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OXIDATION OF CELLULOSE: THE REACTION OF CELLULOSE WITH PERIODIC ACID

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ABSTRACT

An investigation has been made of the mode of attack of cellulose by periodic acid during the early stages of the oxidation (that is, oxidation of approximately 1 percent of the glucose residues). Under these conditions, it is shown that the reaction is confined to oxidation of the secondary hydroxyl groups to aldehyde groups, and results in a rupture in the carbon chain between carbon atoms 2 and 3 of the glucose unit. In accordance with this mechanism it is shown that two moles of aldehyde groups are produced for each mole of oxidant consumed. The aldehyde groups of the periodic acid-oxycellulose can readily be converted to carboxyl groups, titration of which provides an independent check on the content of the former.

Periodic acid-oxycellulose is characterized by its susceptibility to further attack by alkaline solutions. The alkali-sensitivity of these materials, as measured by solubility in hot dilute sodium hydroxide and by cuprammonium fluidity, appears to be proportional to the content of aldehyde groups. However, upon conversion of all of the aldehyde groups to carboxyl groups, the alkali-lability practically disappears. The results suggest that the sensitivity of periodic acid-oxycellulose to alkali does not depend solely on the rupture of the glucose ring between carbon atoms 2 and 3, but is related to the specific instability towards alkali of the dialdehyde formed during the oxidation.

CONTENTS

I. INTRODUCTION

Cellulose can undergo many modifications in oxidizing media, and accordingly the properties of oxidized celluloses, generally referred to as oxycelluloses, vary widely. It appears that the attack on cellulose by oxidizing agents is principally confined to three points: (1) the aldehyde end-groups, of which there are few, if any, in native cellulose [1] [2] and which can be oxidized to carboxyl groups, (2) the primary alcohol groups which can be oxidized to the aldehyde or carboxyl stage, and (3) the glycol group (the 2,3-dihydroxy group) which can be oxidized to the ketone, aldehyde, or carboxyl stage. Until recently,

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[2] Figures in brackets indicate the literature references at the end of this paper.

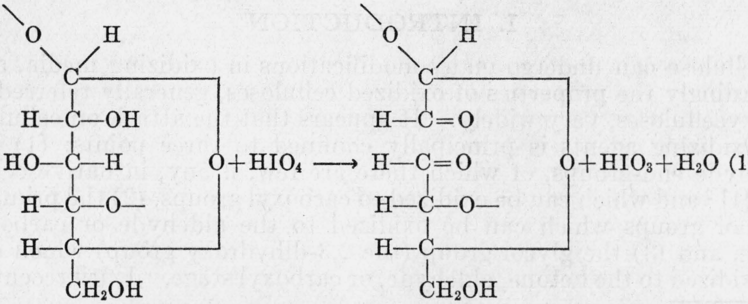
it has generally been assumed that the oxidative attack occurred principally at the primary alcohol groups, a hypothesis which gave rise to considerable confusion. This hypothesis did not adequately explain the different behaviors of oxycelluloses prepared with various oxidizing agents. Thus, whereas Clibbens and Ridge [2] were able to show that treatment of cotton with any acid resulted in the same corresponding increase in cuprammonium fluidity and decrease in tensile strength, a similar general relationship did not exist for all types of oxycellulose. The data in table 1 (from reference [2]) illustrate this point. This apparent anomaly was indeed disturbing, since both the fluidity and strength of cellulosic materials are regarded as functions of molecular chain length.

As a solution to the difficulty, Davidson [3, 4] made the important suggestion, which he later supported by extensive experimental work [5], that some types of oxidation do not result in direct scission of the chain molecules but reduce the chemical stability of some of the linkages in the cellulose chain towards alkali. Types of oxidation which do not rupture the chains would have little or no effect on strength, but if these types of modification result in a material which is unstable towards alkali, the fluidity in the alkaline cuprammonium solution will be high. This then would explain the lack of an identical correlation between strength and cuprammonium fluidity for all types of oxycelluloses similar to the correlation existing for all types of hydrocelluloses.

