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TREATMENT OF CELLULOSE AND OXIDIZED CELLULOSE WITH ACETIC-SULFURIC ACID MIXTURES

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Introduction

It has previously been recorded in the literature that cellulose could be partially converted to the formic acid ester by the action of anhydrous formic acid.¹ Some years later it was shown by Malm and Clarke² that by heating cellulose with glacial acetic acid an acetylcellulose containing approximately one acetyl group for four $C_6H_{10}O_5$ groups could be obtained. This product contained from 6 to 7% of CH_3CO . A recent patent³ has claimed the preparation of a stable tri-formate of cellulose by the action of anhydrous formic acid and zinc chloride on cellulose.

It has been known since 1879⁴ that sulfuric acid is a powerful catalyst in the acetylation of cellulose. Therefore it appeared of interest to investigate the effect of acetic-sulfuric acid mixtures on cellulose. Since none of the previous workers, as far as could be ascertained, had used oxidized cellulose, it seemed that the extension of the investigation to include such products might also be of interest. The oxidation procedures employed were similar to those given in a paper by Murray, Staud and Gray⁵ in which definite oxygen equivalents per $C_6H_{10}O_5$ group were used.

As the method of acetyl determination usually employed appeared open to question for the analysis of the acetyl derivatives of oxidized celluloses, several of the preparations were also analyzed by another method in which the oxidation products were less likely to invalidate the results. The comparison of the data obtained by the two methods appears to be of possible interest.

Experimental

The cellulose employed in this investigation was high grade commercial processed cotton linters prepared by treatment of crude linters with alkali under pressure, followed by mild bleaching. The material had the following constants

Cuprammonium viscosity 9600 centipoises⁶

¹ E. C. Worden and L. Rutstein, *Kunststoffe*, **2**, 325 (1912).

² C. J. Malm and H. T. Clarke, *THIS JOURNAL*, **51**, 274 (1929).

³ British Patent 260,650, June 30, 1925.

⁴ Franchimont, *Compt. rend.*, **89**, 711-712 (1879).

⁵ Murray, Staud and Gray, *THIS JOURNAL*, **52**, 1508 (1930).

⁶ Determined by the method recommended by the Viscosity Committee of the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem. (Anal. Ed.)*, **1**, 49 (1929).

Alpha cellulose content.....	99.1% ⁷
Copper number.....	0.042 ⁸
Ash.....	0.168%
Moisture.....	3.37% ⁹

Oxidations.—(I) One hundred and sixty-two grams of cellulose (1 mole of $C_6H_{10}O_5$), which had been dried at 105° for sixteen hours, was placed in a solution consisting of 31.6 g. of potassium permanganate (Baker's Analyzed C. P.) ($1/2$ available oxygen atom per $C_6H_{10}O_5$) in six liters of normal phosphoric acid for six hours at 20–25°. After filtration on a Büchner funnel, the oxidized material was treated with a dilute solution of sodium bisulfite, approximately 1%, and washed with water until the filtrate after standing in contact with the oxidized cellulose for approximately sixteen hours was neutral to brom thymol blue.

(II) The same procedure was repeated using 63.2 g. of potassium permanganate (one available oxygen atom per $C_6H_{10}O_5$).

(III) One hundred and sixty-two grams of cellulose, dried at 105°, was placed in a solution consisting of 39.2 g. of 85% chromic oxide in six liters of water (CrO_3 content, 33.3 g., $1/2$ available oxygen atom per $C_6H_{10}O_5$) for twenty-four hours at 20–25°. The oxidized cellulose was then washed with water until the filtrate was neutral to brom thymol blue.

(IV) The same procedure was repeated using 156.8 g. of 85% chromic oxide (CrO_3 content 133.3 g., 2 available oxygen atoms per $C_6H_{10}O_5$).

All of the above oxidations were made in duplicate with an interval of several months between the first and second series.

