

TABLE II (Concluded)

Expt.	Ratio			20°	30°	40°	60°	80°	Remarks
	Sod. oleate:	Phenol:	Water						
94	8.00	2.00	90.00	4.32	3.68	3.20	2.47	1.50	Sl. turbidity
95	4.50	0.50	95.00	1.51	1.21	1.01	0.749	0.584	Sl. turbidity
96	4.00	1.00	95.00	1.95	1.58	1.33	1.01	.780	Sl. turbidity
97	3.00	2.00	95.00	1.62	1.29	1.06	0.764	.591	Sl. turbidity
(J) System: Sodium Oleate:Vanillin:Water									
98	9.00	1.00	90.00	4.14	3.49	3.03	2.42	2.29	Sl. turbid, some ppt.
99	8.00	2.00	90.00	3.50	2.98	2.68	2.23	1.98	Sl. turbid, some ppt.
100	4.00	1.00	95.00	1.88	1.53	1.29	0.981	0.846	Sl. turbid, some ppt.
(K) System: Sodium Oleate: <i>p</i> -Hydroxybenzaldehyde:Water									
101	9.00	1.00	90.00	8.16	7.15	6.43	5.42	4.93	Sl. turbid, some
102	8.00	2.00	90.00	2.73	2.31	2.02	1.61	1.41	ppt.

<sup>a</sup> Expts. 1, 11 and 2, 12 were made, respectively, with two different lots of sodium oleate prepared from two lots of oleic acid purified by low temperature recrystallization. The material used in expts. 1 and 11 was used throughout Section A and in Section F, expts. 65-70 inclusive. All other expts. were carried out with the material used in expts. 2 and 12. <sup>b</sup> Sodium oleate was prepared from oleic acid purified by the Skellon barium salt method. <sup>c</sup> Sodium oleate was prepared from a sample of commercial acid.

of Mr. Q. P. Peniston in the preparation of some materials used.

### Summary

1. Using a more rigorously purified sodium oleate, earlier observations on the occurrence of maxima in the viscosity of sodium oleate:phenol:water systems have been checked qualitatively but not quantitatively, the present results indicating the maxima to be even more pronounced than previously reported.

2. On extending the investigation to other phenolic substances it was found that not all produced such maxima in the viscosity of sodium

oleate solutions. The effectiveness of *p*-cresol, guaiacol and creosol in this regard was of the same order as that of phenol, but in the case of catechol, resorcinol and *o*-bromophenol the maxima were not so marked or even, at lower concentrations of sodium oleate, non-existent. Vanillyl alcohol, *p*-hydroxybenzyl alcohol, vanillin and *p*-hydroxybenzaldehyde did not increase the viscosities of the solutions of sodium oleate examined.

3. Evidence is adduced against Weichherz and Saechtling's<sup>2</sup> theory that the formation of acid soaps is a minor cause of the observed maxima in viscosity.

RECEIVED JULY 6, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## The Degradation of Oriented Cellulose Structures by Polarized Ultraviolet Light

By C. W. MASON AND F. B. ROSEVEAR<sup>1</sup>

### Introduction

The photochemical changes produced in cellulose have received attention since Witz<sup>2</sup> in 1883 reported that cotton when exposed to light was changed, in part at least, to "oxycellulose." Although the exact nature of "oxycellulose" can only be inferred at present, and although some reported experiments may have been complicated by effects other than that of light, nevertheless, it appears that a certain portion of the ultraviolet

region does produce physico-chemical changes in the cellulose structure.

The structure of cellulose shows very definite differences in properties, depending upon the direction considered. This is indicated macroscopically by its pronounced fibrous nature, microscopically by its strong double refraction, as well as the production of tiny fibrillae by mechanical treatment, and sub-microscopically by the X-ray deduction of its atomic arrangement.

It is reasonable to expect, then, that the anisotropic properties would include the photochemical

(1) Present address: Procter and Gamble Research Laboratory, Ivorydale, Ohio. [Original manuscript received July 26, 1938.]

(2) Witz, *Bull. soc. ind. Rouen*, II, 190 (1883).

effect, providing the radiation can be rendered directional in those properties which have to do with its photochemical action.

A directional effect of this sort has been found with potassium nitrate and other nitrates. Narayanswamy and Krishnan<sup>3</sup> noted that in the photochemical breakdown of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  in K, Na,  $\text{NH}_4$ , Sr, Ba, Cd, Pb, and Al nitrates, the rate of decomposition with plane polarized light was greater if the plane of vibration of the light was parallel to the plane of the  $\text{NO}_3^-$  groups.

