.5 per cent.

### Acetylation and Methylation of Highly Methylated Celluloses

Inasmuch as there was a possibility that acetylation might activate the tardily reacting hydroxyl groups, an attempt was made to increase the methoxyl content of the highly methylated celluloses described above by reacetylation and subsequent remethylation. The materials used for this were prepared by methylation of the acetone-soluble cellulose acetate (Material 4) by the standard procedure.

For this purpose, 40 grams of the highly methylated cellulose (44.5 per cent methoxyl) were dissolved in 240 cc. of glacial acetic acid into which chlorine had been bubbled for two to three minutes. The material was then cooled to 10° C., whereupon it formed a soft, semisolid mass. One hundred cubic centimeters of acetic anhydride into which sulfur dioxide had been bubbled for six minutes were added gradually with cooling over a period of thirty minutes. The flask was then rotated at room temperature for forty-five minutes, at which time the soft, semisolid material was completely liquefied. A very small amount of insoluble material was removed by centrifuging, and a clear, colorless, viscous solution was obtained. This was permitted to flow in a fine stream into ice-cold water maintained between a pH of 4.5 and 7.0 by simultaneous addition of sodium hydroxide solution, whereby a white asbestos-like product was precipitated. If the precipitating medium was allowed to become more strongly acid, the product redissolved. The product was collected on a 15-cm. Büchner funnel with the aid of suction and washed three times with cold water, and once with acetone;

it was then resuspended in acetone. In this suspension it was methylated according to the standard procedure with the use of 1000 cc. of 30 per cent sodium hydroxide solution and 350 cc. of dimethyl sulfate. The results are shown in Table II.

TABLE II  
METHYLATION OF ACETYLATED, HIGHLY METHYLATED CELLULOSES

Methyl Cellulose	Methoxyl Content %		Degree of Polymerization by Viscosity Method		Combined Acetic Acid Content %	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
At start	44.5	43.5	228	258		
After reacetylation	44.36	—	17	61	1.7	2.3
After remethylation	45.3	45.0	30	50		

The results of this investigation show that, although the methoxyl content is increased nearly to the theoretical by this method, a simultaneous drop in degree of polymerization (as shown by viscosity measurements) also occurs. Thus, it is indicated that the treatment applied here resulted in hydrolytic degradation of the cellulose, which permitted higher methoxyl values to be reached. This result, which seems to confirm those obtained by Karrer and Zecher (4), will be discussed later.

#### THE ROLE OF THE ACETYL GROUPS IN THE METHYLATION OF CELLULOSE ACETATES

Methylations of native cellulose in the form of cotton linters according to the standard procedure--i.e., in one operation--

resulted in a white fibrous product of which the methoxyl content was 34.6 per cent.

The same cellulosic material when converted into the acetone-soluble acetate (Material 2a) having 57.2 per cent combined acetic acid, on subsequent methylation by the standard procedure, gave a product with 44.65 per cent methoxyl. This result seems to show the beneficial effect of using acetone-soluble cellulose acetates as a starting material. However, in this experiment all three of the factors mentioned earlier seemed to be involved. First of all, both chemical activation and the favorable physical state of the material being methylated may play a part in the reaction. The third factor--i. e., the generation of hydroxyl groups--must also be considered.

Indications are that even on the most careful acetylation of native cellulose, under acid conditions, considerable cleavage of glycosidic linkages occurs. In addition, it is likely, that on preparing the acetone-soluble acetate by way of saponification, in which a certain amount of sulfuric acid is added, further degradation takes place. The copper number of the carefully "stabilized" acetone-soluble acetate was found to be 1.8, whereas that of the original cellulose was 0.07. That degradation has taken place is more clearly seen from the degree of polymerization of the acetone-soluble acetate which was found to be 130 (corresponding to a molecular weight of 21,200). A commercial acetone-soluble acetate (see page 23) showed a degree of polymerization of 140 (molecular weight,



22,600), whereas original cellulose showed a degree of polymerisation of about 1,540 (corresponding to a molecular weight of about 250,000).

In comparing these results it would appear that the considerable degradation indicated by the drop in the degree of polymerisation would contribute much to reaching a higher methoxyl content. However, a brief consideration indicates that this is not so.

This is shown by a calculation of the effect which depolymerisation has upon the theoretical methoxyl content. In a cellulose chain molecule there are three hydroxyl groups per glucose unit which may be methylated. In addition there are two other groups in the chain which may be substituted also. One (in the 1-position of the glucose residue) is the hydroxyl group attached to the end carbon atom having the aldehydic function in the open chain configuration; the other is the hydroxyl in the 4-position of the glucose unit on the other end of the chain. Thus, the theoretical number of hydroxyls in a cellulose chain molecule which can be methylated would be  $3 \times \text{degree of polymerization} + 2$ ; and,

$$\frac{(\text{Total No. of hydroxyls}) (\text{OCH}_3) (100)}{C_6H_{10}O_5 + (\text{Total No. of hydroxyls}) (CH_2)} = \text{the theoretical methoxyl content expressed as percentage of the weight of material}$$

When calculated upon this basis, the theoretical methoxyl contents of celluloses at various degrees of polymerization are indicated below:

Degree of Polymerisation	Molecular Weight	Methoxyl Content Which Should Be Attained According to the Theory, %
∞	∞	45.57
1500	244,000	45.60
150	24,400	45.74
50	8,100	46.07

Thus, the influence of cleavage of glycosidic linkages upon the result of methylation is actually small, provided degradation does not occur to a considerable extent.

However, it was thought desirable to reduce that degradation which likely takes place on saponification of the intermediate. It was to be expected that this (i.e., the triacetate) would show less degradation than the acetone-soluble product. That this was so is shown by its degree of polymerization. The nonfibrous triacetate (Material 5, page 27), isolated from the acetylation mixture before saponification, showed a degree of polymerization of 274, corresponding to a molecular weight of 38,000.

The triacetate, isolated as described before, was methylated according to the standard procedure in the form of an air-dry powder. The methoxyl content was found to be only 42.8 per cent--i.e., considerably lower than that obtained with the acetone-soluble acetate (44.65 per cent). However, in view of what has been said before, the decrease in methoxyl content would appear to be too great to be due solely to a smaller degree of degradation.

It will be noticed that the methoxyl content obtained with the triacetate (32.8 per cent) is even less than that obtained with the original cellulose (44.6 per cent). Likewise, when air-dry commercial acetone-soluble acetate (Material 3, page 23) was methylated in the absence of acetone, a methoxyl value of only 27.6 per cent was obtained. The same acetate, when methylated in acetone solution, gave a product with 44.8 per cent methoxyl.\*

The results of these various experiments seem to indicate that, merely by acetylation as a pretreatment of the cellulosic materials, nothing can be gained as regards the efficiency of methylation and that the advantage observed in any cellulose in the form of its acetate is the result of the fact that the cellulosic material is converted into a state of solution in which its intramolecular hydroxyl groups are more easily accessible.

The triacetate used in the experiment described above had been dried before being methylated. Thus, the lower methoxyl content might be due to the fact that the triacetate had lost some of its reactivity on drying. However, this possibility seems to be eliminated in view of the two results obtained on methylation of fibrous acetate, which had not been dried but in which the water had been displaced by alcohol and later by acetone. Methylation of

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\* In the experiment in the absence of acetone the procedure had to be modified inasmuch as the total amount of alkali was added at once to the acetate in order to obtain satisfactory stirring and dispersion of the product. In the first case, the standard procedure was followed--i. e., both alkali and dimethyl sulfate were added simultaneously over the entire period of methylation.

the fibrous triacetate prepared by use of toluene as a nonsolvent and perchloric acid as a catalyst (Material 6) according to the standard procedure resulted in a methoxyl content of only 21 per cent. A similar result was obtained upon methylation of the fibrous diacetate (Material 7) prepared by using pyridine as a diluent at room temperature without a catalyst. This product had 15.8 per cent methoxyl when prepared by the standard methylation procedure.

In comparing the last two methylations with that of cotton linters, we see that the only difference is the presence of acetate groups. The physical form, i.e., the fibrous state, was the same. The degree of degradation in the acetates would be expected to be lower. Especially should this hold true in the case of the fibrous diacetate prepared with acetic anhydride and pyridine--i.e., without the use of any acid catalyst--for Staudinger and Hilers (29) have shown that such a method of acetylation causes no depolymerization of the cellulose. The molecular weight of this product could not be determined because of its insolubility in the usual organic solvents; this is also in accord with Staudinger and Hilers' observations on the acetylated products prepared with acetic anhydride and pyridine. The degree of polymerization of the fibrous triacetate described above was found to be 666 corresponding to a molecular weight of 108,000 which was higher than that of any of the other acetates.

Since methylation of the cellulose acetate in a fibrous form gave lower methoxyl values than methylation of cellulose itself in its fibrous form, chemical activation due simply to the presence

of the acetate group appears rather improbable. Therefore, it was thought desirable to accumulate further evidence to show that it is the physical form rather than the chemical constitution of the modified cellulose which is instrumental for the more rapid attainment of high methoxyl values.

Some of the additional evidence may be derived from the following experiments in which the above nonfibrous and fibrous triacetates were dissolved in chloroform and precipitated in a fine form by means of petroleum ether. The precipitated materials were separated by centrifuging and washed three times with petroleum ether and three times with acetone. They were then worked into a smooth paste with acetone in a mortar. Acetone was gradually added until a fine milky suspension was obtained. Methylation was then carried out on these fine precipitates according to the standard procedure. The results are compared in Table III.

TABLE III

EFFEOT OF PHYSICAL STATE OF CELLULOSE TRIACETATE UPON  
RATE OF METHYLATION

Form of Triacetates	Methoxyl Content %
Nonfibrous	
Dry powder	32.8
Freshly precipitated	40.8
Fibrous	
Fibrous form not dried	21.0
Freshly precipitated	37.0

Clearly, this comparison shows the benefit which may be derived from a suitable physical form. The product resulting from the freshly precipitated nonfibrous triacetate was further (i.e., exhaustively) methylated. However, even after six treatments by the standard procedure, after which the methoxyl content had become constant, a maximum value of only 43.91 per cent was reached, which is still short by 1.66 per cent of the theoretical value of 45.57 per cent. The degree of polymerization of this methylated product was found to be 234. This checks the observation (see page 40) that the triacetate represents a less degraded form than the acetone-soluble, partially saponified acetate and showed that on methylation no further degradation had occurred. Besides, it shows that the degree of polymerization does not seem to change on methylation.