TABLE 1.—*Relation between cuprammonium fluidity and tensile strength of various hydrocelluloses and oxycelluloses*

Cuprammonium fluidity	Loss in tensile strength resulting from—		
	Treatment with any acid	Treatment with $K_2Cr_2O_7+(COOH)_2$	Treatment with NaOCl
Rhes	*Percent*	*Percent*	*Percent*
10	10	1	7
20	34	6	25
30	58	16	47

Davidson's hypothesis was lent considerable support by the investigations of Jackson and Hudson [6], who showed that in the oxidation of cellulose by periodic acid, cleavage of the glucose ring between carbon atoms 2 and 3 occurred with the conversion of the secondary alcohol groups to aldehydes, according to the following scheme:



(1)

A reaction of this type does not result in a scission of the molecular chains, and hence little, if any, loss in strength occurs.

While it appears that periodic acid (at least during the early stages of oxidation) and a few other oxidizing agents may be quite specific in their attack on cellulose, the action of many oxidizing agents to which cellulose is frequently exposed is more complex and less understood. A major difficulty in attempts to ascertain the exact course of the various types of oxidation has been the lack of analytical methods of sufficient specificity and sensitivity to determine quantitatively the various groups which may be formed and to allocate them to their proper positions in the glucose residues. Recently, however, a number of new methods have been developed and accordingly a series of studies of the course of oxidation of cellulose by various reagents was undertaken. The present paper reports the results obtained with periodic acid.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF MATERIALS

Raw cotton was dewaxed by extraction with hot alcohol for 24 hours and then washed thoroughly with cold distilled water. The cotton was further purified by boiling with a 1-percent solution of sodium hydroxide for 8 hours; the procedure was essentially the same as that described by Corey and Gray [7], except that the apparatus of Worner and Mease was used [8].

The oxycelluloses were prepared by steeping samples of the purified cotton in solutions of periodic acid buffered with sodium acetate at pH 4.6. The extent of oxidation was controlled by varying either the concentration of periodic acid or the time of treatment. In most cases, however, a concentration of about 0.025 *N* periodic acid was employed. All treatments were carried out with the ratio of cotton to solution of 1 to 50 and a temperature of 25° C±0.1°. Immediately following the oxidation, the samples were rapidly washed in cold distilled water until a test of the washing for periodate was negative. The materials were then conditioned in the dark, in a room maintained at a temperature of 21° C and 65-percent relative humidity. Under these conditions, it was found that the properties of the oxycellulose did not change over prolonged periods of time.

2. METHODS

The concentration of periodic acid was determined by titration of an aliquot of the solution with sodium arsenite after the addition of sodium bicarbonate and potassium iodide, according to the method of Müller and Friedberger [9]. The number of milliequivalents of oxidant consumed per gram of dry cellulose was calculated from the difference in the amount of arsenite required by a control solution, and by an identical solution containing the sample.

The aldehyde content of the oxycellulose was determined by a modification (described below) of the iodometric method as used for hydrocellulose by Martin, Smith, Whistler, and Harris [1]. This determination depends on the oxidation of the aldehyde groups to carboxyl groups by iodine. The amount of iodine consumed by the oxycellulose was determined as follows: 10 ml of 0.05 *M* sodium borate solution having a pH of 9.2 at 25° C was pipetted into a 125-ml glass-stoppered Erlenmeyer flask and then placed in a thermostat at 25° C. 20 ml of 0.03 *N* iodine solution containing 20 g of potassium iodide per liter, previously brought to 25° C, was then added and approximately 100 mg of the sample to be titrated was immediately introduced. (With this amount of sample, it is important that the oxycellulose contain no more than 0.15 millimole of aldehyde groups per gram; the ratio of milliequivalents of iodine to milliequivalents of aldehyde should not be below 25). After 6 hours, 15 ml of 0.1 *N* HCl was added and the iodine remaining in the solution was measured by titration with standard sodium thiosulfate (about 0.013 *N*) with starch as the indicator. Blank determinations on identical solutions which did not contain cotton were made. From the difference in amount of thiosulfate required by the blank solution and by the solution containing the sample, the milliequivalents of iodine consumed per gram of dry sample were calculated. As explained elsewhere [1], a correction for the iodine consumed by purified cotton in the same time interval must be applied in calculating the aldehyde content of the oxycellulose.

