

were employed and the precision condenser readings were made more precise by methods such as suggested by Hobbs, Jacokes, and Gross.¹⁰

Acknowledgment is made of a grant from the Faculty Research Committee of the University of Pennsylvania which aided in purchase of equipment.

Summary

1. A scheme of capacity measurements at varying frequency has been applied to the com-

(10) Hobbs, Jacokes and Gross, *Rev. Sci. Instruments*, **11**, 126 (1940).

parison method of dielectric constant determination. The principal advantage of this scheme in the case of low dielectric constants is the elimination of certain calibration inaccuracies apt to be present in precision condenser readings made at fixed frequency.

2. The dielectric constant of carbon tetrachloride has been determined at six temperatures from 15 to 40°. The values owe most of their error to the uncertainty in the values of the standard, benzene.

PHILADELPHIA, PENNA.

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The Oxidation of Cellulose by Nitrogen Dioxide*

BY EDWARD C. YACKEL AND WILLIAM O. KENYON

Since the work of Witz¹ on the action of oxidizing agents on cellulose, a vast literature concerning oxidized cellulose has accumulated. A summary of this literature to 1922 has been compiled by Clifford and Fargher.² The oxidizing action on cellulose of numerous oxidants has been studied under widely varying conditions of temperature, pH, time of reaction and concentration. Space does not permit a summary of this phase of the subject, but the investigations of Hibbert and Parsons³ and of Heuser and Stöckigt⁴ illustrate the methods employed. Recently periodic acid has been studied as an oxidant for several carbohydrates.⁵

A rigorous comparison of the various oxidized celluloses reported in the literature is difficult because they are not definite chemical entities. However, two general types are recognized.⁶ One of these, the "methylene blue" type, has a high methylene blue absorption, a low copper number and a low alkali solubility; while the other, the "reducing type," has a low methylene blue number, a high reducing value and a high alkali solubility. An excellent and concise sum-

mary of the present status of the oxidation of cellulose has been given by Heuser.⁷

The major problem in studying oxidized celluloses is the difficulty of producing materials which are homogeneous in chemical and physical properties. Several of the oxidants employed are apparently not selective as to the particular hydroxyl groups of the anhydro-glucose unit in the cellulose molecules which are attacked. Many methods of oxidation are topochemical. When the oxidation is mild, the products usually consist of an oxidized portion and an unchanged residue of unreacted or only slightly modified cellulose. More drastic oxidation produces a larger proportion of oxidized material accompanied by increased degradation. Physical degradation accompanying the oxidation breaks up the cellulose fibers and usually the material is friable and powders easily.⁷

We have found that, under suitable conditions, cellulose may be readily oxidized by nitrogen dioxide to produce a new type of oxidized cellulose.⁸ This method of oxidation is readily controlled to produce oxidized celluloses of various carboxyl group contents. When the degree of oxidation is sufficiently high, the products dissolve rapidly and completely in dilute aqueous alkalis, for example, 2% aqueous sodium hydroxide. Even with high degrees of oxidation, the cellulose remains fibrous and is not friable.

(7) E. Heuser, "Organic Chemistry," H. Gilman, Editor, John Wiley and Sons, New York, N. Y., 1938, Vol. II, pp. 1556-1559.

(8) See U. S. Patent 2,232,990, E. C. Yackel and W. O. Kenyon, February 25, 1941.

* Presented before the Division of Cellulose Chemistry at the St. Louis Meeting of the American Chemical Society, April 10, 1941.

(1) G. Witz, *Bull. Soc. Ind. Mulhouse*, **43**, 334 (1883).

(2) P. H. Clifford and R. G. Fargher, *Shirley Inst. Mem.*, **1**, 118 (1922), and *J. Text. Inst.*, **13**, 189T (1922).

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

(4) E. Heuser and F. Stöckigt, *Cellulosechemie*, **3**, 61 (1922).

(5) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 2049 (1937); **60**, 989 (1938).