Since the conversion of cellulose acetate into a dissolved or at least more finely divided form has facilitated methylation greatly, the same would be expected to be true of unacetylated cellulose.

A very finely divided cellulose was prepared from acetone-soluble acetate (Material 3) by treating the acetone solution used in the standard methylation procedure with an excess of 0.5 N sodium hydroxide. After two hours at 50° C. the precipitated cellulose, which was found to be completely saponified, was filtered off, washed free of alkali, and worked up through a smooth paste into a milky suspension in acetone. However, methylation of this material according to standard procedure resulted in a methoxyl content of only 23.7 per

cent. A similar value (23.0 per cent) was obtained by methylation of finely divided viscose cellulose which had not been dried but in which the water had been displaced by acetone. It will be noted that these values are even considerably lower than those obtained with fibrous cellulose (cotton linters).

Certainly, these results do not coincide with what would be expected since the lower degree of polymerization which must be attributed to these two materials should result in a higher methoxyl content than when fibrous cellulose was used. No definite explanation for this can be offered, but a description of the physical behavior of these materials during methylation may throw some light on this discrepancy. As stated, at the beginning of the methylation a milky suspension of the fine cellulose particles in acetone existed. However, immediately upon the addition of the methylating agents, agglomeration of the cellulosic material began. As the reaction proceeded, this became more and more pronounced and, after about thirty minutes, the cellulosic material had the appearance of a slimy, gelatinous mass which stuck to the bottom of the flask and could not be dispersed in the mixture by stirring. The supernatant acetone which at first had a milky appearance caused by the suspension of cellulose, was then completely clear. During the last one-half hour of the reaction the gelatinous mass again became well dispersed in the acetone.

Since such behavior was not observed during the methylation of the cellulose acetates, it is suggested that the failure of the

finely divided cellulose to respond to methylation may be attributed to these physical phenomena (agglomeration and gelatinization). Obviously, it is the presence of substituted groups which lessens the agglomerating effect of the alkali. The freshly precipitated acetate did not agglomerate on addition of the methylating agents, and the unacetylated cellulose lost its gelatinous character only after a certain number of methyl groups had been introduced. If this is true, then it should be possible to methylate a partially methylated cellulose more readily. In other words, after sufficient methylation of the cellulosic material has caused the product to become suspended in the methylation mixture, methylation should proceed more rapidly. This possibility was investigated in the following experiments.

Finely divided cellulose was regenerated from acetone-soluble cellulose acetate as described on page 42. It was then methylated according to the standard procedure. A sample was removed after fifty minutes, at which time the gelatinized cellulosic material had again become suspended. The methoxyl content at this state was 4.2 per cent. Methylation was then continued in the standard manner, and the methoxyl content of the final product from this two-step methylation was found to be 27.5 per cent--i.e., somewhat higher than the 23.7 per cent obtained in the previous case from a similar material.

The product with 27.5 per cent methoxyl was washed thoroughly with hot water and with acetone and worked up through a smooth paste



into a fine suspension in acetone. It was remethylated, remaining in suspension throughout the entire reaction. The product of this second methylation possessed a methoxyl content of 35.4 per cent.

For comparison a cellulosic material (wood pulp, Material 8) was used which had been converted into a finely divided state by mechanical means--i.e., by grinding. It was subjected to two methylations in exactly the same manner as the material regenerated from the cellulose acetate. As in the latter case, the wood pulp material showed the phenomena of agglomeration and gelatinization. After the first methylation a methoxyl content of 16 per cent had been reached; on the second methylation, during which the material was in a state of suspension in the methylation mixture, this value was increased to 35.7 per cent.

These experiments confirm the hypothesis that the physical phenomena observed during the first methylation reduces the efficiency of methylation of an originally finely divided cellulose. For the first fifty minutes, during which time the material was agglomerated and in a gelatinous state, little methylation took place, the methoxyl content being 4.2 per cent. This is indeed small when compared with 30 per cent (Figure 4) which was obtained upon methylation of fibrous cotton linters for the same length of time. During the last fifty minutes of the reaction the methoxyl content increased to 27.5 per cent, thus showing the beneficial effects where the material is in the form of a suspension. Likewise, as shown in the second methylation of both of the materials investigated above--namely, cellulose

regenerated from acetone-soluble cellulose acetate and ground chemical wood pulp--methylation took place quite readily, and methoxyl contents of 38.4 and 36.7 per cent, respectively, were reached. In both cases the material was well suspended.

In view of the explanation given for the failure of deriving any benefit from freshly precipitated (unacetylated) cellulose as compared with its fibrous origin, it seems justified to interpret the comparison of the behavior of the dry or fibrous with the freshly precipitated cellulose acetates as showing that it is the finely divided form which facilitates methylation.

From a comparison of the two methods--namely, (1) methylation of the acetate in a suitable solvent and (2) methylation of a freshly precipitated acetate in the absence of a solvent--it would appear that the first method should be more efficient, since it would be expected that at least the beginning of the reaction takes place while the cellulosic material is in solution. Only later on, when more methoxyl has been introduced, would the reaction continue on a precipitated material, thereby approaching conditions as they prevail in the second method from the start.

It appeared desirable to see how these assumptions compare with what actually happens. It was thought that a means to this end would be to follow the reaction of methylation by determining the rate of both deacetylation and methylation and, at the same time, to observe the physical changes which were expected to occur in the

mixture while these two processes were in progress.

## MECHANISM OF METHYLATION OF CELLULOSE ACETATE DISSOLVED IN ACETONE

### Rate of Methylation and Demethylation of Cellulose

#### Acetate Dissolved in Acetone

Method 1. This series of experiments was carried out by taking samples of the entire methylation mixture at definite intervals, isolating the cellulose derivatives from the mixture and analysing them for acetyl and methoxyl contents.

For this purpose 35 grams of the commercial acetone-soluble acetate (Material 3) were dissolved in 700 cc. of acetone in a three-liter triple-necked round-bottomed flask immersed in a bath maintained at 54 to 56° C. and fitted with a standard stirrer. Then 420 cc. of dimethyl sulfate and 960 cc. of a 30 per cent sodium hydroxide solution were added simultaneously, drop by drop, at the rate of 0.1 of the total every ten minutes. The actual time of addition of each portion of reagent was about eight minutes. During the interval between additions, a sample of the contents of the flask was removed. The samples thus obtained were treated with an equal volume of warm water and the acetone removed under vacuum. The cellulosic material was collected on a filter, washed free of sulfate with hot water, and dried in the open air. Methoxyl and acetyl were determined as described above. The results are given in Table IV and reproduced in Figure 2.

TABLE IV

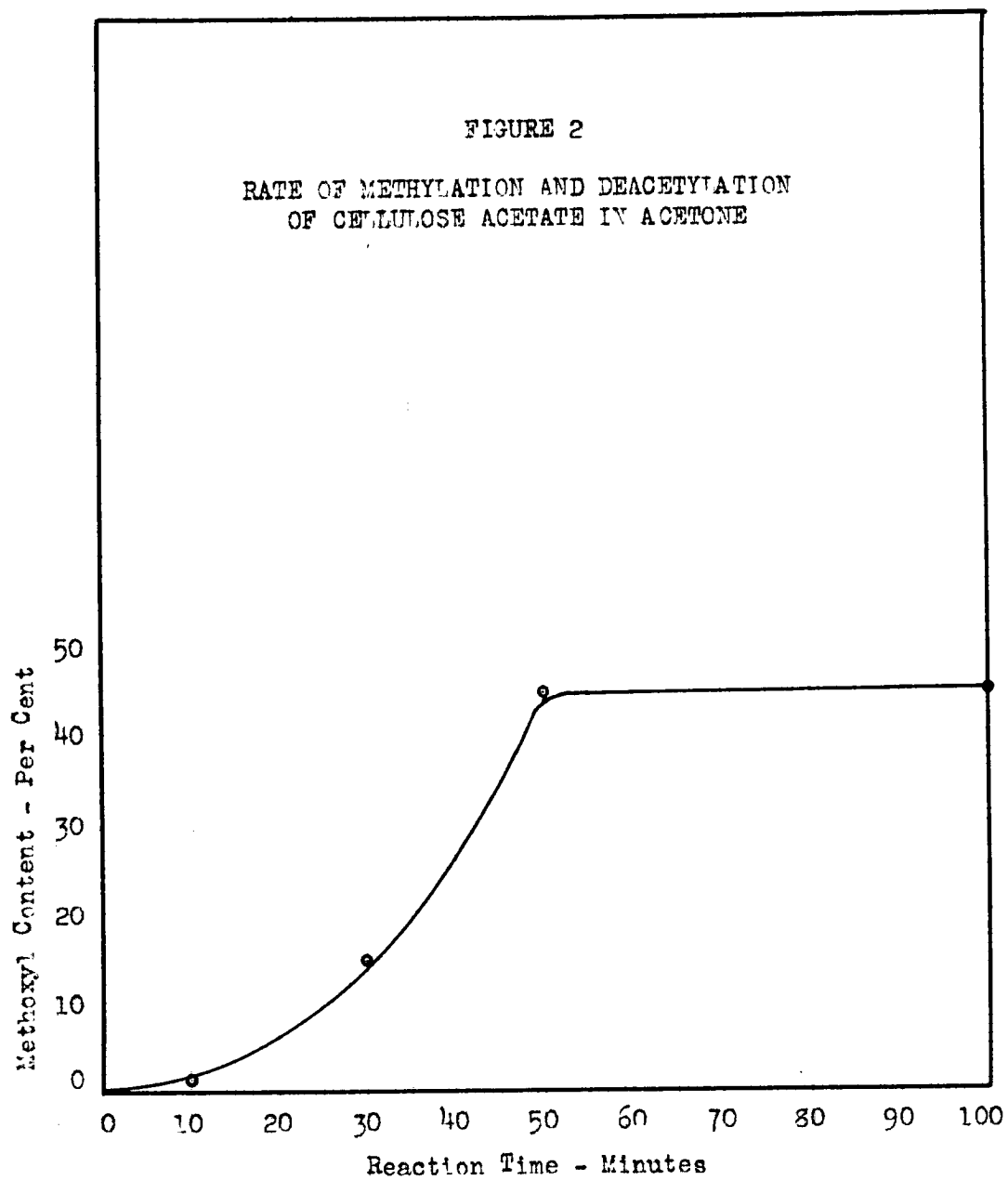
RATE OF METHYLATION AND DEMETHYLATION  
OF CELLULOSE ACETATE IN ACETONE

## Method 1

Reaction Time min.	Methoxyl Content %	Combined Acetic Acid Content %
0	----	56.00
10	1.10	44.80
30	14.60	-----
50	44.60	0.00
100	44.80	----

No definite conclusions regarding the process of demethylation can be drawn from the acetyl determinations of which, for technical reasons, only two could be made: one on samples taken after ten minutes and another on samples taken after fifty minutes. The combined acetic acid contents of these samples were 44.8 per cent and zero. However, the possibility existed that during isolation of the cellulose product the sodium hydroxide present may have effected further saponification.