The pleochroism of sodium nitrate and potassium nitrate in the ultraviolet, investigated earlier by Krishnan and Dasgupta,<sup>4</sup> supports the observations on decomposition. A selective absorption at about 3000 Å. occurs in solutions of sodium and potassium nitrates. With crystals and plane polarized light, this band is evident if the light is vibrating parallel to the plane of the  $\text{NO}_3$  groups, while light vibrating perpendicular to the plane of the  $\text{NO}_3$  groups is freely transmitted. A similar effect is noted at about 2600 Å.

Padoa<sup>5</sup> observed that the rate of photochemical decomposition of crystalline *o*-nitrobenzaldehyde, in polarized light, differs with the direction of vibration of the light. Weigert<sup>6</sup> found a similar effect, with tetrachloro- $\alpha$ -cetonaphthalene.

## Experimental

**I. Selection and Preparation of Cellulose.**—Ramie was used, for X-ray evidence indicates that in ramie the molecular chains are not only parallel to each other, but essentially parallel to the fiber axis, rather than spiral as in many fibers.<sup>7-10</sup>

"Degumming" of ramie, following the mechanical "decortication," is accomplished commercially by a wide variety of methods,<sup>11,12</sup> so that even though some available samples of commercial ramie sliver gave a very low copper number, indicating high purity of their cellulose, it was thought best to follow a known procedure, as follows:

Raw, dried, decorticated ramie was: (1) extracted three times with boiling water; (2) refluxed for fifteen-minute periods with three changes of 1% sodium hydroxide; and (3) washed successively with water, 5:95 acetic acid, 1:99 acetic acid, 95% alcohol, absolute alcohol, and ether.

(3) (a) Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411-1412 (1935); *C. A.*, **30**, 386; (b) Krishnan and Narayanswamy, *Current Sci.*, **3**, 417 (1935).

(4) Krishnan and Dasgupta, *Nature*, **126**, 12 (1930).

(5) Padoa, *Atti Accad. Lincei*, **28**, II, 372 (1919).

(6) Weigert, *Z. Elektrochem.*, **24**, 222 (1918).

(7) Clark, *Ind. Eng. Chem.*, **22**, 474-487 (1930).

(8) Herzog, *J. Phys. Chem.*, **30**, 457 (1926).

(9) Sponser and Dore, *4th Colloid Symposium Monograph*, 174-202 (1926).

(10) Polanyi, *Naturwissenschaften*, **9**, 337 (1921).

(11) Mathews, "Textile Fibers," John Wiley and Sons, New York, N. Y., 1924, p. 780.

(12) Carter and Norton, *Univ. Louisiana Studies*, No. 26 (1936).

The resulting product was free from the yellowish-brown color of the raw ramie. It showed a copper number of 0.10-0.12 as compared to a value of 0.08 for the commercial sliver.

**II. Production of Plane Polarized Ultraviolet Light.**—Preliminary exposures beneath ordinary glass, Pyrex, and vitreous silica, using Harrison's reagent<sup>13</sup> as a staining test, indicated that only the latter material had sufficient transmission (below 3300-3400 Å.) to permit marked degradation.

**A. The Light Source.**—The features of the quartz-enclosed mercury vapor arc as well as others are discussed in the First Report of the Committee on Photochemistry, National Research Council.<sup>14</sup> The mercury spectrum, while not continuous, has a rather large number of lines of high intensity distributed throughout the ultraviolet region. As the light source for the experiments, a Hanovia "Advanced Research Model" SC2601-A (110 volts, D.C.) quartz-enclosed mercury arc was used. This lamp gives an arc 6-7 cm. long and about 1 cm. in section.

Decrease in intensity of the arc with age was not found to cause trouble during the exposures. After some 1700 hours, the radiations still had a pronounced photochemical effect on cellulose, and the bulb showed no visible coating, or serious spectral alteration. The fact that the samples for light vibrating perpendicular and parallel to the fibers were run simultaneously renders unimportant any decrease other than a virtual elimination of the active wave lengths, and also any fluctuations in intensity.

**B. The Polarizer.**—Maximum cross section of the illuminating beam was necessary, to irradiate a quantity of fibers sufficient for analysis. For this and other reasons, polarizing prisms were inadequate; polarizing filters absorb ultraviolet completely.