TABLE I

WEIGHTS OF THE OXIDIZED CELLULOSE RECOVERED BY THE VARIOUS OXIDATIONS

Oxidation procedure	Weight in grams of starting material	Weight in grams of oxidized cellulose recovered	% loss
$KMnO_4$			
$1/2$ available oxygen atom per $C_6H_{10}O_5$ (6 hours, 20–25°)	I 162	150	7.4
	II 162	147	9.3
1 available oxygen atom per $C_6H_{10}O_5$ (6 hours, 20–25°)	I 162	138	14.8
	II 162	137	15.4
CrO_3			
$1/2$ available oxygen atom per $C_6H_{10}O_5$ (24 hours, 20–25°)	I 162	157	3.1
	II 162
2 available oxygen atoms per $C_6H_{10}O_5$ (24 hours, 20–25°)	I 162	160	1.2
	II 162

Treatment with Acetic-Sulfuric Acid Mixtures.—Fifty grams of oxidized cellulose from each of the treatments described above and 50 g. of unoxidized cellulose were dried at 55–60° for twenty-four hours and placed in 3-liter balloon flasks, each containing 1500 cc. of glacial acetic acid (99.6–99.8% CH_3COOH) and 15 cc. of concentrated sulfuric acid (specific gravity 1.84). After stoppering, the flasks were maintained at 20–25°

⁷ Determined by Method IV as recommended by the Alpha Cellulose Committee of the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem. (Anal. Ed.)*, 1, 52 (1929).

⁸ Determined by the method of Staud and Gray, *Ind. Eng. Chem.*, 17, 741 (1925).

⁹ Determined by drying for twelve hours at 105°.

with occasional shaking. Approximately seven gram samples were removed after various intervals of time. The maximum time of treatment was 335 hours.

The samples were washed with water until the wash water in contact with the products remained neutral to brom thymol blue for sixteen hours. In some cases the products were treated with dilute sodium bicarbonate solutions for a few minutes, in the early stages of washing, followed by washing to neutrality with distilled water.

After washing, the samples were dried at 55–60° for twenty-four to forty-eight hours. The products from the first series of oxidations were analyzed for acetyl content by the modified Knoevenagel method given below. Those from the second series were subjected to acetyl determination by two methods: (A) the modified Knoevenagel procedure and (B) a method for determining acetic acid in the presence of other acidic groups. These methods are given in detail below.

Acetyl Content of Cellulose and Oxidized Cellulose Treated with Acetic-Sulfuric Acid Mixtures

(A) **Modified Knoevenagel Method.**¹⁰—Approximately one-half gram samples weighed to the nearest centigram are placed in a weighing bottle and dried at 105° for at least four hours. They are then cooled in a desiccator and the bottle and contents weighed to one-tenth milligram. The dried material is transferred to a 250-cc. Erlenmeyer flask and the weight of the sample taken for analysis determined by difference.

Twenty cubic centimeters of 75% by weight aqueous ethanol is added and the flask placed in a 56 ± 1° bath for thirty minutes. Twenty cubic centimeters of *N*/2 sodium hydroxide is added and the flask again placed in the 56° bath for fifteen minutes, after which it is allowed to stand at 20–25° for twenty-four to forty-eight hours. The flasks are kept tightly stoppered during this period and the contents stirred occasionally by gentle shaking. The sides of the flasks are finally washed down with distilled water and the excess alkali is titrated with standard *N*/2 hydrochloric acid. The acetyl percentage is calculated by the formula

$$\text{Percentage acetyl} = \frac{\text{cc. of } N/2 \text{ NaOH used} \times 0.0215 \times 100}{\text{Weight of sample}}$$

(B) **Method for Determining Acetic Acid in the Presence of Other Acidic Groups.**¹¹—The neutral solutions obtained at the conclusion of analysis by the modified Knoevenagel method are transferred to a one-liter distilling flask and acidified with 25 cc. of 20% tartaric acid. Tartaric acid is used because it is strong enough to free acetic and formic acids from their salts, but not of sufficient strength to liberate hydrochloric and sulfuric acids. The volatile acids, which are freed from their salts in this way, are then steam distilled from the solutions. They are for the most part acetic and formic acids. One liter of distillate is usually required for their complete removal, which is determined by testing the distillate with litmus paper as it drops from the condenser and then distilling 200 to 300 cc. additional.