Method 2. In order to check the results of the previous experiment and in the hope of avoiding saponification of the acetate during isolation of the reaction product, the alkali was neutralized with dilute sulfuric acid immediately after the time specified for methylation had elapsed. For this purpose individual methylations of the cellulose acetate in acetone solution were carried out according



to the standard procedure up to the time intervals specified. At the end of that time interval the reaction mixture was placed in a salt-ice bath, and the alkali was neutralized with dilute sulfuric acid. This required the relatively long time of seven minutes in order to prevent the temperature from rising above 30° C. The acetone was then distilled off under vacuum, the mixture brought up to 70° C., and filtered. The product of the reaction was washed thoroughly with hot water until free of sulfate and air dried. The results of the acetyl and methoxyl analyses are shown in Table V and in Figure 3.

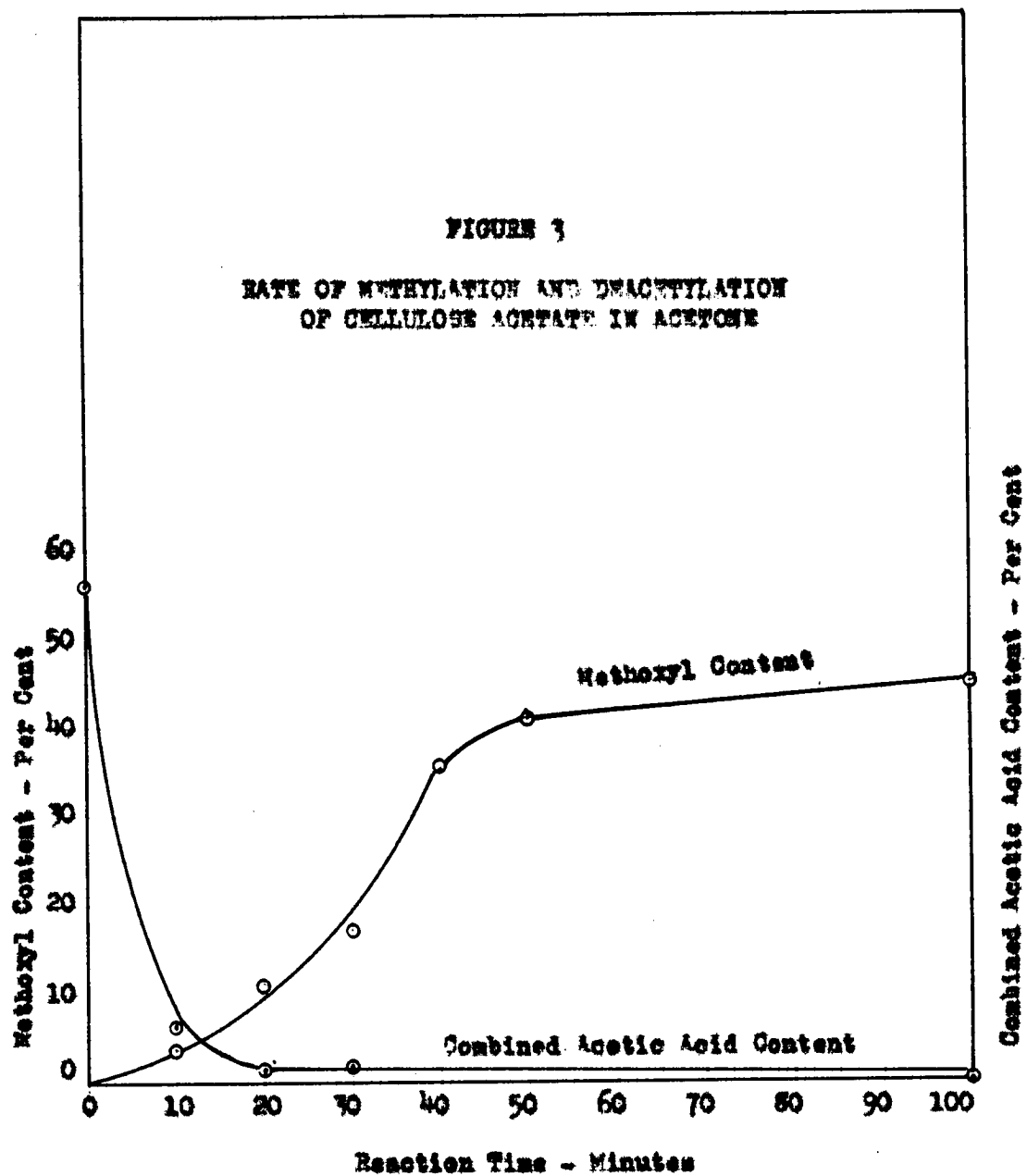
TABLE V

RATE OF METHYLATION AND DEMETHYLATION OF  
CELLULOSE ACETATE IN ACETONE

Values obtained on products isolated from individual methylations after the caustic soda had been neutralized

## Method 2

Reaction Time min.	Methoxyl Content %	Combined Acetic Acid Content %
0	0.00	56.00
10	3.98	6.20
20	11.20	1.60
30	17.00	2.00
30	17.20	----
40	35.10	0.00
50	41.00	1.00
100	44.80	0.00



Again it is seen that the acetyl values are very low, and the suspicion arose that saponification may have occurred during the neutralization caused by either the sulfuric acid or by unneutralized alkali. In order to check these possibilities, the following three experiments were carried out.

(1) A 0.5-gram sample of acetone-soluble cellulose acetate was dissolved in 20 cc. of acetone. Twenty-five cubic centimeters of 0.5 N sulfuric acid were added at 55° C. Precipitation of cellulosic material took place. After five minutes the solid material was filtered off and washed thoroughly with water. It was then redissolved in 50 cc. of acetone and treated for fifteen minutes at 55° with 0.5 N sodium hydroxide. Back titration of the alkali revealed that the cellulosic material still contained 51 per cent combined acetic acid after treatment with sulfuric acid. (The original acetate had contained 56 per cent combined acetic acid.) Thus, under the conditions applied, very little deacetylation could be attributed to the action of the sulfuric acid during neutralization of the sample.

(2) In a similar experiment an acetone solution of the acetate was treated with a known quantity of sodium hydroxide solution of the same concentration as used for methylation (30 per cent). The observation was made that globules of sodium hydroxide were formed which were not dispersed on gentle shaking. However, during back-titration of the sodium hydroxide with standard acid the globules broke up and precipitation of fine white cellulosic material took place. From the amount of sodium hydroxide consumed, it was found



that about 55 per cent of the acetyl groups had been saponified. About the same amount of acetyl groups are saponified if dilute sodium hydroxide solution is added to the acetate solution in acetone and the amount of unconsumed sodium hydroxide is determined immediately by back-titration.

(3) In the third experiment, an acetone solution of the acetate was treated with a solution of the 70 per cent sodium hydroxide as in Experiment 2. But this time the globules were separated from the acetone solution by filtration. Determination of the alkali content of the globules remaining on the filter paper, which was 99.2 per cent of the amount added, revealed that practically none of the alkali had been consumed by the acetate. Correspondingly, analysis of the filtrate containing the bulk of the acetate showed that the majority of the acetyl groups were still in combination with the cellulose.

This result shows that the alkali saponifies the acetyl groups only if and when it comes into sufficiently close contact with these groups. Such contact is established if dilute acid is added to the mixture, which results in a breaking up of the globules.

Thus it is more than probable that, on neutralization of the methylation mixture (Method 2, page 45), the majority of the acetyl groups were saponified while contact between the alkali and the acetate was being established. Since, as we have seen, considerable time was required for neutralization, sufficient

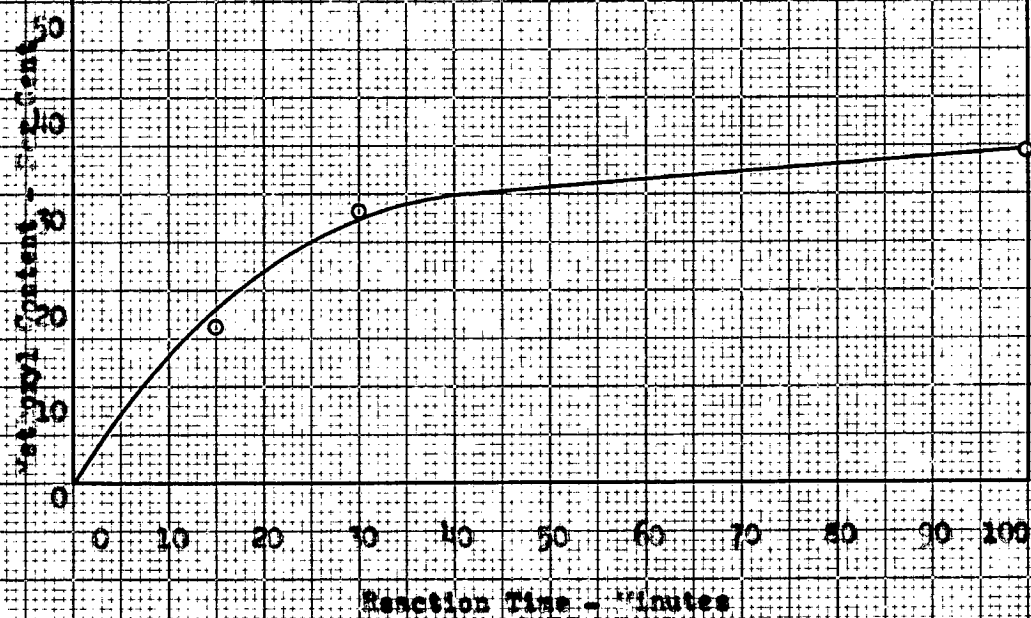
alkali was present to accomplish saponification long before neutralization was completed.