(6) J. T. Marsh and F. C. Wood, "An Introduction to the Chemistry of Cellulose," D. Van Nostrand Co., New York, N. Y., 1939, Chapter 8, pp. 153 *et seq.*

The present paper describes methods for oxidizing cellulose by nitrogen dioxide, the characteristics of these oxidized celluloses, and the methods for determining the carboxyl group contents. In a subsequent paper⁹ studies of the structure of this type of oxidized cellulose will be reported.

Experimental

Eastman Filtration Cotton (abbreviated as E. F. C.), a combed long fiber cellulose, was used in all experiments except oxidations 32-36 inclusive, Table VI, in which cotton linters were used. Analyses of the cotton linters and an average analysis of the various batches of E. F. C. are as follows:

	E. F. C.	Linters
Cuprammonium viscosity, cp. ¹⁰	5500	13,300
Copper number ¹¹	<0.1	
Alpha cellulose, % ¹²	>98.0	98.1
Ash ¹³	<0.1	
Moisture, % ¹⁴	3.0-4.0	4.3

The nitrogen dioxide (b. p. 21°) was freshly distilled from phosphorus pentoxide. The term nitrogen dioxide refers to the equilibrium mixture of nitrogen dioxide with its dimer nitrogen tetroxide.

Methods of Oxidation.—Two different methods, the static and the cyclic, were employed. In the former the apparatus of Fig. 1 was used. The oxidizing chamber A was connected to the nitrogen dioxide reservoir B, the size of A being appropriate to the amount of cellulose used (Table VI). After introducing the cellulose through C, sealing this off, and evacuating through D, the desired amount of nitrogen dioxide was placed in D and drawn into the apparatus. The apparatus was maintained at room temperature in the position shown, any unvaporized nitrogen dioxide collecting in C. At the end of the oxidation

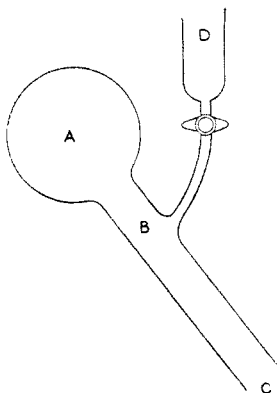


Fig. 1.—Apparatus for oxidation by static method.

period the bulk of the nitrogen oxides was removed by suction at D. The sealed end C was cut off, the apparatus filled with distilled water and the oxidized cellulose removed. It was washed with distilled water until the washings were no longer acidic, then air dried. The amount of oxidized cellulose was at least as great as the amount of cellulose used.

(9) C. C. Unruh and W. O. Kenyon, *THIS JOURNAL*, **63**, 127 (1941).

(10) Cellulose Division Am. Chem. Soc. method, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).

(11) C. J. Staud and H. LeB. Gray, *Ind. Eng. Chem.*, **17**, 741 (1925).

(12) Cellulose Division Am. Chem. Soc. method, *Ind. Eng. Chem., Anal. Ed.*, **1**, 52 (1929).

(13) By ignition.

(14) Determined by drying for sixteen hours at 105°.

This method proved inconvenient on a large scale due to the pressure of nitric oxide formed, and the cyclic method (Fig. 2) was devised. Fifty to 100 g. of well picked or fluffed cellulose was inserted into the 22.5-liter flask A, care being taken to avoid packing. In B were placed 250 g. of dry nitrogen dioxide and 150 g. of phosphorus pentoxide. Reservoir B was warmed by an electric bulb of low wattage. The gaseous nitrogen dioxide enters A through tube C. The spent gases pass through D to condenser E. Unreacted nitrogen dioxide condensed, was dried in B and recycled. Nitric oxide escaped through the condenser.

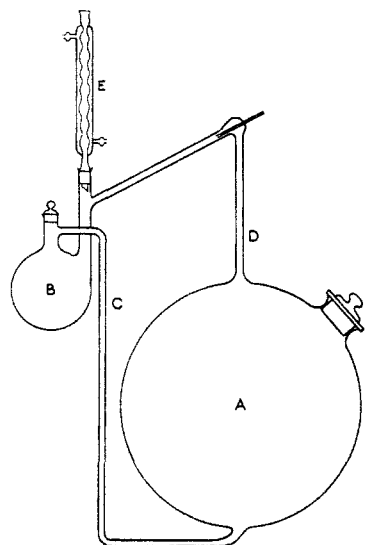


Fig. 2.—Apparatus for oxidation by cyclic method.