An independent check on the iodine method was made by analyzing for carboxyl content after oxidation of the aldehyde groups with chlorous acid. This substance is particularly useful for this purpose in view of the selective action towards aldehyde groups observed by Jeanes and Isbell [18] in their work on the oxidation of certain aldoses. A 0.4 *M* solution of chlorous acid was prepared immediately before use by the acidification of a solution of technical sodium chlorite to pH 2.5 with the appropriate quantity of glacial acetic acid. The oxycellulose was treated with this solution at 25° C.

The carboxyl content was determined by measuring the amount of silver bound by the fiber from a solution of silver *o*-nitrophenolate according to the procedure described by Sookne and Harris [10].

Two types of fluidity measurements were made. The first consisted in measurements on dispersions of cellulose in cuprammonium hydroxide solution by the method of Clibbens and Geake [11] as modified by Mease [12]. The second involves the nitration of the cellulose, as recommended by Berl [13], and the determination of the fluidities of dispersions of the nitrocellulose in acetone. The necessity for making both types of fluidity measurements was made clear in the extensive investigations by Davidson, who showed that a measure of the true chain length of certain oxycelluloses containing alkali-sensitive linkages could not be obtained by dissolution of the material in an alkaline solvent such as cuprammonium hydroxide solution. In order to avoid the degradation that occurs when the oxycellulose is dispersed in such alkaline solutions, recourse was had to the nitrocellulose method.

The nitrocellulose fluidities were calculated from the times of flow of solutions through an Ostwald viscometer at 20° C. To reduce the time required to make measurements, solutions containing 0.1 g (rather than 0.25 g) of nitrocellulose per 100 ml of acetone were used. To render the results comparable to the findings published by others, fluidities were calculated for solutions having a concentration of 0.25 g per 100 ml, by means of Hess and Philipoff's modification [14] of Baker's equation:

$$\eta^{1/8}_{\mathrm{rel}}=1+\frac{[\eta]}{8}c,$$

in which η_{rel}=relative viscosity; $[\eta]$=a constant; c=concentration in g/100 ml of solvent.

The fluidities were readily calculated from the η_{rel}. The fluidity of the solution having the concentration of 0.25 g per 100 ml of solvent is referred to as the "nitrocellulose fluidity." The nitrocelluloses derived from samples which had consumed more than 0.05 milliequivalent of oxidant per gram were not completely soluble in acetone [15]. The nitrocellulose fluidity of the soluble portion was determined after removing the insoluble material by centrifuging and making the necessary corrections for concentration. It is recognized that the solution thus obtained is not representative of the entire material. It is noteworthy that when the aldehyde groups are oxidized to carboxyl groups, the derived nitro-celluloses are completely soluble.

The sensitivity of periodic acid-oxycellulose to alkalies is indicated by the increase in nitrocellulose fluidity that occurs when such materials are treated with dilute sodium hydroxide [15]. Preliminary experiments showed that the maximum increase in nitrocellulose fluidity was obtained by a 1-hour boil (under reflux) in 0.25 *N* NaOH, the ratio of sample to solution being 1 to 200. The scission of all alkali-labile linkages is completed under these conditions. The "alkali boil" referred to hereafter represents such a treatment, and the loss in weight that occurs during the treatment, expressed in percentage, is hereafter referred to as "alkali solubility." It should be further pointed out that while the nitrocellulose fluidity does reach a maximum and constant value after a 1-hour boil in the alkali, the alkali-solubility value rises rapidly during the first hour but continues to rise at a very much slower and diminishing rate thereafter. Even after 8 hours the slow dissolution of the cellulose continues to take place.