Final proof of this interpretation is derived from the fact that dilute alkali, which is miscible immediately with the acetone solution, effected nearly complete saponification at once.

The curves representing the rate of methylation show that little methylation took place at the very beginning of the reaction (see Figures 2 and 3). This result is in contrast to the values which were obtained by methylation of cotton linters by the standard procedures for intervals as shown in Figure 4. In the latter case the rate of methylation was more rapid at the very beginning of the reaction, then decreased and was nearly complete after about fifty minutes. In the case of the acetates dissolved in acetone, the reaction was comparatively slow at the beginning but became very rapid after about thirty minutes and was again nearly complete after fifty minutes. The difference in the rate of methylation during the first part of the reaction seems to find its explanation as follows.

In the methylation of the acetate in solution, the period of increased speed of reaction appears to coincide with a visible change in the appearance of the reaction mixture. As soon as the dimethyl sulfate and sodium hydroxide are added to the acetone solution of the acetate, small globules are formed. Evidently these globules consist of sodium hydroxide solution surrounded by a thin film of cellulosic material. These globules withstand stirring up to about

Figure 1

RATE OF ACTIVATION OF PEARL COTTON  
FIBERS IN THE

thirty to forty minutes, when they are gradually broken up and droplets of sodium hydroxide, no longer surrounded by solid cellulosic material, are visible. At the same time, a fine white precipitate forms and the reaction mixture soon acquires the appearance of a cream-like, white emulsion which does not separate if stirring is stopped. At a time soon after this increased turbidity, between about twenty and fifty minutes, the temperature of the reaction mixture increases rapidly as shown in Figure 5. When comparing the latter with Figures 2 and 3, it will be seen that the increased temperature corresponds to a more rapid rate of methylation, which seems to indicate the existence of a condition in which the alkali enters more thoroughly into the reaction. At this point the considerable amount of dimethyl sulfate which has been added and rapid saponification of the acetate apparently permit methylation to proceed quickly.

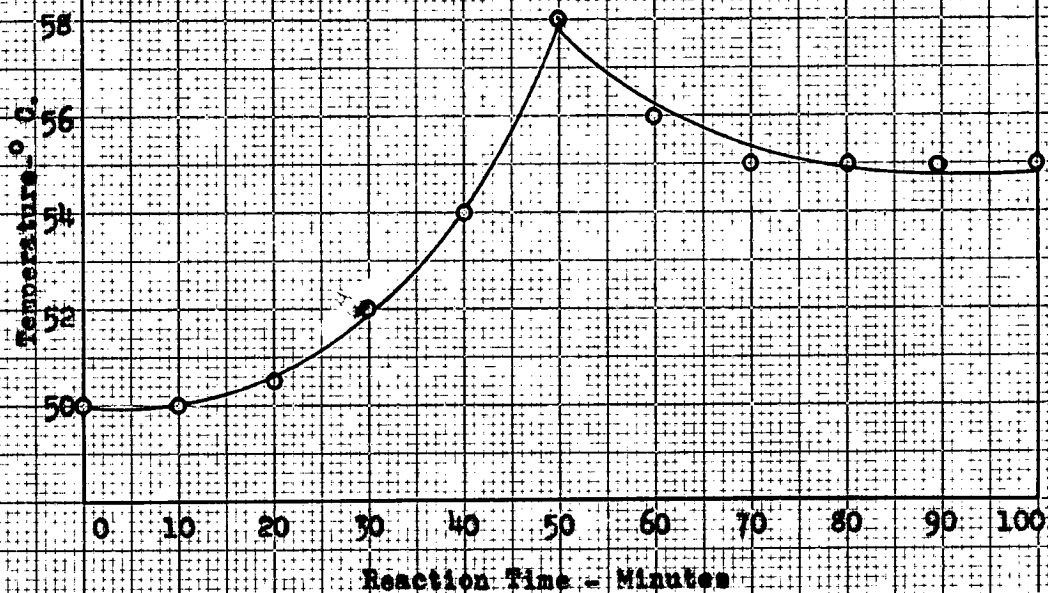
The Physical State of the Cellulosic Material During the Methylation of Cellulose Acetate Dissolved in Acetone

It still remains to be shown to what extent methylation proceeds while the cellulosic material is in solution and to establish the relation of the physical phenomena to the rate of methylation and deacetylation.

Separation of Soluble and Insoluble Portion during Methylation. In order to answer the above questions, use was made of the phenomenon described above--namely, that during the early stages of methylation the alkali settles out in the form of globules which, as

FIGURE 5

TEMPERATURE CHANGES DURING NITRILATION OF  
CELLULOSE ACETATE DISSOLVED IN ACETONE



may be concluded from Experiment 2, page 52, probably could be separated from the solution by filtration.

Individual portions were methylated according to the standard procedure and, after the times specified (twenty, thirty, and forty minutes) the methylation mixtures were separated by filtration into (1) a residue consisting of sodium hydroxide globules which, as described previously, were surrounded by a film of cellulosic material and (2) the acetone solution. The residue (1) was washed free of sodium hydroxide by hot water and air dried. The cellulosic material from the acetone solution (2) was obtained by precipitation with cold water; the precipitate was collected on a Büchner funnel with the aid of suction, washed with cold water, and air dried. The cellulosic materials, both from the residue (which amounted to only 10 per cent or less of the original material) and from the solution, containing the majority, were separately analysed for methoxyl and combined acetic acid contents. The results are shown in Table VI and Figure 6.

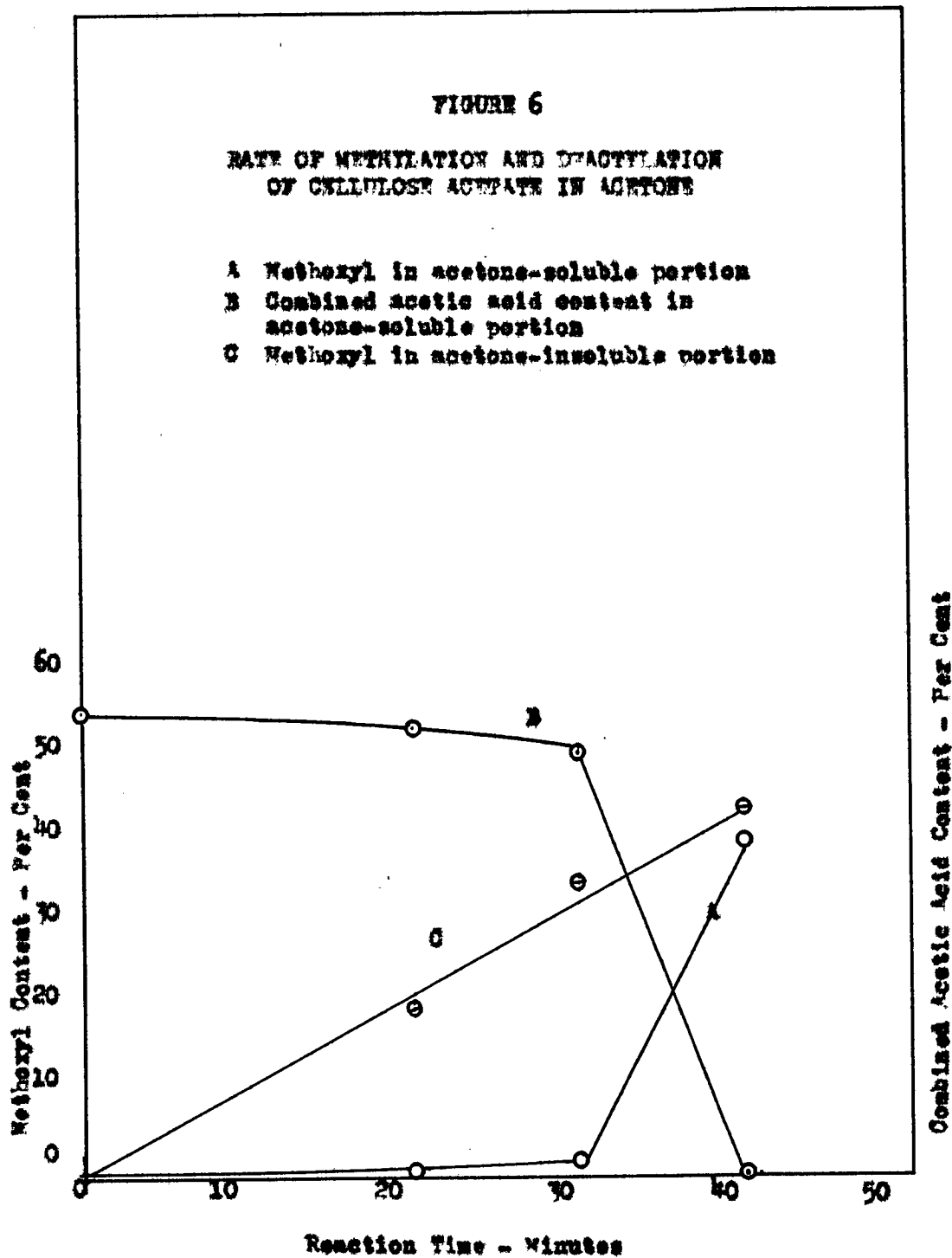
The curve of the methoxyl content for the methylcellulose isolated from the solution shows that very little methylation takes place up to thirty minutes, whereas at forty minutes a methoxyl content of 40.2 per cent had been reached. This result confirms those previously obtained (see Figures 2 and 3). Likewise, as seen from Curve B, very little deacetylation takes place up to thirty minutes, whereas at forty minutes it is complete.