The internal temperature of A increased by ten to fifteen degrees at the start of the reaction but soon subsided. An internal temperature of 21°, or slightly less, gave the best results. Under these conditions, a green condensate appeared on the surface of the fibers. Too low a temperature may cause sufficient condensate to collect in C to interfere with circulation of gas, and excessive condensation on the fibers may produce a less uniform product. Uniformity of oxidation is aided by stirring the cellulose periodically through the opening F. Upon completion of the reaction, excess nitrogen dioxide was removed by a current of air, and the product was rinsed rapidly in distilled water. It was washed as described in the static method. The amount of oxidized cellulose was at least as great as the amount of cellulose used. The degree of oxidation is controlled by the time of oxidation. A more extended investigation of this cyclic method is given in the succeeding paper.⁹

Analytical Methods.—The first method tried was as follows. One-half-gram samples of the oxidized cellulose were treated with 20 cc. of 75% aqueous alcohol and 20 cc. of 0.5 N aqueous sodium hydroxide solution. After standing for a time, the excess alkali was titrated and the carboxyl group content was calculated from alkali consumption. This method gave variable results, depending on the time of contact with the alkali and on the temperature. At 25° one sample of oxidized cellulose showed 11.8% of carboxyl after standing for twenty-seven minutes in the alkali, and 13.4% carboxyl after two hours' contact.

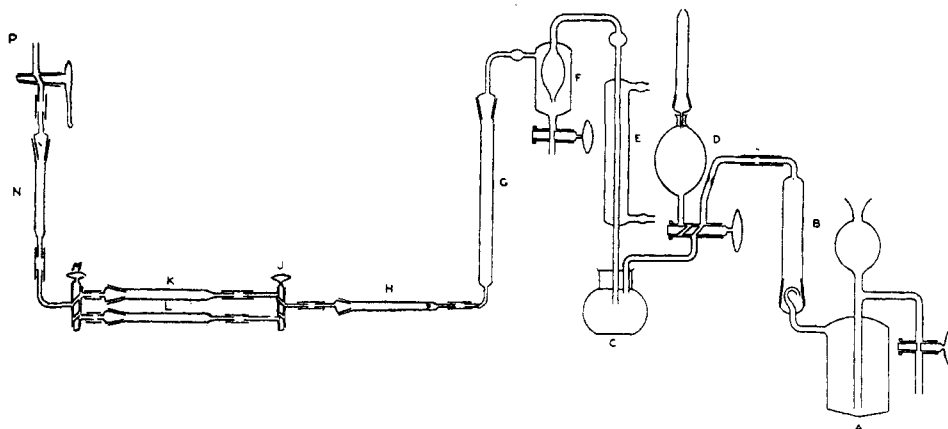


Fig. 3.—Apparatus for analysis of oxidized celluloses by carbon dioxide evolution method.

At 53° the same sample showed 14.6% carboxyl after twenty-six minutes, and 22.86% after two hours. An ultimate analysis showed 42.60% carbon and 5.62% hydrogen. From the carbon analysis the sample has a calculated carboxyl content of 13.3%, based on the assumption that the primary hydroxyl groups are oxidized to carboxyl groups.

The carboxyl groups of the oxidized celluloses react with the salts of weaker acids such as calcium acetate, forming a salt of the oxidized cellulose and releasing an equivalent amount of the weaker acid. On this basis the

following method of carboxyl group estimation was developed which is a modification of a published method¹⁵ for determining acidity in regenerated cellulose fibers. To 0.5-g. samples of the oxidized cellulose were added 50 cc. of carbon dioxide-free distilled water and 30 cc. of calcium acetate solution. After standing with frequent shaking to facilitate completion of the interchange, 30-cc. portions of the liquid were titrated with 0.1 *N* sodium hydroxide, using phenolphthalein indicator. The carboxyl contents are calculated as follows,

$$\frac{\text{cc. of 0.1 } N \text{ NaOH} \times 0.0045 \times 100 \times 8}{\text{wt. sample} \times 3} = \% \text{ COOH (by wt.)}$$