The polarizer, based on the "pile of plates" principle, was constructed as follows. Two sets of eight polished vitreous silica plates (25 × 50 × 1 mm.) were cleaned carefully, piled face to face and the edges of the piles coated with warm "Piceine." This material when warmed was sufficiently fluid to adhere to the edges of the plates, without creeping between them, and on cooling served to hold the plates together, and to prevent reflection at their edges, because of its blackness and optical contact with the glass. When placed side by side, the two piles composed a reflector 50 × 50 × 8 mm., which was mounted in a duralumin frame so that the incident and reflected beams travelled parallel to the plane separating the two 8-plate halves of the polarizer.

It was found by measurement that the use of more than eight or ten plates added little to the quantity of reflected plane polarized light. A similar conclusion was reached regarding a "pile of plates" polarizer for microscopes.<sup>15</sup>

For the wave length range between 3400 Å. (the approximate upper limit of the spectral region active in degrading cellulose) and 2000 Å. (the approximate transmission limit of vitreous silica) the refractive index of vitreous silica varies from 1.479 to 1.547, corresponding to a variation in polarizing angle of only  $\pm 0.5^\circ$ . By reflection at the polarizing angle of  $56^\circ$ , all wave lengths in the region will be almost completely polarized, over a  $1^\circ$  range.

(13) Harrison, *J. Soc. Dyers Colourists*, **28**, 359 (1912).

(14) Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

(15) Johnson, *J. Roy. Microscop. Soc.*, 147 (1921).

Reasonably perfect and economical collimation was obtained by means of a set of narrow, flat, blackened, metal plates lying parallel to the length of the arc and to the direction of the desired light beam (see Fig. 1, p. 10). This produced three parallel channels for the light, 4 mm. wide and 120 mm. long, so that a ray of light from any point on the arc to the polarizing plates deviated not more than  $2^\circ$  from the desired  $56^\circ$  angle of incidence. A collimated beam of light  $35 \times 75$  mm. in cross section was thus obtained.

Due to displacement by the multiple reflection, the polarized beam varies from a maximum intensity on one side, to minimum on the other. This non-uniformity and the difference in intensity between the center and the ends of the beam were taken into account by turning the exposure cell end for end each day, and also in the method of sampling.

**III. Method of Exposure.**—While the nature of the photochemical degradation of cellulose is by no means clear, it is also true that any observed degradation might be due in part to chemical influences, non-directional in effect.

Cunningham and Doree<sup>16</sup> found that ozone, when passed over cotton fabric, changed it into "oxycellulose." Oguri<sup>17</sup> exposed filter paper to light from a quartz mercury vapor arc, and found that the copper number was definitely lower when ozone was eliminated. Joachim-Henk,<sup>18</sup> and Barr and Hadfield<sup>19</sup> consider the presence of oxygen to be essential, and the action of ultraviolet light one of oxidation. Cunliffe<sup>20</sup> also showed the importance of oxygen and moisture.

Obviously, the *secondary* actions upon cellulose of ozone, hydrogen peroxide, acids, or other products would be wholly independent of the plane of vibration of the incident radiation, and if the primary action of light were to be studied, these complicating factors should be minimized.

An airtight cell, shown in Fig. 1, was used. A duralumin frame formed three chambers, each designed to take a  $25 \times 50$  mm. vitreous silica slide as front window and a glass microscope slide as back window. In each chamber a glass plate carried a thin layer of parallel fibers of purified ramie, half oriented parallel to the vibration direction of the polarized light, and the other half perpendicular to the vibration direction. All the fibers were drawn over the ends or sides of the supporting plates and held in place at the back by a very small amount of glue. Sodium wire in each chamber served to remove oxygen, ozone, water, and carbon dioxide from the air left in the fibers and in the cell after sealing it, and also volatile reaction products of the degradation.

After extruding the sodium wire into each compartment the back windows of the cell were sealed with Apiezon-Q (Shell Oil Co.), a sealing plastic of very low vapor pressure, which can be used like putty. The tightness of these seals was indicated by the fact that during the runs of 500 hours or more, the only change in the sodium was some clouding

of the surface; an excess of metallic sodium was present throughout the runs.

Before irradiation, two days' time was allowed for removal of the oxygen, carbon dioxide, and water from the air and fibers in the cell.

With this cell, it was found possible to irradiate a total sample of about 0.1 g., in layers only a few fibers thick.