III. RESULTS AND DISCUSSION

1. ESTIMATION OF OXIDANT CONSUMED BY CELLULOSE

As indicated in figure 1, the consumption of periodic acid during the early stages of oxidation (that is, the oxidation of less than 2 percent of the glucose residues) is directly proportional to time. It was observed, however, that an initial rapid disappearance of a small

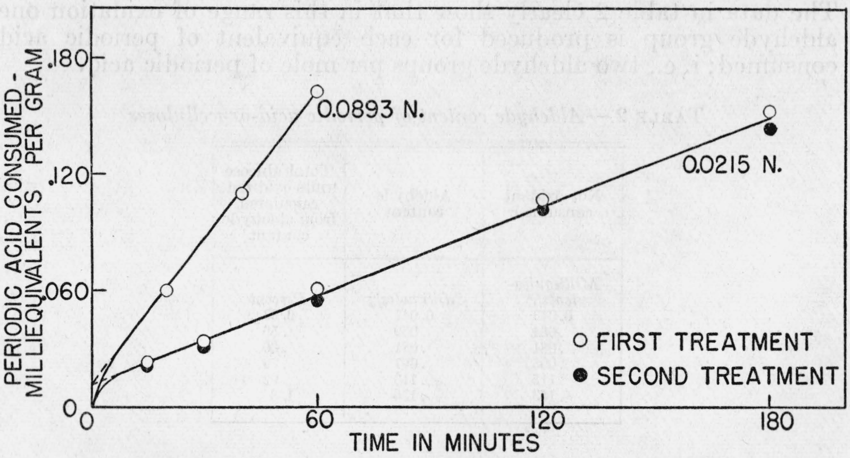


FIGURE 1.—*Rate of consumption of periodic acid by purified cotton from solutions at* pH *4.6 and 25° C.*

portion of the oxidant always occurred. This could conceivably be due either to the oxidation of some rapidly oxidizable material, or to some unexplained adsorption of the oxidant by the fibers. That the latter is the case was indicated by the following experiment. A sample of purified cotton was subjected to two consecutive oxidations with a 0.0215 *N* solution of periodic acid at pH 4.6. The results shown in the lower curve in figure 1, indicate the absence of an easily oxidizable substance, since the same initial rapid disappearance of periodic acid was observed on the second treatment. As also indicated in the figure, a fourfold increase in the concentration of periodic acid did not appreciably alter the amount of oxidant initially taken up. Extrapolation of the straight-line portion of the curves to zero time indicated that 0.012 milliequivalent of periodic acid per gram of cellulose has apparently been adsorbed by the fibers in this manner, and accordingly this amount is deducted from the total apparent amount of oxidant consumed in order to obtain a measure of the periodic acid which has been utilized in the oxidation of the cellulose.

The adsorption noted is not unique with periodic acid, since similar adsorptions by cellulose of other oxidizing agents such as hypochlorite [16], chromic acid [17], and iodine [1] have been reported in the literature.

2. COURSE OF OXIDATION OF CELLULOSE BY PERIODIC ACID

It would be expected that complete oxidation of cellulose by periodic acid, according to eq 1, would require one atom of oxygen per glucose unit. However, as shown by Jackson and Hudson [6], the actual consumption of oxidant considerably exceeds this theoretical amount, a fact which led these investigators to the conclusion that secondary reactions undoubtedly occurred during prolonged contact of the cellulose with the oxidant. This conclusion was supported by the work of Davidson [15], who found that on extensive oxidation appreciable quantities of formaldehyde, formic acid and carbon dioxide were formed.

On the other hand, it appears that during the early stages of oxidative attack, the reaction does proceed principally according to eq 1. The data in table 2 clearly show that in this range of oxidation one aldehyde group is produced for each equivalent of periodic acid consumed; i. e., two aldehyde groups per mole of periodic acid.

TABLE 2.—*Aldehyde content of periodic acid-oxycelluloses*

Net oxidant consumed	Aldehyde content	Total glucose units oxidized, calculated from aldehyde content
Milliequivalents/g	*Millimoles*/g	*Percent*
0.043	0.041	0.33
.064	.069	.56
.081	.081	.66
.095	.097	.79
.115	.113	.92
.153	.156	1.3

The aldehyde groups in oxycellulose were determined by measuring the iodine consumed during the quantitative oxidation of aldehyde groups to carboxyl groups, according to the modified procedure described in section II, 2. The method is similar to that used in the estimation of aldehyde groups in hydrocellulose [1] and it was expected that, similarly, an analysis for carboxyl groups in the fiber after treatment with iodine would also demonstrate that the consumption of iodine was due to reaction with aldehyde groups. Unfortunately, when the oxycellulose was placed in the mildly alkaline buffer used in the iodine titration, reducing groups were dissolved, so that the carboxyl groups left in the fiber could not be equivalent to the reducing groups originally present. However, a check of the oxidation reaction was made by the method described below.