TABLE I
EFFECT OF CONDITIONS ON CARBOXYL GROUP VALUES AS DETERMINED BY THE CALCIUM ACETATE METHOD

Normality of calcium acetate	Temp., °C.	Time, min.	Titration, cc. 0.1 <i>N</i> NaOH	COOH, % by wt.
1.0	25	8	7.10	17.1
1.0	25	16	7.12	17.1
1.0	25	40	7.10	17.1
1.0	25	60	7.20	17.3
1.0	25	120	7.20	17.3
1.0	25	1050	7.43	17.9
0.5	25	17	7.10	17.1
.5	25	49	7.04	16.9
.5	25	120	7.15	17.2
.5	25	1050	7.18	17.3
.1	25	7	6.10	14.7
.1	25	18	6.70	16.1
.1	25	59	6.88	16.5
.1	25	121	7.00	16.8
.1	25	1050	7.12	17.1
1.0	70	20	7.83	18.8
1.0	70	43	8.24	19.8
1.0	70	60	8.30	20.0
1.0	70	130	8.86	21.3
1.0	70	220	9.27	22.3
0.5	70	60	7.95	19.1
.25	70	60	7.75	18.6
.125	70	60	7.65	18.4
.1	70	22	7.40	17.8
.1	70	40	7.50	18.0
.1	70	87	7.65	18.4
.1	70	172	7.88	18.9

The effect of several analytical variables is shown in Table I using the same oxidized cellulose throughout.

From these results a temperature of 25°, a time of two hours, and a calcium acetate concentration of 0.5 *N* were chosen as standard conditions for subsequent analyses. Since the calcium acetate solution is present in considerable excess, the exact normality is of no consequence. The titrations were corrected for the amount of alkali necessary to bring the calcium acetate to a phenolphthalein end-point in the absence of oxidized cellulose. The Eastman Filtration Cotton used for the oxidations showed apparent carboxyl group contents of 0.1% or less by this method.

Later, a modification of the carbon dioxide evolution method used for combined uronic acids¹⁶ was developed. The apparatus (Fig. 3) is a modification of a microanalytical apparatus^{17,18} for carbonate determinations. The oxidized cellulose sample, dried for twenty-four hours *in vacuo* over phosphorus pentoxide, is placed in the 50-cc. Pyrex flask C. By a vacuum applied at P, air is drawn through the apparatus for thirty minutes to sweep out carbon dioxide. The carbon dioxide absorption tubes K and L are removed, weighed and replaced in the absorption train. These are microanalytical absorption tubes of standard design filled with 20-mesh ascarite and a small amount of phosphorus pentoxide.¹⁸ An excess of 12%

(15) M. Ludtke, *Z. angew. Chem.*, **41**, 650 (1935).

(16) C. Doree, "The Methods of Cellulose Chemistry," D. Van Nostrand Co., New York, N. Y., 1933, pp. 371 *et seq.*

(17) G. Kemmerer and L. T. Hallett, *Ind. Eng. Chem.*, **19**, 1352 (1927).

(18) W. O. Kenyon and H. LeB. Gray, *THIS JOURNAL*, **58**, 1422 (1936).

carbon dioxide-free hydrochloric acid is admitted into C from reservoir D which is protected by an ascarite guard tube. Carbon dioxide-free air is drawn through the apparatus at such a rate that about 100 bubbles per minute are formed in bubble counter F which contains aniline sulfate-concentrated sulfuric acid solution to absorb furfuraldehyde. Flask C is boiled gently by a micro-burner. The contents of A, B and G have been previously described.¹⁸ Tube H contains phosphorus pentoxide for removing moisture. J and M are double stopcocks which permit the absorbing tubes K and L to be used alternately; N is a phosphorus pentoxide guard tube. The rubber connections in the apparatus are made with tubing designed expressly for microanalytical work. The rubber stopper in flask C should be renewed frequently and a ground-glass stopper at this point is preferable. Various batches of E. F. C. showed apparent carbon dioxide contents varying from 0.2 to 0.35% in this determination. Comparative tests using air and nitrogen as carrier gases for the carbon dioxide were without significant differences. With oxidized celluloses of high degrees of oxidation, samples varying in size from 35 mg. to 1 g. have been used. If good microanalytical technique is employed in handling and weighing the absorption tubes, the smaller samples are satisfactory. The larger amounts permit more uniform sampling and are usually employed. The absorption tubes are weighed alternately at hourly intervals until carbon dioxide evolution ceases. The results of a typical analysis are shown in Table II and Fig. 4.