TABLE VI

RATE OF METHYLATION AND DEACETYLATION OF  
CELLULOSE ACETATE DISSOLVED IN ACETONE

Values obtained on products isolated from acetone-soluble and -insoluble portions

Reaction Time min.	Acetone-Soluble Portion		Acetone-Insoluble Portion	
	Methoxyl Content %	Combined Acetic Acid Content %	Methoxyl Content %	Combined Acetic Acid Content %
0	-----	56.0	-----	0
20	0.91	54.8	20.1	0
30	1.45	53.3	45.5	0
40	2.20	51.0	-----	0
40	40.20	0.0	44.2	0





The curve for the methoxyl contents of the acetone-insoluble portion indicates much more rapid methylation during the first part of the reaction than in the case of the portion in solution. It is probable that this result is due to a more intimate contact which existed between the alkali and the surrounding cellulosic material from the beginning of the reaction.

In drawing conclusions from the deacetylation curve (B) the difficulty of isolating the major part of the reaction product (2) without losing acetyl has to be taken into consideration. The fact that the product isolated at forty minutes was still in solution, although analysis revealed a high methoxyl content but no acetyl, seems to indicate that at the time the product was isolated it still possessed a small amount of acetyl which enabled it to remain in solution, <sup>for</sup> highly methylated celluloses are insoluble in acetone. However, while the product was being isolated, saponification was completed. This view is also supported by the following observations. At the twenty- and thirty-minute intervals, filtration yielded a clear solution; moreover, this solution showed acid reaction after it had been poured into water for the purpose of precipitating the cellulosic material. This observation indicates that the acetone solution (2) contained very little alkali, most of it having been removed with the globules. In the case of the forty-minute interval, however, a turbid filtrate was obtained which remained alkaline throughout the isolation of the product of reaction. Obviously the alkali had mixed with the solution, and it was no longer possible to

separate them. Consequently, saponification took place.

The rates of methylation and deacetylation appear to be in direct relation to the phenomena observed during the methylation operation, and one may visualize the mechanism to be as follows. At the beginning of the reaction most of the acetate remains in solution but, owing to the "globulation" of the sodium hydroxide, sufficiently close contact is not established with the alkali. Moreover, very little saponification takes place, and methylation is much impeded. However, as soon as the globules start to break, more intimate contact is achieved and saponification and methylation become more rapid. In agreement with the decreasing acetyl content and the increasing methoxyl content of the product of reaction is the previously described appearance of the mixture. As more methoxyl enters the cellulose, the product of reaction would be expected to become more and more insoluble in acetone and hence to precipitate from the solution. Thus, the latter part of the reaction would take place on the precipitated, but still very finely divided material.

Acetone Solubility of Methylcellulose Acetates. While the acetate is being methylated, it passes through a number of intermediate stages--i.e., methylcellulose acetates of decreasing acetyl and increasing methoxyl contents are being formed. In view of the probability that the greater part of the cellulosic material remains in solution during most of the reaction period, it was thought that the mechanism could be still further elucidated by preparing some of the probable intermediates and by studying their solubility in acetone.

Completely substituted methylcellulose acetates of increasing methoxyl content were prepared from the commercial acetone-soluble acetate (Material 3). In preparing such mixed ether-esters, it is necessary to etherify first and then esterify, for, if the reverse procedure were applied, the ester group would inadvertently be saponified by the alkali of the methylation mixture. In order that the cellulosic material would be the same as that which existed in the methylation reactions, the acetone-soluble acetate was chosen as a starting material.

(a) Methylations. The cellulose constituent was regenerated from the acetate as follows. Twenty-five grams of the acetate were suspended in 300 cc. of 30 per cent sodium hydroxide in a triple-necked two-liter round-bottomed flask and stirred for one-half hour in order that the surfaces of the particles would be uniformly wetted by the solution. For the purpose of methylation, the flask was then surrounded by a bath maintained at  $54$  to  $56^{\circ}$  C., and the requisite amount of dimethyl sulfate added at the rate of 30 cc. per ten minutes. Stirring at this temperature was continued for two hours. The methylated product was collected on a Büchner funnel with the aid of suction and washed with hot water until free of sulfate. It was washed with acetone and air dried to a white granular product which showed no acetate groups by the standard method of analysis.

(b) Acetylations. The methylcellulose preparations of increasing methoxyl contents were suspended or, if soluble, dissolved in 160 cc. of pyridine and allowed to rotate on a wheel overnight.

The mixture was then treated with 100 cc. of acetic anhydride without the use of an acid catalyst and, after mixing for twenty-four hours at room temperature, was allowed to remain in a bath at 60° C. for nine days. At the end of this time the acetylation solution was filtered and the filtrate allowed to drop slowly into 2 liters of cold water for precipitation. The product thus obtained was collected and washed with cold water on a Büchner funnel with the aid of suction. It was redissolved in pyridine and precipitated again into water, isolated as before, allowed to air-dry, and placed in a vacuum desiccator over phosphorus pentoxide at 56° C. for the final drying.

The solubility in acetone was determined by extraction of the material (about 1 gram) in a Soxhlet extractor with 150 cc. of the solvent, evaporation of the acetone and drying to constant weight at room temperature. The experimental results and observations are presented in Table VII.

By observation of Table VII it is seen that the solubility in acetone of the methylcelluloses increased as methylation proceeded. Comparison of the actual methoxyl and combined acetic acid contents with the theoretical values shows that complete substitution had taken place. The somewhat greater discrepancy in case of Product 1 may possibly be accounted for by the fact that at the end of the acetylation some of the product insoluble in the acetylation mixture was removed by filtration. This is also reflected in the low yield for Product 1.

TABLE VII

## DATA CONCERNING NITRYLOXIMINOSE ACETATES

Product	1	2	3	4
Appearance of acetylation mixture after one day and solubility in writhings	Reddish brown; contained much insoluble material	Reddish brown; some insoluble material	Reddish brown; some insoluble material	Reddish brown; practically no insoluble material
After nine days	Brown, a little insoluble material	Brown, completely dissolved	Brown, completely dissolved	Brown, completely dissolved
COCH <sub>3</sub> before acetylation, per cent	13.74	19.2	26.0	39.17
Theoretical for-	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 743$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 1.090$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 1.540$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 2.404$
	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 2.257$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 1.910$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 1.460$	$\text{C}_6\text{H}_7\text{O}_2-(\text{OCH}_3)_2 \cdot 516$
COCH <sub>3</sub> after acetylation, per cent	7.60	13.1	18.8	34.60
COCH <sub>3</sub> based on theoretical formula, per cent	8.60	13.0	19.4	35.10
Acetic acid found, per cent	52.00	44.0	37.0	14.60
Acetic acid based on theoretical formula, per cent	50.50	44.5	35.7	14.10

TABLE VII (Continued)

Product	1	2	3	4
Soluble in acetone, per cent	51.7	51.8	71.5	55.4
COH <sub>3</sub> in the insoluble portion, per cent	1.98	7.9	13.8	39.9
COH <sub>3</sub> in the soluble portion, per cent	12.40	17.7	19.7	29.5
Yield - per cent of theoretical	86.5	91.0	91.5	90.0

\* Based on the methoxyl content before acetylation and on the assumption that three hydroxyl groups per glucose unit in the final product are substituted. For example, in case of Product 1, let  $\bar{x}$  = number of methoxyl groups, then  $3 - \bar{x}$  = number of acetyl groups. In case of the methylated cellulose before acetylation:

$$\frac{(\bar{x})(\text{COH}_3)(100)}{162 + \bar{x}(\text{OH}_2)} = 13.74\% \text{ methoxyl} \quad \text{or} \quad \frac{(\bar{x})(\bar{y})(100)}{162 + (\bar{x})(14)} = 13.74\% \text{ methoxyl}$$

$\bar{x} = .743$  = number of methoxyl groups theoretically present in the final product

$\bar{y} = 2.257$  = number of acetyl groups theoretically present in the final product

Although none of these compounds were 100 per cent soluble in acetone, analysis of the acetone-soluble and -insoluble portions still reveals much concerning the solubility of the cellulosic material during methylation of an acetone-soluble acetate in acetone solution.

It is seen that the insoluble portions of Products 1 and 2 are rather low in methoxyl content and should, therefore, be high in acetyl content. This would not be surprising if one considers that highly acetylated celluloses are, in general, not soluble in acetone. The insoluble portion of Product 3 may be a combination of material representing a high acetyl and a low methoxyl content. Inversely, when the methoxyl content is high and the acetyl content low, the product is again insoluble, as is the case of the insoluble portions of Product 4. This is in accord with the fact that, in general, methylcellulose of any methoxyl content is insoluble in acetone.

Thus the results indicate, in general, that completely substituted methylcellulose acetates will be soluble in acetone except those portions that possess (1) low methoxyl (high acetyl) and (2) high methoxyl (low acetyl) contents. The reason that complete solubility was not shown by the methylcellulose acetates prepared here is probably due to the fact that the methods used resulted in very heterogeneous products which still contained varying amounts of the two above-mentioned portions. The insoluble portion (1) would probably not come into consideration in connection with the

solubilities of the methylcellulose acetates possibly present during methylation. Acetone-soluble acetates are already partially deacetylated so that the insoluble products, such as Product 1, probably do not exist. However, the products in the class of Product 2 may exist in the methylation reaction as it proceeds toward a product of high methoxyl and low acetyl contents. This shows that precipitation would take place before methylation and deacetylation were complete. The final methylation then must take place upon a finely precipitated cellulosic material.

Efforts to Bring the Sodium Hydroxide in Closer Contact with an Acetate Dissolved in Acetone. In view of the fact that globulation slows down the rate of methylation, it was logical to study possibilities of dispersing the globules or of preventing their formation from the start.