This distillate is then made alkaline with sodium carbonate and evaporated to dryness on a steam-bath. The alkaline residue is taken up with approximately 25 cc. of distilled water and to it are added 10 cc. of approximately *N*/10 potassium permanganate. The solution is heated on a steam-bath for a few minutes to assure complete oxidation of the formic acid. This solution is next acidified with dilute sulfuric acid

¹⁰ Knoevenagel, *Cellulosechemie*, 3, 119 (1922).

¹¹ "The Acid Value of Cellulose Fatty Acid Esters and a Rapid Method for the Analysis of Certain Cellulose Acetates," by T. F. Murray, Jr., C. J. Staud and H. LeB. Gray, to be published presently as Communication No. 461 from the Research Laboratories of the Eastman Kodak Company.

(15% by volume) and the excess potassium permanganate destroyed with a slight excess of *N*/10 oxalic acid. This excess of oxalic acid is in turn removed by *N*/10 potassium permanganate until a very faint pink color remains. The solution is then made faintly alkaline with 5% sodium hydroxide for the purpose of converting all acids into the sodium salts. Finally this solution is again acidified with 25 cc. of 20% tartaric acid, when again only those acids weaker than tartaric are freed from their salts. The acids volatile with steam are distilled as before. The distillate should contain only acetic and carbonic acids at this point. This distillate is refluxed for ten to fifteen minutes to remove the dissolved carbon dioxide, cooled to room temperature and the solution titrated with standard *N*/10 alkali using phenolphthalein as indicator. From the amount of alkali used, the amount of acetyl in the sample is calculated.

It is necessary to make a correction for acids in the reagents. This is done by carrying out the determination using water and the reagents only. This correction factor is expressed in centimeters of *N*/10 alkali and is applied before final calculation is made.

Acetyl Content of Products.—The values obtained by analysis of the various oxidized celluloses using the modified Knoevenagel method described above are given for the first series of oxidations in Table II.

TABLE II

Treatment, hours	Unoxidized cellulose, % acetyl		RESULTS OF ANALYSES Cellulose oxidized with CrO ₃ Available oxygen atoms per C ₆ H ₁₀ O ₅				Cellulose oxidized with KMnO ₄ Available oxygen atoms per C ₆ H ₁₀ O ₅			
	I	II	1/2		2		1/2		1	
			I	II	I	II	I	II	I	II
0	0.0		1.3	1.6	6.4	6.5	4.2	4.1	4.7	4.9
24	0.68	0.64	2.4	2.2	4.5	4.5	2.1	2.2	3.3	3.4
72	1.70	2.00	4.5	4.5	5.0	4.3	2.5	2.4	3.3	3.4
120	2.40	2.80	5.8	5.9	5.5	5.8	2.4	2.5	3.0	3.2
168	4.10	4.90	6.6	6.5	6.0	6.4	2.7	2.6	3.4	3.5
216	5.00	5.10	6.6	6.6	6.2	6.0	2.8	2.9	3.0	3.1
263	5.30	5.40	6.9	6.8	6.5	6.5	2.8	2.7	3.2	2.8
335	6.20	6.20	6.8	6.7	6.5	7.0	3.1	3.1	3.6	3.4

Determinations were made in duplicate and all values are given in Table II. The average values are given graphically in Fig. 1.

The values obtained upon analysis of the second series of oxidations are given in Table III and Fig. 2.