TABLE II
RATE OF EVOLUTION OF CARBON DIOXIDE IN 50.0-MG.

Time, hours	SAMPLE		Total CO ₂ , %
	CO ₂ liberated/unit weight, mg.	%	
1	3.893	7.79	7.79
2	2.841	5.68	13.47
3	1.205	2.41	15.88
4	0.422	0.84	16.72
5	.350	.70	17.42
6	.373	.76	18.18
7	.129	.26	18.44

The carboxyl content of this sample, 18.85% by weight, is obtained by multiplying the per cent. of carbon dioxide by the factor 45/44. A com-

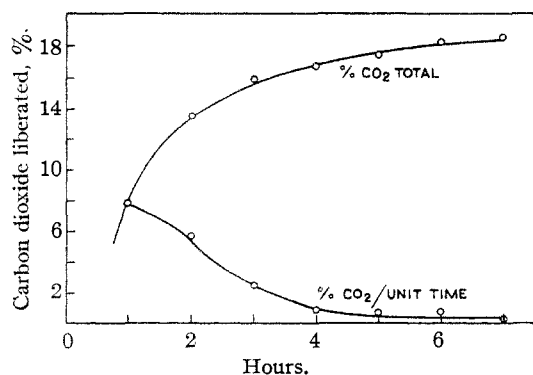


Fig. 4.—Curve of carbon dioxide evolution from oxidized cellulose.

parison of the results obtained using the calcium acetate and the carbon dioxide evolution methods on several oxidized celluloses is shown in Table III.

TABLE III
COMPARISON OF CARBOXYL GROUP VALUES AS DETERMINED BY CARBON DIOXIDE EVOLUTION AND CALCIUM ACETATE METHODS

Sample	% COOH by weight	
	Calcium acetate method	CO ₂ evolution
1	6.6	6.9
2	11.8	11.9
3	16.2	15.8
4	18.5	20.5
5	18.6	22.4

Oxidation Studies.—All of the analyses in Tables IV, V and VI are by the calcium acetate method.

A series of oxidations were run, using E. F. C. dehydrated by various methods as shown in Table IV. Five-gram samples were oxidized by the static method in 500-cc. flasks for sixty-four hours at 23–25°, using 3 g. of nitrogen dioxide as the oxidant.

TABLE IV
EFFECT OF MOISTURE CONTENT ON DEGREE OF OXIDATION

Expt.	Conditions of drying	H ₂ O remaining, %	COOH formed, % by wt.
1	Dehydrated by benzene	1.2	12.5
2	Dehydrated over P ₂ O ₅ in vacuo	0.1 (App.)	13.2
3	110°C. for 24 hr.	..	12.1
4	110°C. for 4 hr.	..	12.2
5	Check, no drying	3.05	13.6

In Table V is shown a study of the rate of oxidation at 22 to 25° by the static method of E. F. C. (undried), using 10-g. samples in 500-cc. flasks with 7.5 g. of nitrogen dioxide. These data are shown graphically in Fig. 5.

TABLE V
RATE OF OXIDATION OF CELLULOSE BY NITROGEN DIOXIDE USING STATIC METHOD

Expt.	Time, hr.	NO ₂ /cellulose ratio (by wt.)	COOH formed, % by wt.
6	2	0.75	3.0
7	4	.75	5.7
8	8	.75	9.1
9	15.5	.75	10.5
10	52	.75	13.7

In Table VI are shown the results of several oxidation series, by the static method at 22–25° in which the size of sample, size of apparatus, nitro-