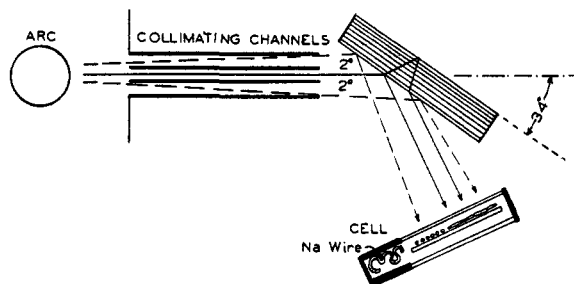


Fig. 1.—Polarizing system for ultraviolet irradiation of fibers.

The fibers present a series of parallel, roughly cylindrical surfaces, on each of which the beam is incident at every angle from perpendicular to grazing incidence. Penetration of light is less efficient than with a plane surface; with polarized light the penetration of light varies, depending upon whether the light vibrates parallel or perpendicular to the axis of the cylinders.

Elimination of reflection factors by immersion in a medium transparent to ultraviolet of appropriate refractive index would introduce prohibitive chemical complications. Consequently the fibers were exposed directly, and a correction computed as follows.

In the method of exposure used, light vibrating lengthwise of the fiber ( $n_y$ ) vibrates perpendicular to the "plane of incidence" (the plane containing the incident and refracted rays); light vibrating crosswise of the fiber ( $n_x$ ) vibrates in the plane of incidence. The first case involves more loss by reflection.

For a plane surface, Fresnel developed mathematical expressions relating the quantity of incident, reflected and transmitted light for each case.<sup>21-23</sup> Vibrations perpendicular to plane of incidence:

$$b = -a \frac{\sin(i - r)}{\sin(i + r)}$$

$$c = 2a \frac{\cos i \sin r}{\sin(i + r)}$$

(21) Preston, "The Theory of Light," Macmillan and Co., London, 1921, pp. 342-354.

(22) Houstoun, "A Treatise on Light," 4th edition, Longmans, Green and Co., New York, 1925. Identical equations are obtained in a more rigorous way by applying the principles of the electromagnetic theory of light, *op. cit.*, pp. 418-421.

(23) Wood, "Physical Optics," 1911, p. 338.

(16) Cunningham and Doree, *J. Chem. Soc.*, **101**, 497 (1912).

(17) Oguri, *J. Soc. Chem. Ind. Japan*, **37**, Suppl. 620-621 (1934).

(18) Joachim-Henk, *Melliand Textil-Ber.*, **18**, 521 (1937); *Am. Dyestuff Repr.*, **27**, 318 (1938).

(19) Barr and Hadfield, *Dept. Sci. Ind. Res. 2nd Rept. Fabr. Cobrd. Res. Comm.*, 95 (1930).

(20) Cunliffe, *J. Text. Inst.*, **19**, T169 (1928).

Vibrations in plane of incidence

$$b = -a \frac{\tan(i - r)}{\tan(i + r)}$$

$$c = \frac{2a \cos i \sin r}{\sin(i + r)\cos(i - r)}$$

Since light intensity is proportional to the square of the amplitude

$$I_a I_b : I_c = a^2 : b^2 : (c^2 \tan i \cot r)$$

where  $a$ ,  $b$ , and  $c$  are the amplitudes of the incident, reflected, and refracted beams,  $I_a$ ,  $I_b$ ,  $I_c$  the corresponding intensities, and  $i$  and  $r$  the angles of incidence and refraction, respectively. The term,  $\tan i \cot r$ , is applied to the refracted beam, to take into account the refractive index of the medium<sup>21</sup> (p. 93) which the light is entering.

For a cylindrical surface,  $i$  varies from 0 to 90° on either side of perpendicular incidence. Hence, by evaluating the term  $c^2 \tan i \cot r$  in terms of  $a^2$  and summing over the angular range 0 to 90°, values for the intensity of refracted (penetrating) light, in terms of the incident intensity, are obtained.

For light vibrating perpendicular to the plane of incidence ( $n_\gamma$ )

$$I_c \text{ is proportional to } \int_0^{\frac{\pi}{2}} a^2 \frac{\sin 2i \sin 2r}{\sin^2(i + r)} di$$

For light vibrating in the plane of incidence ( $n_\alpha$ )

$$I_c \text{ is proportional to } \int_0^{\frac{\pi}{2}} a^2 \frac{\sin 2i \sin 2r}{\sin^2(i + r)\sin^2(i - r)} di$$

These summations were evaluated graphically. The intensity terms were calculated for several angles of incidence, the values being recorded in Table I and plotted in Fig. 2.