It was attempted to do this by adding the sodium hydroxide in the form of a finely atomized spray instead of allowing it to drop freely from a separatory funnel. Such a condition should bring about better contact between the sodium hydroxide and the acetone solution. Atomization was accomplished by drawing out the outlet tube of the separatory funnel to a capillary. Another capillary, through which a stream of air was blown, was then placed alongside the first capillary so that the jet of air disintegrated a fine stream of sodium hydroxide solution. Such a device produced a very fine spray which could be introduced into the methylation mixture. Yet the formation of globules could not be avoided, although they



were much smaller. The resultant methoxyl content was 41.5 per cent--i.e., no higher than when no precautions to minimize globulation were taken (44.65 per cent).

In view of other experiments which seemed to promise more success, further attempts of preventing the formation of globules or of dispersing them were omitted.

#### METHYLATION OF CELLULOSE IN SOLUTION

If it is probable that the good results obtained by methylating cellulose acetate dissolved in acetone are due to the elimination of nearly all of the solid phase for the greater part of the methylation reaction, the same effect should be produced by methylation of an unacetylated cellulose dissolved in a medium, unless chemical activation caused by the presence of acetate groups actually exist. Cellulose dispersed in a quaternary ammonium base is a suitable material for such a reaction. Here we not only may eliminate the solid phase for at least a considerable portion of the reaction, but one liquid phase as well, since the organic base itself will take the place of the inorganic base. The material used here (previously described as Material 5) was a solution of wood pulp in a 40 per cent aqueous solution of trimethylbenzylammonium hydroxide. The cellulose content was 1.9 per cent. In some cases solutions prepared in the laboratory were used.

Information available concerning the methylation of cellulose in solution applies only to the preparation of water-soluble

products of low methoxyl contents (Beck, 11). No attempt at exhaustive methylation nor a study of the effect of various conditions upon the reaction have been reported. In the present work it was necessary to study some of the various factors involved, so that experimental procedures could be developed which would represent optimum conditions for exhaustive methylation of cellulose in solution.

The factors studied were as follows: (1) reaction temperature, (2) cellulose concentration, (3) time of reaction after addition of methylating agent, and (4) rate of addition of methylating agents.

For this purpose a series of methylations were carried out in which one factor at a time would be varied. The experimental conditions and results are summarized in Table VIII.

In experiments T-a through T-d, 151.5 grams of the Triton B cellulose solution containing 3.9 grams of cellulose were placed in a 400-cc. Tallform beaker surrounded by a water bath. A small variable speed stirrer was then introduced. The propeller of this stirrer was as large as the dimensions of the beaker permitted and was shaped so that the material was forced downward at the center. With such a propeller, efficient stirring may be obtained at a slow rate of speed. If a high speed is used, foaming may become critical because air is whipped into the mixture. At a temperature of 25° C., 24 cc. of dimethyl sulfate were added drop by drop at the rate of 4 cc. per ten minutes. This quantity of dimethyl sulfate was chosen, because it represented a good part of the maximum amount which could

TABLE VIII

## FERTILIZATION OF CHLOROPHYLL IN TILTON 3

Expt- iment	Di- methyl Sulfate cc.	Rate of Addition of Dimethyl Sulfate cc. per 10 min.	Time of Stirring after Ad- dition of Temper- ature Dimethyl Sulfate °C.	Initial Concen- tration of Cellu- lose in Tilton 3 %	Friton 3 Added cc.	Manner of Addition	Percent- age OCH <sub>3</sub> of Product	Remarks
2-a	24	4	2 hr.	25	3.9	0	26.3	Product isolated by means of pre- cipitation with acetone
2-b	24	4	2 hr.	25	1	450	7.17	Product isolated by means of pre- cipitation with acetone
2-c	24	4	overnight	25	3.9	0	26.9	Product isolated by means of pre- cipitation with acetone
2-d	24	4	2 hr.	55-60	3.9	0	22.6	Product isolated by means of pre- cipitation with acetone
2-e	12	12	2 hr.	25	3.9	0	12.8	Product isolated by means of pre- cipitation with acetone

TABLE VIII (Continued)

Experiment	Di-methyl Sulfate cc.	Date of Addition of Dimethyl Sulfate cc. per 10 min.	Time of Stirring after Addition of Dimethyl Sulfate	Temperature cc.	Initial Concentration of Cellulose in Triton B %	Triton B Added cc.	Manner of Addition	Percent-age of Product	Remarks
2-1	36	12	2 hr.	25	3.9	0	-	11.9	Product isolated by means of precipitation with acetone
2-j	24	4	2 hr.	25	3.9	50	added after 30 min. to facilitate stirring	13.6	Product isolated by means of precipitation with acetone
2-g	24	4	2 hr.	25	3.9	50	added after 30 min. to facilitate stirring	13.6	Product isolated by means of precipitation with acetone
2-f	120	4	overnight	25	3.9	100	50-cc. portions after 1 1/2 hr.	19.8	Filtered directly without use of acetone

*Cellulose compound in great amount*

TABLE VIII (Continued)

Experi- ment	Di- methyl Sulfate cc.	Rate of Addition of Dimethyl Sulfate cc. per 10 min.	Time of stirring after ad- dition of Dimethyl Sulfate	Temper- ature °C.	Initial Concen- tration of Collu- lose in Friton 3 %	Friton 3 Added cc.	Number of Addition	Percent- age CO <sub>2</sub> ; of Product	Remarks
2-g	180	4	stirred 2 hr. stood overnight	25	3.9	600	dropwise after ½ cc. di- methyl sulfate was added	79.8	Filtered direct- ly without use of acetone
2-h	180	12	2 hr.	25	3.9	600	dropwise after ½ cc. di- methyl sulfate was added	79.5	Filtered direct- ly without use of acetone
2-b-1	24	4	2 hr.	25	remethylation of 2-h, 150 cc. Friton 3 added at first			40.6	Filtered direct- ly without use of acetone
2-a	180	12	2 hr.	25	3.9	600 cc. 2. ½ M NaOH substituted for Fri- ton 3 added dropwise		79.5	Filtered direct- ly without use of acetone
2-c	120	12	0	55	3.9	50	at begin- ning, 120 cc. ½ M NaOH	72.8	Filtered hot

TABLE VIII (Continued)

Expt- Invent	Date of Addition of Dimethyl Sulfate cc. per 10 min.	Time of Stirring after Ad- dition of Dimethyl Sulfate	Temper- ature °C.	Initial Concen- tration of Cellu- lose in Triton B Added cc.	Percent- age OOH, of Product	Remarks
2-p	120	12	overnight -2 to +5	3.9	0	at begin- ning, 320 cc. 30% NaOH
2-q	180	12	2 hr.	3.9	600	Filtered direct- ly without use of acetone
2-r	180	12	2 hr. -2 to +5 stood overnight	3.9	700	Filtered direct- ly without use of acetone
2-s	120	24	2 hr. -30 to -80 stood overnight	3.9	700	Filtered direct- ly without ad- dition of acetone
2-t	180	12	overnight -2 to +5	3.9	400	Filtered direct- ly without ad- dition of acetone

Cellulose solution prepared in Triton B from acetone-soluble cellulose acetate - Material 3

2-t	180	12	overnight -2 to +5	3.9	400	Filtered direct- ly without ad- dition of acetone
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be added without complete neutralization of the existing organic base. At the end of the methylation the remaining Triton B was neutralized with dilute hydrochloric acid. No precipitate was formed at this stage, but a white flocculent precipitate appeared when the volume was brought up to 2 liters by the slow addition of acetone, accompanied by moderate mechanical stirring. This cellulosic material could then be collected on a 9-cm. Büchner funnel with the aid of suction. It was washed on the filter with acetone, mixed thoroughly in a Hamilton Beach Model 25 malted milk mixer with 200-cc. portions of acetone. The residue was dried in a vacuum desiccator over calcium chloride to a white crumbly solid which could be powdered. (If allowed to dry in the open air, condensation of water owing to cooling effects of the evaporating acetone will give a sticky and even gelatinous material in case of water-soluble products.)

Variation of the conditions resulted in different effects as shown in Table VIII. In general, it may be said that it is better to work at normal rather than higher temperatures and that there is very slight advantage to prolonged stirring after complete addition of the methylating agent.

#### Experiments T-a and T-b

A 1 per cent solution of cellulose, produced by the addition of more Triton B, does not methylate nearly as well as a 3.9 per cent solution, only 7.17 per cent methoxyl being obtained compared with about 23 to 27 per cent for the higher concentration. This shows that

in cases where greater quantities of the methylating agent is to be used and addition of more Triton is necessary in order to maintain alkalinity, it would be best to add this Triton as needed, rather than at the beginning of the methylation. In all experiments of this series the methylated products remained in solution throughout the whole procedure.

#### Experiments T-2 and T-1

The quantity of dimethyl sulfate was varied in these experiments. Again, at the end of the methylation procedure, the products were still dissolved in the liquid, which shows that the reaction takes place upon a dissolved cellulose at least thus far--i. e., up to the introduction of about 12 per cent methoxyl.

#### Experiment T-1

The experiments thus far have dealt with methylation of cellulose dissolved in Triton. It was thought to be of interest to know exactly what effect this state of solution has upon the methylation. A direct comparison may be obtained from consideration of T-1. Here 6.06 grams of cotton linters were suspended in 145 grams of Triton B and methylation was begun at once without solution of the cellulose. (Cotton linters are very difficult to dissolve in Triton B. Even under the most vigorous agitation with a "Lightnin'" mixer, several days may be required to bring about solution.) Although partial solution of the cellulose material occurred during the reaction, the low methoxyl content of the product (13.6 per cent), when compared



with that of the product resulting from Experiment T-a (methoxyl content, 26.3) shows at once the beneficial effects of having the cellulose completely dissolved in the Triton B.

#### Experiment T-f

In the previous experiments, the amount of dimethyl sulfate had been limited to 24 cc. in order to ensure alkaline reaction under the conditions chosen. It was likely that this amount did not represent the necessary excess to produce high methylation. Therefore, in the present experiment 120 cc. of dimethyl sulfate were used. This necessitated an addition of the base. Before this was added, it had been observed that the base available in the 3.9 per cent solution became neutralized after 36 to 40 cc. of dimethyl sulfate had been added. In contrast to the previous experiments, this time--i.e., using 120 cc. of dimethyl sulfate--the product of reaction had precipitated at the end of the operation and could therefore be filtered off directly (without the addition of acetone) on a 9-cm. Mohner funnel with the aid of suction. It was washed thoroughly with hot water and acetone and dried as previously described. The beneficial effect of the excess of dimethyl sulfate is shown in the increased methoxyl content of 39.8 per cent.