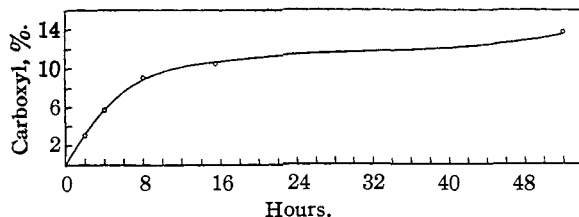


Fig. 5.—Typical curve of oxidation of cellulose by nitrogen dioxide vs. time.

gen dioxide/cellulose ratio and time of oxidation were varied. Undried E. F. C. was used. In the column "NO₂ concentration (g./cc.)" are the calculated concentrations of nitrogen dioxide in grams per cubic centimeter of space in the oxidation flask, assuming complete vaporization. With large amounts of nitrogen dioxide, some remained unvaporized in the reservoir B (Fig. 1). These data are shown graphically in Fig. 6.

Properties of the Oxidized Celluloses.—The oxidized celluloses produced by this method having carboxyl group contents up to about 15% are fluffy, white materials which cannot be distinguished from the original cellulose by visual examination. These products are not friable like other oxidized celluloses and may be handled with-

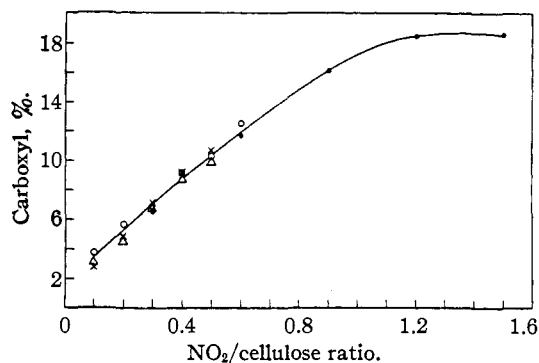


Fig. 6.—Relationship of COOH contents of oxidized celluloses and the NO₂/cellulose ratio used in the static method oxidation: ●, Expts. 11-15; ×, Expts. 16-20; Δ, Expts. 21-25; ○, Expts. 26-31.

out the fibers breaking up. Materials having carboxyl contents greater than 15% maintain their fiber structure but there is some shrinkage accompanied by surface hardening. This behavior is possibly the result of enhanced water-susceptibility due to the high proportion of carboxyl groups. Certain highly water-susceptible cellulose derivatives and synthetic resins show this phenomenon of shrinkage and surface glazing, or even coalesce, on drying. Air-dried oxidized

TABLE VI

SUMMARY OF OXIDATION OF CELLULOSE BY NITROGEN DIOXIDE UNDER VARIOUS EXPERIMENTAL CONDITIONS, STATIC METHOD

Expt.	Cotton, g.	NO ₂ , g.	Size of oxidation chamber, cc.	NO ₂ /cellulose ratio (by wt.)	NO ₂ concentration, g./cc.	Time of oxidation, hours	COOH formed, % by wt.
11	5	1.5	500	0.3	0.003	64	6.5
12	5	3.0	500	.6	.006	64	11.8
13	5	4.5	500	.9	.009	64	16.2
14	5	6.0	500	1.2	.012	64	18.5
15	5	7.5	500	1.5	.015	64	18.6
16	15	1.5	2000	0.1	.00075	64	2.8
17	15	3.0	2000	.2	.0015	64	4.8
18	15	4.5	2000	.3	.00225	64	7.1
19	15	6.0	2000	.4	.003	64	9.1
20	15	7.5	2000	.5	.00375	64	10.7
21	30	3.0	2000	.1	.0015	64	3.1
22	30	6.0	2000	.2	.003	64	4.6
23	30	9.0	2000	.3	.0045	64	6.9
24	30	12.0	2000	.4	.006	64	8.8
25	30	15.0	2000	.5	.0075	64	9.9
26	30	3.0	2000	.1	.0015	90	3.7
27	30	6.0	2000	.2	.003	90	5.6
28	30	9.0	2000	.3	.0045	90	6.9
29	30	12.0	2000	.4	.006	90	9.0
30	30	15.0	2000	.5	.0075	90	10.3
31	30	18.0	2000	.6	.009	90	12.6
32	180	18.0	12000	.1	.0015	72	3.0
33	180	36.0	12000	.2	.003	72	4.4
34	180	54.0	12000	.3	.0045	72	6.7
35	180	72.0	12000	.4	.006	72	8.4
36	180	90.0	12000	.5	.0075	72	9.8