TABLE III

Treatment, hours	Unoxidized cellulose, % acetyl		RESULTS OF ANALYSES Cellulose oxidized with CrO ₃ Available oxygen atoms per C ₆ H ₁₀ O ₅				Cellulose oxidized with KMnO ₄ Available oxygen atoms per C ₆ H ₁₀ O ₅			
	I	II	1/2		2		1/2		1	
			I	II	I	II	I	II	I	II
0	0.0		2.6	2.8	8.6	8.4	5.6	5.7	6.6	6.4
44	3.8	3.8	6.1	6.1	7.8	...	4.2	3.8	4.5	5.4
95	5.5	5.5	6.7	7.3	8.5	8.2	4.2	4.4	5.1	5.6
162	7.4	7.4	8.8	8.8	8.7	8.4	4.3	4.5	6.1	6.1
210	8.2	8.4	7.8	7.8	8.4	8.5	5.4	4.9	6.3	6.9
258	8.3	7.8	7.9	7.9	8.8	8.9	4.9	4.8	6.4	6.1
330	8.9	8.2	8.0	8.0	9.1	9.3	4.8	4.9	6.2	6.1

Four samples from each of the groups analyzed by the modified Knoevenagel method, given in Table III, *i. e.*, the unoxidized cellulose and prod-

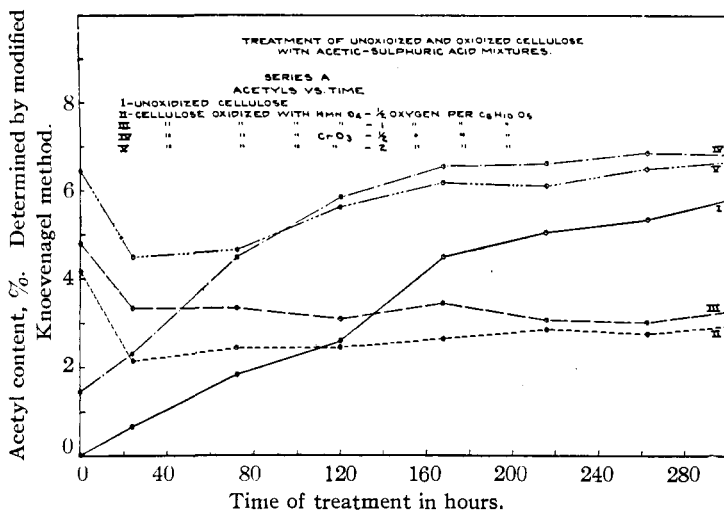


Fig. 1.

ucts from the second series of oxidation experiments after treatment with the acetic-sulfuric acid mixture, were also analyzed by the second method

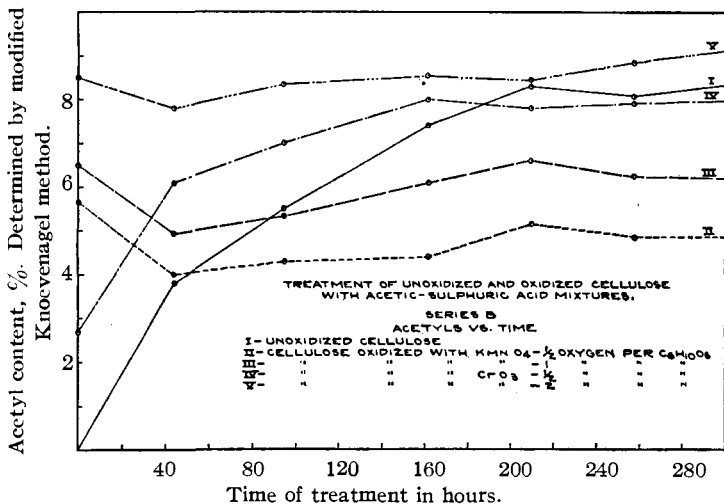


Fig. 2.

given above for the determination of acetic acid in the presence of acidic groups, which will hereinafter be called the "Distillation Method." The results are given in Table IV and Fig. 3.