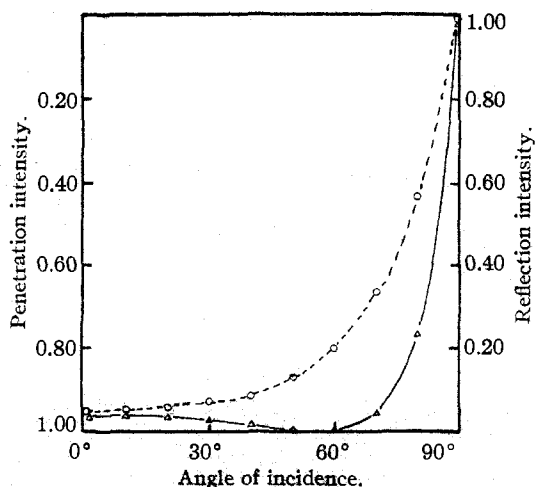


Fig. 2.—Intensity of penetration and of reflection of light, as a function of angle of incidence.

TABLE I  
CALCULATED VARIATION IN INTENSITY OF REFRACTED BEAM WITH ANGLE OF INCIDENCE

$i$	$I_c$ for light vibrating lengthwise ( $n$ )	$I_c$ for light vibrating crosswise ( $n$ )
0°	0.952	0.956
10°	.948	.957
20°	.942	.963
30°	.930	.973
40°	.908	.984
50°	.870	.995
60°	.800	1.000
70°	.663	0.959
80°	.436	.765
90°	.000	.000

In calculating values for the first column, the refractive index used was  $n_\gamma = 1.568$ , for the second column,  $n_\alpha = 1.530$ , both values for 5893 Å. The corresponding refractive indices in the ultraviolet are not known, but the absorption spectrum of cellulose does not exhibit any marked bands that might indicate anomalous dispersion, and comparison of Fig. 2 with a similar published diagram for crown glass ( $n = 1.523$ )<sup>24</sup> will show that refractive index variations of the magnitude involved make practically no difference in the shape and position of the curves.

Since the value of  $(c^2 \tan i \cot r)$  for  $i = 0^\circ$  is indeterminate, it must be obtained from the relationship  $a^2 = b^2 + c^2 \tan i \cot r$  and Young's equation<sup>21</sup> (p. 352). No data on possible ultraviolet pleochroism of cellulose fibers have been determined, but even if this exists it is unlikely that the differences in the absorption coefficient for the two orientations would have sufficient influence on the reflection factor to render these curves inapplicable, especially since the absorption of cellulose is relatively low in the spectral region used.

If the total area of the graph represents one intensity unit of incident light, the curve divides this area into the relative amounts penetrating (above) and reflected (below). By planimetry the areas above the curves are: 0.77 for light vibrating parallel to  $n_\gamma$ , 0.91 for light vibrating parallel to  $n_\alpha$ .

Thus, the fibers oriented parallel to the vibration direction of the incident light were penetrated by only 0.77/0.91 or 0.85 as much light as those lying perpendicular. The degradation values for fibers in the latter orientation were therefore reduced by the factor, 0.85.

(24) Hardy and Perrin, "Principles of Optics," McGraw-Hill Book Co., New York, N. Y., 1932, p. 28.

Actually, the effective penetration, for vibrations either crosswise or lengthwise of the fibers, is probably greater, because of imperfections in their assumed cylindrical surfaces, and because adjacent fibers may absorb some light that would otherwise be lost by the first reflection. The difference in penetration may therefore be somewhat less than the factor 0.85 indicates.

**V. Determination of Amount of Degradation.**—Of the common criteria for evaluating the degradation of cellulose, copper number was selected, as the most adaptable to the very small samples available.

A critical survey of methods up to 1931 is given by Burton and Rasch.<sup>25</sup> Doree<sup>26</sup> summarizes several methods which are in favor in the textile industry. Probably the most important variation from the original method is the elimination of strongly alkaline  $\text{Cu}^{++}$  solution containing tartrate, in favor of a solution made alkaline with  $\text{Na}_2\text{CO}_3$ - $\text{NaHCO}_3$  as proposed by Braidy<sup>27</sup> and Koehler and Marquoyrol.<sup>28</sup>

Amick<sup>29</sup> concludes that the copper number method for evaluating glucose is too much subject to variations in conditions to have any significance in expressing structural changes in glucose, but if conditions are fixed rigidly, analytical results can be duplicated.