#### Experiments T-g and T-h

In Experiment T-g, still greater amounts of dimethyl sulfate and Triton B were used. The latter agent was also added dropwise to make sure that no interruption in maintaining alkalinity occurred.

Experiment T-h showed that it made practically no difference if the rate of addition of dimethyl sulfate was increased and the prolonged stirring after addition eliminated.

#### Experiment T-h-1

The product from T-h was suspended in Triton B (in which it was insoluble) and remethylated. The methoxyl content of 40.6 (an increase from 39.5) per cent shows that such remethylation possessed little if any advantage over the one methylation operation; nor is there any advantage to be seen in comparing these results with those which were obtained when fibrous cellulose was methylated and remethylated by the usual procedure. Further, there was little reason to expect that more than one remethylation would bring the methoxyl content up to the theoretical since such methylation would take place upon solid methylated cellulose.

#### Experiments T-n, T-p, and T-e

Replacing the additional amount of Triton B by sodium hydroxide solution of the same normality as the Triton B, as shown in T-n, yielded identical results as T-h. Very similar results were also obtained with a 30 per cent sodium hydroxide solution if the temperature was kept low, as shown in Experiment T-p. If the temperature was higher, as in Experiment T-e, lower methoxyl values were obtained.

Experiments T-m, T-o, and T-s

Since previous experiments indicated that lower temperatures are beneficial for the methylation of cellulose dissolved in Triton B, Experiments T-m, T-o, and T-s were carried out as indicated in the table. It was found that at a temperature from  $-2$  to  $+5^{\circ}$  C. a value of 43.3 per cent methoxyl could be reached. When the same reaction was carried out at a temperature of  $-20$  to  $-40^{\circ}$  C. (which is the lowest temperature possible without freezing the mixture), as in T-s, a value of 43.5 per cent methoxyl was obtained. Since these results were obtained on one methylation (as were the others, if not otherwise specified), it may be regarded as the highest value ever reported for methylcellulose prepared by only one methylation from fibrous cellulose which had not been converted into a derivative. This is so, even if it is considered that the cellulosic material contained in the Triton solution was wood pulp--i. e., a material of a lower degree of polymerization than cotton linters. The degree of polymerization of the product from T-m was 164 (corresponding to a molecular weight of 26,500), which compares quite well with that of products obtained from cellulose acetates (see page 11). A brief consideration of the results discussed earlier leads to the conclusion that a marked influence of the degree of polymerization can only be expected if the latter were much lower. It should be added here that the figure 164 was found on the product which had been precipitated from its solution in Triton B. Since it is likely that the original wood pulp used had a higher degree of polymerization, it is probable that the material was

degraded while being dissolved or while being kept in solution. This would confirm the observation made by other investigators.

#### Experiment T-r

In Experiment T-r, 10 grams of a commercial acetone-soluble acetate (Material 3) were dissolved in 145 grams of Triton B and methylated as shown in Table VIII. The material was completely deacetylated when it dissolved in the strong base and before the methylation was started. This is true, since it was shown experimentally that the Triton B may be substituted for sodium hydroxide in the determination of acetyl groups by alkaline saponification methods. However, the methoxyl content obtained was not higher than that obtained in the case where unacetylated cellulose was the starting material, as in Experiments T-a and T-e, but lower, namely, 42.7 per cent. Thus, we may conclude that there is definitely no other advantage in the use of cellulose acetate as a starting material than that of improved physical conditions.

When comparing the behavior of the cellulosic materials--the acetate dissolved in acetone and the cellulose dissolved in the organic base--we note great similarity. In both cases, the greater part of the reaction occurs on the cellulosic material which is in solution; in both cases, the latter part of the reaction, where the methylated products become more and more insoluble in their respective solvents, proceeds on solid (although finely divided) materials. In this way the speed of reaction decreases markedly. Thus, the result obtained with unacetylated cellulose in solution supports the previously

expressed opinion, according to which the advantage of using an acetone-soluble acetate as a starting material is due to the fact that the reaction proceeds to a large extent on cellulose in the state of solution. From this point of view, both methods appear to be equivalent. In pursuing this line of thought, one would expect to be able to overcome the obstacle which becomes noticeable during the latter part of the reaction by preventing the reaction product--both the acetate and the unacetylated cellulose--from precipitating--i. e., by keeping the products in solution. If this could be done, better results would surely be obtained.

## SUMMARY

## THE ROLE OF ACETYL GROUPS IN CELLULOSE DURING METHYLATION

The literature reveals the fact that it is difficult, if not impossible, to methylate native cellulose to the theoretical methoxyl content of the tri-ether. This theoretical value, however, may be obtained if cellulose is used in the form of its acetate.

It has been suggested that this result might be due to activation of the hydroxyl groups--i.e., the acetyl groups would be more easily substituted than the former.

It is likely that the acetates which are reported to have been converted into trimethylcellulose were of a low degree of polymerization, and this suggests that the result is due to degradation of the cellulose because the number of hydroxyls is thereby increased.

The fact that some of the investigators carried out the methylation reaction on acetates dissolved in acetone suggests that it might be the state of solution rather than activation which is responsible for the better results.

Degradation of Cellulose as a Reason for Increased  
Degree of Methylation

It was not possible to reach the theoretical methoxyl content with acetylated cellulose. The highest value obtained with an acetate prepared in the laboratory was, after three methylations,

44.5 per cent, which did not increase upon a further methylation (the theoretical value is 45.6 per cent). This result does not confirm that obtained by Haworth and co-workers (2, 3), but it does confirm the results of various subsequent workers who used Haworth's method. A commercial acetate dissolved in acetone gave practically the same results, namely, 44.8 per cent.

However, when a highly methylated cellulose (44.5 per cent) was again acetylated and then remethylated, almost the theoretical methoxyl content (45.3 per cent) was obtained. Since the acetate, after reacetylation, had a very low degree of polymerization it is very likely that this high value was due to degradation which the cellulose suffered during reacetylation. This result appears to confirm Karrer and Escher's concept (4) that the theoretical value can be reached only on cellulose in a state of degradation. However, degradation has to be quite considerable, otherwise the corresponding increase of hydroxyl groups will have hardly any effect on the result of methylation. This is shown by a calculation of the magnitude of this effect (see page 37).

Whereas the main degradation occurred during the acetylation process proper, an additional decrease of chain length took place during saponification--i.e., while the acetyl content of the acetate in the acetylation mixture was being reduced to the point at which the acetate becomes acetone soluble. Correspondingly, the triacetate which was isolated from the acetylation mixture possessed a higher degree of polymerization than the acetone-soluble acetate; the

latter was very nearly the same as that of a commercial acetone-soluble acetate. This is in accord with observations of Yarsley (13) who found that the viscosity of the partially saponified acetates were generally lower than that of the parent triacetate.

Similarly, if acetylation was carried out under mild conditions in which the cellulose maintained its fibrous form, the degree of polymerization of the resulting acetate was appreciably higher than that of the nonfibrous triacetate. It is likely that the acetate of limited acetyl content which had been prepared by partial acetylation with acetic anhydride and pyridine, without the use of an acid catalyst, possessed the highest degree of polymerization of all acetates used.

The degree of polymerization of the methylcellulose samples prepared from the acetone-soluble acetates during this investigation, with the exception of one mentioned above, ranged from 120 to 2<sup>nd</sup>—i. e., about 1/10 to 1/15 of that of the original cellulose. The data are compiled in Table IX. This table also contains the results of the previously quoted investigators.

Thus, the possibility that cellulose in the form of its acetate reaches the theoretical methoxyl content because the cellulose constituent is in a state of degradation seems to exist only in cases in which degradation has actually gone very far. However, when this is not so, degradation as a cause of increased methoxyl content appears to be practically eliminated.



TABLE IX

## EXHAUSTIVE METHYLATION OF CELLULOSE ACETATES

Starting Material	Degree of Polymerization	Maximum Methoxyl Content of Product %	Degree of Polymerization of Product	Investigators	Remarks
Acetone-soluble cellulose acetate, Material 2a	171	44.75	120	Author	Standard procedure, i.e., by method of Haworth, Hirst, and Thomas (2)
Acetone-soluble cellulose acetate, Material 2b	142	44.50	130	Author	Standard procedure, i.e., by method of Haworth, Hirst, and Thomas (2)
Commercial acetone-soluble cellulose acetate, Material 3	162	44.80	172	Author	Standard procedure, i.e., by method of Haworth, Hirst, and Thomas (2)
Acetone-soluble acetate from cotton linters	-	45.6	-	Haworth, Hirst and Thomas (2)	Standard procedure, i.e., by method of Haworth, Hirst, and Thomas (2)
Acetone-soluble acetate from "good grade of cellulose"	-	45.0	-	Haworth and Machemer (1)	Standard procedure, i.e., by method of Haworth, Hirst, and Thomas (2)

TABLE IX (Continued)

Starting Material	Degree of Polymerization	Maximum Methoxyl Content of Product %	Degree of Polymerization of Product	Investigators	Remarks
Commercial acetone-soluble acetate (Cellite)	-	42.0	-	Hess and coworkers (8)	Standard procedure, i.e., by method of Henth, Hirst, and Thomas (2)
Acetone-soluble cellulose acetate prepared from wood pulp	-	45.6	-	Sperin (22)	Standard procedure, i.e., by method of Henth, Hirst, and Thomas (2)
Acetone-soluble cellulose acetate from cotton linters	-	42.2	-	Karrer and Facher (4)	Standard procedure, i.e., by method of Henth, Hirst, and Thomas (2)
Commercial acetone-soluble acetate	350	43.44	-	Wolfram, Sweden, and Lassettre (20)	Standard procedure, i.e., by method of Henth, Hirst, and Thomas (2)
Acetone-soluble acetates from cotton	13-150	44.41	-	Staudinger and Scholz (21)	Standard procedure, except at 20° in place of 55°

\* Result of one methylation, i.e., product was not exhaustively methylated.