celluloses containing 15% of carboxyl or less were found to have moisture contents of about 4 to 6% by weight as determined by drying for sixteen to twenty-four hours *in vacuo* over phosphorus pentoxide. The more highly oxidized celluloses apparently retain more moisture when air dried at a relative humidity of 20 to 30%; for example, oxidized celluloses of about 20% COOH content had moisture contents of 13 to 15%. With materials of greater carboxyl contents, it is questionable whether the retained moisture can be completely removed by drying *in vacuo* over phosphorus pentoxide.

The oxidized celluloses have a great affinity for basic dyes. Preliminary tests indicate that the methylene blue absorption is a function of carboxyl group content. They readily absorb basic dyes which are present in aqueous solution as salts of weak acids. For example, oxidized celluloses of moderate degrees of oxidation quickly and completely remove the color from a dilute aqueous solution of rosaniline acetate, the basic dye forming a salt with the carboxyl groups of the oxidized cellulose liberating acetic acid. The dye can be displaced by treatment of the dyed material with a dilute aqueous mineral acid.

A variety of salts of the oxidized celluloses have been produced. The materials of 13% carboxyl group or greater dissolved quickly and completely in aqueous alkalies such as 2% aqueous sodium hydroxide, dilute ammonia, sodium carbonate, warm aqueous pyridine or in aqueous solutions of quaternary ammonium hydroxides. In general, these salts may be obtained as white, water-soluble solids by pouring their aqueous solutions into ethyl alcohol or other suitable water-miscible non-solvents. In preparing the salts, it is advisable to add a few drops of dilute acetic acid to the aqueous salt solution to neutralize excess base prior to precipitation. Oxidized celluloses containing less than about 13% of carboxyl form gelatinous, swollen masses with the above-mentioned bases.

With polyvalent cations, the oxidized celluloses form insoluble salts even when the degree of oxidation is high. For example, the addition of barium acetate to an aqueous solution of the sodium salt of an oxidized cellulose precipitates the white, insoluble barium salt. This insolubility of oxidized cellulose salts of polyvalent cations is probably due to the fact that the cation forms a cross link between the oxidized cellulose mole-

cules, resulting in a three-dimensional structure. In a similar manner, the salts of cellulose acetate phthalate and of polymethacrylic acid with polyvalent cations are insoluble. Oxidized celluloses should therefore always be washed with distilled water to prevent calcium salt formation by tap water.

It has been mentioned that the oxidized cellulose can displace acetic acid from its salts. This method is convenient for the preparation of salts of oxidized cellulose with retention of fibrous structure. For example, 1.5 g. of oxidized cellulose of 17.2% COOH was treated with an excess of 0.5 *N* barium acetate solution at room temperature for several hours. The fibrous barium salt was filtered, washed free of excess barium acetate in distilled water, and dried. The product weighed 1.877 g., which is an increase of 0.377 g. The calculated increase in weight on forming the salt is 0.388 g. This method can be employed to form the salts of other cations.

A number of the oxidized celluloses were analyzed for combined nitrogen by the micro-Dumas method. None were found within the limit of accuracy of this method.

Discussion

A comparison of the properties of various oxidized celluloses reported in the literature, and the properties of those oxidized by nitrogen dioxide, indicates that these latter materials are unique. They retain their fibrous structure while, as Heuser⁷ has pointed out, other methods of oxidation produce physically degraded materials. While the greater portion of the work reported was done with Eastman Filtration Cotton, similar results were obtained with linters and wood pulp.