The recent work of Jeanes and Isbell [18], showing that aldoses are readily oxidized to the corresponding aldonic acids by treatment with chlorous acid at pH 2.2 provided a means for oxidation in acid solution. Thus, treatment of the samples for 40 to 60 minutes with chlorous acid resulted in quantitative oxidation of the aldehyde groups to carboxyl groups as shown in table 3. Furthermore, the estimation of the latter affords an independent check on the aldehyde content obtained by the iodine method.

TABLE 3.—*Aldehyde and carboxyl contents of periodic acid-oxycellulose after chlorous acid treatment*

1	2	3	4
Initial aldehyde content	Aldehyde content after $HClO_2$	Carboxyl content after $HClO_2$	Sum of columns 2 and 3
Millimoles/g	*Millimoles/g*	*Millimoles/g*	*Millimoles/g*
0.041	0.000	0.037	0.037
.095	.000	.097	.097
.156	.010	.141	.151
.041	.011	.026	.037
.095	.012	.086	.098
.156	.022	.125	.147

In samples where the oxidation of the aldehyde groups was not completed, it may be seen that the sums of the carboxyl and aldehyde contents after the chlorous acid treatments agree within the experimental error with the aldehyde contents of the periodic acid-oxycelluloses found by the idodine method of analysis. This may be taken to indicate that no new reducing or acidic groups are formed in the oxycellulose as a result of the chlorous acid treatment. Finally, it was found that a similar chlorous acid treatment had no measurable effect on purified cotton cellulose.

3. RELATION BETWEEN ALDEHYDE CONTENT AND ALKALI-SENSITIVITY

As already noted by Davidson, the most characteristic property of the periodic acid-oxycelluloses is the ease with which they are degraded by alkaline solutions. This instability is explained by the fact that rupture of a glucose residue according to eq 1 results in the formation of alkali-sensitive linkages which undergo a scission in alkaline solutions. Thus, Davidson was able to show that periodic acid-oxycelluloses exhibited low nitrocellulose fluidities (long chains) and high cuprammonium fluidities (short chains). When the samples were subjected to an alkali boil, the nitrocellulose fluidities were considerably increased, but the cuprammonium fluidity remained unchanged. In other words, the treatment with alkali resulted in scission of all of the alkali-labile linkages, a process that is also accomplished in the highly alkaline cuprammonium solution.

Further support for this explanation was obtained in the present investigation. As shown in figure 2, there is only a slight increase in nitrocellulose fluidity with increase in aldehyde content (curve 1) of a series of oxycelluloses, indicating that although an appreciable number of glucose rings had been ruptured, the molecular chain length had not been correspondingly shortened. That the chains contained alkali-labile linkages, however, is suggested by the high nitrocellulose fluidities of a similar set of samples after the alkali boil treatment (curve 2). In contrast, the cuprammonium fluidities (fig. 2) increased rapidly with increasing aldehyde content, regardless of whether the samples were subjected to preliminary alkali treatment, indicating as pointed out earlier, that scission of all alkali-labile linkages in this type of oxycellulose is completed during dissolution of the oxycellulose in cuprammonium solution.