TABLE IV

Treatment, hours	Unoxidized cellulose, % acetyl	RESULTS OF ANALYSES			
		Cellulose oxidized with CrO_3		Cellulose oxidized with KMnO_4	
		Available oxygen atoms per $\text{C}_6\text{H}_{10}\text{O}_5$		Available oxygen atoms per $\text{C}_6\text{H}_{10}\text{O}_5$	
		$\frac{1}{2}$	2	$\frac{1}{2}$	1
0	0.0	0.22	0.12	0.44	0.23
44	2.7	3.00	.23	0.50	0.28
162	6.2	5.10	.82	0.72	0.90
330	6.4	4.80	.51	1.63	1.35

The relationship of the severity of oxidation and the acetyl content of the products as determined by the distillation method is shown in Fig. 4.

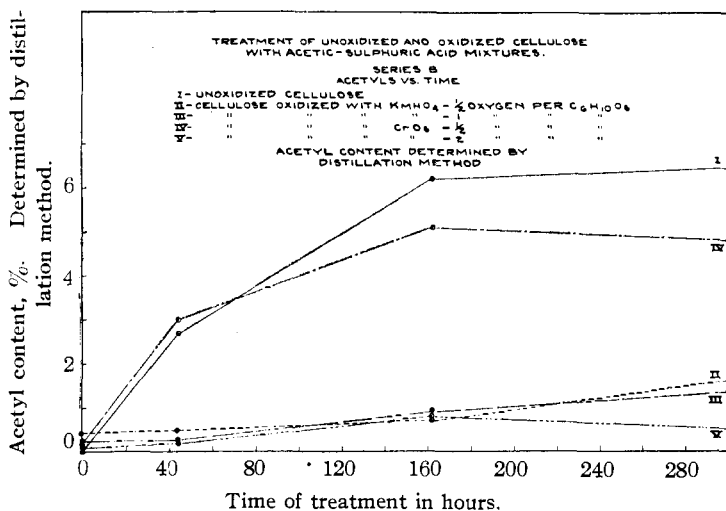


Fig. 3.

Discussion

From an examination of Table I it is seen that the yield of oxidized cellulose is an inverse function of the severity of the oxidizing solutions employed. This confirms the results of Hibbert and Parsons¹² and also that of Murray, Staud and Gray.⁵

When the results of acetyl determinations of the first and second series of unoxidized cellulose and oxidized celluloses, after treatment with acetic-sulfuric acid mixtures, are considered, as given in Tables II and III and in Figs. 1 and 2, at least three points are evident. First, when unoxidized cellulose is used, the acetyl content after 330 and 335 hours approximates that obtained by Malm and Clarke² by the action of boiling acetic acid on cellulose. This appears to be another indication that in the reaction between unoxidized cellulose and acetic acid, there is one hydroxyl group

¹² Hibbert and Parsons, *J. Soc. Chem. Ind.*, **44**, 473T (1925).

per $C_{24}H_{40}O_{20}$ which behaves in a different manner from the other eleven as indicated by the cellulose formula put forward by Gray.¹³

The second point is that in both series of experiments the acetyl content, as determined by the modified Knoevenagel method, of the materials which had been oxidized using chromium oxide, for 330 and 335 hours, approximates more closely that of the unoxidized cellulose. The third point is that the most vigorously oxidized celluloses show the least acetyl content.

The fact that in many cases the apparent acetyl contents of the starting materials were higher than values subsequently obtained and that these appeared to show correlation with the vigor of the oxidizing solution, led to the trial of the distillation method of determination of acetyl content. It seemed fairly obvious that during the oxidation groups showing acidic reaction had been produced in the cellulose which were of course titrated as acetyl content in the modified Knoevenagel method.