TABLE II (Continued)

Starting Material	Degree of Polymerization	Maximum Methoxyl Content of Product %	Degree of Polymerization of Product	Investigator	Remarks
Highly methylated cellulose ( <u>see page 74</u> )	228	45.70	70	Author	Acetylated to give product of degree of polymerization of 17, then methylated by standard procedure
Highly methylated cellulose ( <u>see page 74</u> )	258	45.00	510	Author	Acetylated to give product of degree of polymerization of 61, then remethylated by standard procedure
Cellulose triacetate from cotton linters	274	47.91	274	Author	Methylated by standard procedure but was not in solution
Dimethyl cellulose monoacetate from viscose	-	45.42	-	Henzer and Hiemer (1)	Not done according to standard procedure above. Solid material methylated without the use of acetone
Cellulose triacetate from cotton	-	44.98	-	Henzer and Hiemer (1)	Not done according to standard procedure above. Solid material methylated without the use of acetone

Activation of Hydroxyl Groups as a Cause  
for Improved Methylation

If activation of the hydroxyl groups of the cellulose by way of acetylation were the cause for reaching the theoretical methoxyl content, the triacetate in which all three hydroxyl groups per glucose residue must be assumed to be acetylated, ought easily to be converted into trimethylcellulose. This, however, was not the case. As was shown on triacetates of varied degree of polymerisation, the methoxyl content remained far below the theoretical requirements. In view of the results obtained on the triacetates, it was not surprising that diacetates behaved in the same way.

The failure to introduce into cellulose without difficulty the theoretical number of methyl groups after the theoretical number of acetyl groups had once been introduced remains hard to understand, unless one postulates that the hydroxyl groups are less reactive to methylation than to acetylation, no matter whether they react as such or in the form of acetyl groups--i. e., whether or not the intramolecular system of the fiber has been made more accessible by way of acetylation.

Physical Conditions as a Cause of Improved Methylation

The acetone-soluble acetate dissolved in acetone took up in one methylation almost 29 per cent more methoxyl than fibrous cellulose under the same conditions. However, when the same acetone-soluble acetate was methylated without being dissolved in acetone,

it took up almost 40 per cent less methoxyl than in the dissolved state. Since the probability that degradation and activation as possible causes for increased methoxyl content have been greatly reduced, the above-mentioned facts seem to indicate that it is the state of solution which is responsible for the improved results that are obtained by using cellulose in the form of its acetone-soluble acetate dissolved in acetone.

Although the state of solution does not exist throughout the whole process of operation, the reaction product becoming more and more insoluble in the acetone-methylation mixture, yet the reaction, now proceeding on the precipitated reaction product, is still more efficient than it is with cellulose in fibrous form. This conclusion is drawn by a comparison of the results which were obtained on a dried fibrous triacetate with the same product in the form of a fine precipitate, the methoxyl content of the latter being 76 per cent higher than that of the former. The same beneficial effect of the physical state in which the cellulosic material is exposed to the methylating agents is seen from a comparison of the results on a finely precipitated nonfibrous triacetate with those on the same material in the form of a dry powder.

An attempt to utilize such improved physical conditions on cellulose itself was unsuccessful since the material (regenerated cellulose), although originally in a state of fine subdivision, agglomerated and gelatinized under the influence of the methylating agents under the conditions used. The fact that such disturbances

did not occur when utilizing the improved physical conditions in the case of the acetate may be valued as an additional advantage in using the latter. No doubt, the reason for this difference in the behavior of the two types of cellulosic material lies in the presence or absence of substituted hydroxyl groups. This is further borne out by the fact that the regenerated cellulose lost its gelatinous character toward the end of the reaction and became well suspended in the agents, similarly as though the acetate had been the starting material. When this stage was reached, methylation became more efficient. Thus, finely divided cellulose regenerated from an acetone-soluble acetate yielded a product with 27.8 per cent methoxyl content after one methylation and with 38.4 per cent after a second methylation. Likewise, very finely ground pulp (chemically unmodified) yielded a product with a methoxyl content of 16 per cent after one methylation and 35.7 per cent after two methylations.

Summing up the results discussed so far, it appears quite certain that the advantage observed in the methylation of cellulose in the form of its acetate is due neither to degradation nor to activation, but to the improved physical conditions under which the reaction takes place.

#### THE RELATION BETWEEN PHYSICAL PHENOMENON OBSERVED DURING THE REACTION AND THE RATE OF DEACETYLATION AND METHYLATION OF CELLULOSE ACETATE DISSOLVED IN ACETONE

Contrary to anticipation, the rate of methylation of the acetate dissolved in acetone was slow at the beginning of the reaction,

even slower than on fibrous unacetylated cellulose. This result is explained by the observation that the sodium hydroxide solution, in spite of efficient stirring, does not mix with the acetone solution of the acetate, the former separating in the form of globules. After a while, however, the alkali globules break up and the mixture acquires the appearance of an emulsion. As soon as the contact between the alkali and the acetate was established, the rate of methylation increased rapidly. With this increase coincided a change of the emulsion into a suspension of a finely divided precipitate within the methylation mixture. But soon after, the rate of methylation slowed down considerably and remained so, apparently, indefinitely. This interpretation of the course of the reaction is also supported by the type of the curve representing the heat generated during the reaction as plotted against time.

Difficulties were encountered in following the rate of deacetylation because the products of reaction, isolated at certain time intervals, lost their acetyl groups very rapidly while they were being prepared for analysis. It was shown that this occurred upon neutralisation of the excess alkali, and it would also probably occur during the usual operations of filtering and washing. However, from the results of a number of blank experiments it is very probable that, while the alkali globules existed in the methylation mixture, most of the acetyl groups were still in combination with the cellulose and were saponified only if and when contact was established.

That these conclusions are correct is seen from the results

obtained when the process of methylation was followed by utilising the experience gained on the blank experiments. In the earlier stages of methylation the alkali globules could be separated from the solution by filtration. It was found that the acetone solution contained the bulk of the reaction product with most of its acetyl groups intact. As methylation proceeded, separation was no longer possible, and the product of the reaction was shown to have lost most of its acetyl groups.

While the acetate is being methylated it passes through a number of intermediate stages, these intermediates being products of decreasing acetyl and increasing methoxyl contents and, therefore, doubtless of varying solubilities in acetone. Results of experiments, in which some of the probable intermediates were prepared and their solubility in acetone determined, shed further light on the mechanism of the methylation reaction. The results of these experiments permit the contention that in the methylation mixture, precipitation takes place before all acetyl groups are saponified and that the final phase of the reaction thus occurs on a precipitate of high methoxyl and low acetyl contents.

Attempts to disperse the alkali globules and thus to establish contact between the alkali and the acetate in solution at the beginning of the reaction were not successful, but it would appear probable that such means could be found.



## METHYLATION OF CELLULOSE IN SOLUTION

If the advantage of using cellulose in the form of its acetate is due to the fact that the methylation reaction takes place, at least partly, on cellulosic material in solution, this advantage should be also obtained by using unacetylated cellulose in solution. At the same time the results would show whether the acetate offers, after all, any additional advantage. So far, methylation of cellulose in solution, for instance in a quaternary ammonium base, has been studied only in view of producing water-soluble methylcelluloses of the lowest possible methoxyl content. The aim of the present investigation was, of course, to reach the theoretical methoxyl content required for trimethylcellulose. The effect of various influences were studied and conditions were established by which the highest methoxyl content was obtainable. Most pronounced was the influence of temperature, lower temperature yielding a higher methoxyl content. But even under apparently the most favorable conditions, the methoxyl content reached only 43.3 per cent. Still, this value appears to be the highest ever reported for methylcellulose prepared by a single operation from fibrous cellulose--i.e., without using an intermediate derivative.

As regards the mechanism of methylation of cellulose in solution, there appears to be great similarity with the methylation of an acetone-soluble acetate. Here, also a great part of the reaction takes place on cellulose while it is in solution. During the latter part, however, the cellulosic material has to be reacted

upon while it is in the form of a precipitate, although in a finely divided state. This could be assumed to cause the slowing down of the reaction so that the methoxyl content remained (by about 2 per cent) below the theoretical value. If this were true, one ought to be able to introduce the last percentage of methyl groups if it were possible to find a solvent which would be capable of maintaining the cellulosic materials--i.e., the methyl-acetyl derivatives as well as the fibrous partially methylated cellulose--in solution throughout the whole operation.

As we have seen, it is the introduction of methyl groups which gradually leads to precipitation of the product of reaction. Moreover, it is likely that it is not alone the fact that the reaction continues on solid material which is responsible for the difficulty of introducing the last relatively small percentage of methyl. Some deliberation on the probable nature of the solid material seems to offer a direction in which an explanation might be found.

In the case where fibrous cellulose is dissolved in the organic base, it is surprising that not even this powerful agent is capable of keeping the product of reaction dispersed. Obviously, forces of expansion exerted by the organic base are not capable of overcoming the forces of cohesion which bind the chain molecules together in the partially methylated cellulose. It may be assumed that the forces of cohesion increase considerably on methylation.

This is illustrated by the behavior of partially methylated cellulose with sodium hydroxide solutions of mercerizing strength. For example, dimethylcellulose does not swell at all in caustic soda solution; it does not form an alkali cellulose compound and no xanthate (viscose) (see Houser and Hiemer (1)). This is due to the fact that the derivative above a certain methoxyl content becomes hydrophobic. Such a property ought to favor the development of cohesive forces between individual chain molecules--i.e., between hydroxyl groups not yet covered by methyl. On this assumption the difficulty of introducing the last percentage of methyl groups into a system, which may be regarded as an association of molecules having lost most of its hydrophilic properties and exhibiting strong forces of mutual attraction, could be quite well understood.

Such a conception would also be in accord with the observation that the introduction of more methyl into an already highly methylated product is facilitated by lowering the temperature, for at low temperatures the system regains some of its lost ability to swell in strong alkali.

Further work might be based on the conception explained above--i.e., on a search for ways and means of reducing the tendency of the partially methylated cellulose chains to develop such forces of mutual attraction which may be assumed to decrease considerably the reactivity of the intermediate product of reaction.

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