Alkali solubility has been employed extensively by various workers as a test of oxidation of cellulose. Relatively concentrated sodium hydroxide, such as 10% or sometimes greater, is commonly employed, and heat is often necessary to cause solution. The products of mild oxidation are usually only partially soluble, indicating heterogeneity. The products of vigorous oxidation, while dissolving completely, are extensively degraded.⁷ When concentrated alkalies or high temperatures are used, it is difficult to determine whether solubility is due to carboxyl groups or to degradation products of low molecular weights. Cellulose acetate phthalate or polymethacrylic acid dissolve readily in dilute alkalies by virtue

of carboxyl groups present, even though they are of high molecular weights. In a similar manner, the celluloses oxidized by nitrogen dioxide dissolve in dilute aqueous solutions of inorganic or organic bases when the carboxyl group content is above about 13%. Products with less than about 13% of carboxyl do not dissolve, probably because there are insufficient carboxyl groups to bring the macromolecules into solution. Additional proof of carboxyl groups is given by the great absorptive capacity for basic dyes and the formation of salts by removal of cations from salts of weaker acids.

As shown by Fig. 5, a typical oxidation curve for the static method, the nitrogen dioxide rapidly oxidizes the cellulose in the early stages of the reaction, and then oxidation practically ceases. The experiments of Table VI, using various nitrogen dioxide/cellulose ratios in containers of various sizes, were run for extended periods of time so that the oxidations would reach completion. When the carboxyl group contents of the oxidized celluloses of Table VI are compared with the nitrogen dioxide/cellulose ratios, the composite graph obtained (Fig. 6) shows a good correlation between the various series.

Though the calcium acetate method of analysis gave results in good agreement with the results of the carbon dioxide evolution method when using celluloses of low degrees of oxidation (Table III), we believe that the latter method is more reliable

at present. Recently, a critical study has been made of the application of the carbon dioxide evolution method to the determination of uronic acids in cellulose materials.¹⁹ A further study of the calcium acetate method might show suitable conditions which would render it satisfactory. This method involves a heterogeneous reaction between a liquid and a solid phase. Complete penetration of the calcium acetate solution into the fibers is necessary for complete reaction with the carboxyl groups. Occlusion or preferential absorption of acetic acid by the fibers would also produce low values.

Summary

1. Methods for oxidizing cellulose by nitrogen dioxide are described.
2. The properties of the oxidized celluloses thus obtained are described.
3. The ability of these oxidized celluloses to dissolve in dilute aqueous alkalies, to absorb large amounts of basic dyes and to replace weaker acids such as acetic acid from their salts indicates extensive carboxyl group formation during oxidation.
4. The analyses of the oxidized celluloses by carbon dioxide evolution by reaction with calcium acetate are reported.
5. The production of salts of the oxidized celluloses by various methods is described.

(19) R. L. Whistler, A. R. Martin and M. Harris, *J. Res. Natl. Bur. Stds.*, **24**, 13 (1940).

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Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. I*

By CORNELIUS C. UNRUH AND WILLIAM O. KENYON

Little is known concerning the structure of oxidized celluloses because various oxidants may simultaneously attack one or more of the hydroxyl groups of the anhydro-glucose units in the cellulose molecule to produce a complicated structure containing carboxyl, aldehyde and ketone groups, or possibly mixtures thereof.¹ Also the products of oxidation are usually heterogeneous and degraded.² An exception appears to result when

* Presented before the Division of Cellulose Chemistry at the St. Louis meeting of the American Chemical Society, on April 10, 1941.

(1) G. F. Davidson, *Silk J.*, **13**, 21-25, No. 145 (1936); *Textile Mfg.*, **62**, 233 (1936); *J. Textile Inst.*, **27**, 144-158 (1936); **29**, 195-218T (1938); *J. Soc. Dyers and Colourists*, **56**, 58-63 (1940).

(2) E. Heuser "Organic Chemistry," H. Gilman, Editor, John Wiley and Sons, New York, N. Y., 1938, Vol. II, pp. 1556-1557.

periodic acid is the oxidant, in which case the secondary hydroxyl groups are preferentially attacked.³

The oxidized celluloses prepared by using nitrogen dioxide as the oxidant⁴ offer unique possibilities for structural studies. Products covering a wide range of degree of oxidation can thus be prepared, and above a certain degree of oxidation the products are completely soluble in dilute aqueous alkali. Retention of fiber structure and lack of friability of these materials indicate little apparent

(3) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 2049 (1937); **60**, 989 (1938).

(4) E. C. Yackel and W. O. Kenyon, *ibid.*, **63**, 121 (1941).