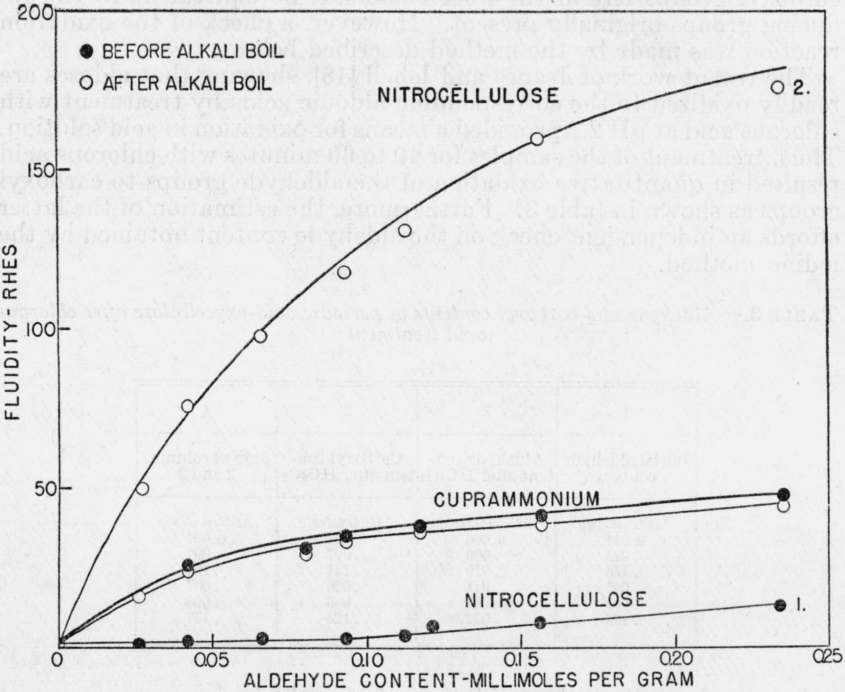


FIGURE 2.—*Fluidities of periodic acid-oxycelluloses, oxidized to various aldehyde contents, before and after boiling in 0.25 N* NaOH *for 1 hour.*

The question arises as to whether the sensitivity to alkalies of this type of oxycellulose depends on the rupture of the glucose ring between carbon atoms 2 and 3 or on a specific instability towards alkali of the dialdehyde formed in the oxidation process. In order to throw some light on this question, samples of oxycelluloses were treated with chlorous acid in order to oxidize the aldehyde groups to carboxyl groups.

As shown in figure 3, the effect of this treatment in every case was to lower the alkali-solubility to nearly zero. If the alkali-solubility values represented a true solubility phenomenon, it might have been expected that conversion of aldehyde to carboxyl groups would have resulted in an increase in solubility. Since this is not the case, it is concluded that the relatively high alkali-solubilities of the original oxycelluloses are related to a specific instability, involving the presence of aldehyde groups, of the products toward alkali. Further support for this conclusion is found in figure 4. Whereas the nitrocellulose fluidities of the oxycelluloses are greatly increased by an alkali boil, treatment of the oxycellulose with chlorous acid yielded products whose nitrocellulose fluidity was much less affected. The results leave little doubt that the sensitivity to