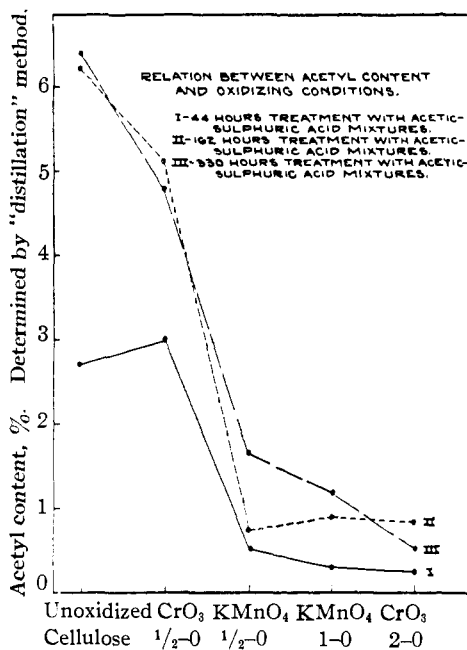


Fig. 4.

It was believed that the presence of combined sulfuric acid might be a factor in the results, but the results given in Table V do not indicate this.

TABLE V
PERCENTAGE OF COMBINED SULFURIC ACID

	Treatment with $CH_3COOH-H_2SO_4$		
	Before	After 44 hours	After 330 hours
Unoxidized cellulose	0.0	0.03	0.33
Cellulose oxidized, $\frac{1}{2}$ available oxygen atom per $C_6H_{10}O_5$ using CrO_3	.0	.08	.30
Cellulose oxidized, 2 available oxygen atoms per $C_6H_{10}O_5$ using CrO_3	.0	.07	.50
Cellulose oxidized, $\frac{1}{2}$ available oxygen atom per $C_6H_{10}O_5$ using $KMnO_4$.0	.08	.30
Cellulose oxidized, 1 available oxygen atom per $C_6H_{10}O_5$ using $KMnO_4$.0	.0	.24

When the distillation method was used in the analysis of the products,

¹³ Gray, *Ind. Eng. Chem.*, 18, 811 (1926).

the results given in Table IV and in Fig. 3 illustrate a striking difference from those obtained when the modified Knoevenagel method was used. Although the untreated materials did not give zero results, indicating the probable presence of other volatile materials of acid character not oxidized by potassium permanganate, the values are very much nearer zero and there is a much greater divergence between the acetyl content of the unoxidized and oxidized celluloses.

It is observed in this instance that the values for the acetyl content of the unoxidized cellulose after treatment with acetic-sulfuric acid mixture again approximate that of $C_{24}H_{39}O_{19}(O-CO-CH_3)$. It is also seen that the esterification is in an inverse ratio to the severity of the oxidizing conditions employed in the preparation of the oxidized cellulose, as shown in Fig. 4, which leads to the tentative conclusion that the hydroxyl group which is most readily acetylated is also probably the most easily oxidized.

Finally, the data obtained by the modified Knoevenagel method offer possible evidence that the acidic groups produced by the oxidation of cellulose are partially converted to non-acidic form by the action of the acetic-sulfuric acid mixture as indicated by the decreased values obtained after forty-four hours of treatment as compared with the apparent acetyl content of the starting materials as shown in Tables II and III and Figs. 1 and 2.

Summary

Cellulose in the form of cotton linters has been oxidized using chromic oxide in amounts of one-half and two available oxygen atoms per $C_6H_{10}O_5$ group and by potassium permanganate at concentrations of one-half and one available oxygen atom per $C_6H_{10}O_5$ group in *N* phosphoric acid.

The unoxidized and oxidized celluloses have been treated with acetic-sulfuric acid mixtures with the removal of samples at intervals during approximately 330 hours.

The products from the treatment of unoxidized and oxidized celluloses after treatment with acetic-sulfuric acid mixtures have been analyzed by two methods.

The results are given.

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