Results on cellulose likewise can be duplicated if conditions are maintained comparable, but where variations in the history and condition of sample as well as differences in conditions of the experiments are introduced, absolute interpretations are not justified. The chief value of the copper number determination is in making comparisons of an empirical nature.

Heyes<sup>30</sup> gives a micro-method for copper number, which requires 0.25 g. By modifying the Heyes method, sufficiently accurate checks could be obtained on 0.01 g. of exposed ramie, permitting several determinations on the 0.1-g. samples.

The method finally adopted follows.

Solutions used were:

A. Carbonate-bicarbonate: 150 g. anhydrous sodium carbonate, 50 g. anhydrous sodium bicarbonate in 1 liter of solution.

(25) Burton and Rasch, *Bur. Standards J. Research*, **6**, No. 4, 603-19 (1931).

(26) Doree, "Methods of Cellulose Chemistry," Chapman and Hall, London, 1933.

(27) Braidy, *Rev. gén. mat. color.*, **25**, 35 (1921).

(28) Koehler and Marquoyrol, *Mém. poudres*, **18**, 73 (1921).

(29) Amick, *J. Phys. Chem.*, **31**, 1441 (1927).

(30) Heyes, *J. Soc. Chem. Ind.*, **47**, 90T (1928).

B. Copper sulfate: 100 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in 1 liter of solution.

C. Ferric sulfate: 4 g.  $\text{Fe}_2(\text{SO}_4)_3$  and 100 cc. concd. sulfuric acid per liter of solution.

D. Sulfuric acid for washing:  $\text{H}_2\text{SO}_4:\text{H}_2\text{O} = 10:90$ . (Solutions C and D as well as all distilled water used, were boiled free of air to minimize the possibility of oxidation of cuprous oxide.)

E. Standard potassium permanganate solution: approximately 0.004 *N*.

Such a low normality was chosen by experiment since it gave, for the sample weight used, the best compromise between a high buret reading and a sharp end-point. The solution was standardized against sodium oxalate, according to the method of Fowler and Bright.<sup>31</sup>

0.009-0.011 g. of the fibers in cuttings about 1 mm. long, were weighed into a dry 15 × 15 cm. test-tube; moisture "regain" was slight enough to be negligible. To this was added 10 ml. of digestion mixture (9.5 ml. solution A and 0.5 ml. of solution B) which had been preheated in a boiling water-bath for ten minutes previously. A stirring rod with a bent lower end, and short enough not to protrude, was inserted into each test-tube. A small glass crucible in the mouth of the tube served as a reflux condenser. The tube was supported in the boiling water-bath so that the digestion mixture was completely below the level of the liquid, and with the aid of forceps to grasp the rod, its contents were stirred gently (in order to avoid beating in air) every ten minutes for three hours.

Ten minutes before the close of the digestion period, the stirring rod was removed, and the carbonate adhering to it was washed into a sintered glass filtering funnel.

When the three-hour digestion was complete, the tube was cooled in cold tap water for five minutes, and the supernatant liquid poured into the filter funnel. The fibers were washed once with 3 cc. of distilled water, by decantation, and the washings added to the digestion liquor. To the washed fibers 1 ml. of ferric sulfate solution C was added, rinsing down the sides, and the tube of fibers was replaced in the water-bath for five minutes. During this time almost all of the digestion liquor was filtered with suction, leaving just enough in the funnel to cover the few fibers present. To the funnel, arranged over a filtering bell jar, and covered with a watch glass, was added 2 ml. of 10:90 sulfuric acid from a pipet. (It is important that all the residual alkali be destroyed by this step, as it was found that local neutralization of the next solution containing  $\text{Fe}^{++}$  ions precipitated ferrous hydroxide, which is very susceptible to oxidation.)

The  $\text{Fe}^{++}$ - $\text{Fe}^{+++}$  solution was transferred to the funnel, and filtered into a 25-ml. Erlenmeyer flask under the bell jar; the fibers in the test-tube and funnel were washed with 1 ml. of ferric sulfate solution, then with three 2-ml. portions of 10:90 sulfuric acid, and finally with water.

Titration was done promptly with the 0.004 *N* potassium permanganate, using a micro-buret with a drawn-out tip, which delivered a drop of 0.014 ml. volume.