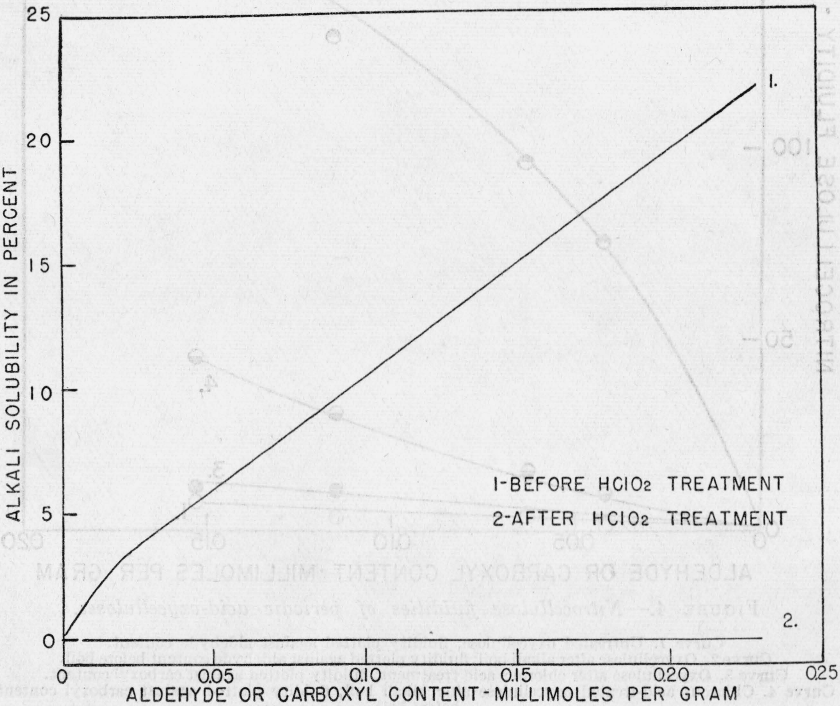


FIGURE 3.—*Percentage weight loss caused by treatment of oxycelluloses with boiling 0.25 N* NaOH *for 1 hour:*

Curve 1. Periodic acid-oxycellulose; percentage weight loss plotted against aldehyde content.
Curve 2. Periodic acid-oxycellulose oxidized further with chlorous acid; percentage weight loss plotted against carboxyl content.

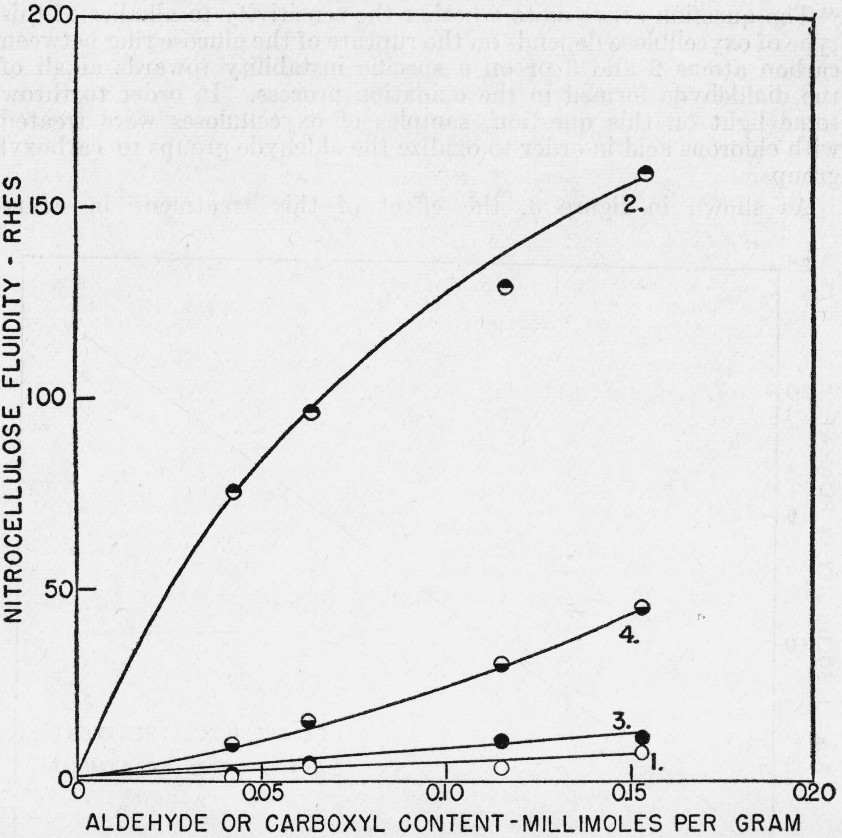


FIGURE 4.—*Nitrocellulose fluidities of periodic acid-oxycelluloses.*

Curve 1. Untreated oxycellulose; fluidity plotted against aldehyde content.
Curve 2. Oxycellulose after alkali boil; fluidity plotted against aldehyde content before boil.
Curve 3. Oxycellulose after chlorous acid treatment; fluidity plotted against carboxyl content.
Curve 4. Chlorous acid-treated oxycellulose after alkali boil; fluidity plotted against carboxyl content before boil.

alkali of these oxycelluloses does not depend solely on the rupture of the glucose ring between carbon atoms 2 and 3, but is related to the specific instability towards alkali of the oxidation product formed according to eq 1.

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