The end-point is a colorless solution produced by neu-

(31) Fowler and Bright, *Bur. Standards J. Research*, **15**, 493 (1935).

tralization of the faint blue color of the solution with the excess potassium permanganate. Further potassium permanganate produces a pink tint. Since all of these colors are very faint, the titration was carried out by artificial light with a Daylite glass filter, in a screened compartment. Comparison was made with distilled water containing one drop of potassium permanganate solution, and with an untitrated copper number solution. With such control, the end-point could be duplicated to plus or minus one drop ( $\approx 0.014$  ml.).

The ferric sulfate solution proposed by Heyes was too concentrated for this titration, masking the faint end-point with a yellow-green color. The solution used contained one-tenth as much ferric sulfate.

A micro-buret which did away with the troubles of lubricating a stopcock of small bore, and which delivered a drop of 0.014 ml. volume was improvised as follows. A 1-ml. graduated pipet was drawn out in a flame to a finer tip. This buret was then clamped vertically, a thin-walled rubber tube fixed to the upper end, and passed down to the desk top and under a weighted roller, by the movement of which liquid could be drawn up or expelled.

The blank for the determination was obtained on 10 cc. of digestion mixture without fibers, going through the actual procedure from the first filtration on. Three drops of potassium permanganate were required to produce the colorless end-point, this being equivalent to 0.04 ml., a value which was deducted from all final buret readings. On the basis of a 10-mg. sample, the blank was equivalent to a copper number of 0.11-0.12.

$$\text{Cu no.} = \frac{\text{ml. of KMnO}_4 \times \text{Normality} \times 0.0635}{\text{Weight of sample in grams}}$$

The accuracy obtainable is indicated by the following values on ramie sliver after exposure through vitreous silica, without the polarizer

15 hours: (at 15 cm. distance) 0.658, 0.637, 0.647, 0.555, 0.643.  
10 hours: (at 15 cm. distance) 0.513, 0.580, 0.582.  
7 hours: (at 5 cm. distance) 3.68, 3.58, 3.68.

### Results

The first run of five hundred and thirty-five hours of irradiation, gave rather erratic results for the determination of copper numbers:

Vibrations lengthwise ( $n_\gamma$ )  
0.316, 0.317, 0.254, 0.265, av. 0.29  
Vibrations crosswise ( $n_\alpha$ )  
0.373, 0.269, 0.487, 0.257, 0.572, av. 0.39  
Average, corrected by reflection factor 0.85 = 0.33

The inconsistency of these results is ascribed to poor samplings of the fibers, and to partial reoxidation of hydroxide as mentioned in the analytical procedure. In a second run, care was taken to avoid this by acidifying before adding  $\text{Fe}^{+++}$  solution to the cuprous oxide-stained fibers, and better mixing of the sample was obtained by agitating the cuttings of fibers by an air jet.

The second run, lasting eight hundred and forty hours, yielded more consistent copper numbers.

Vibrations lengthwise ( $n_\gamma$ )  
0.37, 0.41, 0.33, 0.32, av. 0.36  
Vibrations crosswise ( $n_\alpha$ )  
0.56, 0.67, 0.60, 0.49, 0.43, av. 0.55  
Average corrected by reflection factor 0.85 = 0.47

Longer exposures, giving large copper numbers, would have emphasized the difference in degradation with orientation. (Measured by the amount of degradation, eight hundred and forty hours of exposure to the rather weak polarized light used was roughly equivalent to less than fifteen hours exposure to unpolarized light at 15 cm. distance.)

The exposed material might have been divided into fewer and larger samples for analysis, minimizing the error in the determination, but it was thought that, in view of the lack of high precision of the method, a larger number would be more significant, if they showed a consistent trend. This is certainly the case in the second run, for although the values show a considerable spread, none of the results for one orientation overlap those for the other, and the increase in copper number is roughly proportional to the longer time of irradiation.

The evidence presented for the greater photochemical degradation by light vibrating crosswise of the fibers, although definite, is only qualitative. The optical complexity of the specimen, so different from the transparent plane parallel surfaced ones ordinarily used in photochemical experiments, the non-uniform distribution of illumination and penetration, the probable presence of cellulosic material not oriented parallel in the fiber—all these factors would tend to minimize the difference of degradation for the two orientations, so that the observed difference of approximately 25% is far from insignificant.

### Discussion

Photochemical action is initiated by absorption of light energy. For any substance, inorganic or organic, where absorption arises from the arrangement of atoms in a fixed structure such as a molecule or crystal lattice, the absorbed activating energy is very probably applied to deformation of this structure. If the light energy is polarized, the direction of maximum deformability should be that of strongest absorption, and of most pronounced photochemical action, as was found in the photolysis of inorganic nitrates.<sup>2-4</sup>

Cellulose is believed to be built up of "glucose residues," chained end to end by a hemiacetal

linkage, as in cellobiose. The molecules are arranged parallel to the fiber length; lateral spacings between chains are relatively great. In agreement with Wooster's<sup>32</sup> and Bragg's<sup>33</sup> generalizations, the highest refractive index is found for vibrations lengthwise of the chain structure. Greatest deformability, and the consequent maximum photochemical degradation, should take place crosswise of the chains, since their length and parallelism would prevent lengthwise deformation.

It is generally accepted that photochemical degradation of cellulose fibers results in shortened chain length with an increase in reducing and acidic properties due to the breaking of oxygen linkages, and a consequent increase in copper number. Comparisons of chain length by viscosity, etc., were not feasible on the small samples irradiated, but the chemical changes observed correspond to those to be expected from the above process, if the light energy by virtue of its transverse vibrations breaks some of the oxygen links in the cellulose chain.

The present work illustrates qualitatively the generalization that the properties of crystalline

(32) Wooster, *Z. Krist.*, **80**, 495 (1931); "Crystal Physics," Cambridge Univ. Press, Cambridge, 1938, pp. 175-187.

(33) Bragg, "The Crystalline State," Vol. I, G. Bell and Sons, London, 1933, p. 186; "Atomic Structure of Minerals," Cornell Univ. Press, Ithaca, 1937, p. 120.

matter differ with direction, a factor that should never be ignored in dealing with ordered structures. With the recent development of methods for producing oriented aggregates of other long chain compounds such as oils, the study of the anisotropic photochemical properties of their molecules becomes possible.

**Acknowledgment.**—This work was carried out under a Fellowship supported by the Procter and Gamble Company. The authors are also indebted to E. B. Ashcraft for valuable advice.

### Summary

Using a silica "pile of plates" polarizer, to give polarized ultraviolet light, parallel ramie fibers were irradiated, in a cell containing metallic sodium, to eliminate air or moisture that might cause secondary non-directional reactions. With light vibrating crosswise of the fibers, degradation was greater than with vibrations lengthwise, by about 25%, as measured by copper number determined on 10-mg. samples. From analogy with simpler compounds, it is concluded that photochemical degradation of cellulose chains is greatest if they are oriented so that the light energy vibrates in the direction in which they are most deformable.

ITHACA, N. Y.

RECEIVED SEPTEMBER 2, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

## A Simple Wet Combustion Method for the Determination of Carbon, Oxygen Equivalence and Empirical Formula by Iodic Acid Oxidation\*

BY BERT E. CHRISTENSEN AND J. FRED FACER

More work pertaining to organic combustions has been described in the literature than perhaps any other single analytical procedure. The fact that so much attention has been devoted to this determination testifies to its importance. The problem of determining carbon and hydrogen has been approached in several ways.<sup>1-6</sup> In spite of all these developments there is still need for simpler techniques, less expensive equipment and

methods by which the occasional determination can be made with some degree of ease.

A study of the means by which the above problem may be answered leads to one possibility, the wet combustion process. This would entail the measurement of "oxygen consumed" as an alternative for the determination of moisture. Dichromate and iodate have been cited as excellent reagents for this purpose. Of these iodate is outstanding<sup>7</sup> since little, if any, decomposition (unless carried out above 200°) or carbon monoxide formation accompanies its reduction.

A survey of the literature reveals that Strebinger<sup>8</sup>

(\* Published with the approval of the Monographs Publication Committee, Oregon State College, Research paper No. 24, School of Science, Department of Chemistry.

(1) Glocker and Roberts, *THIS JOURNAL*, **50**, 828 (1928).

(2) W. R. Kirner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 358 (1934).

(3) H. Lieb and H. G. Krainick, *Mikrochemie*, **9**, 367 (1931).

(4) J. Lindner, *Ber.*, **59**, 2561, 2806 (1926).

(5) M. Nicloux and A. Boivin, *Compt. rend.*, **184**, 890 (1927).

(6) E. Sucharda and B. Bobranski, *Z. anal. Chem.*, **77**, 462 (1929).

(7) Christensen, Williams and King, *THIS JOURNAL*, **59**, 293 (1937).

(8) Strebinger, *Z. anal. Chem.*, **58**, 97 (1919).