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An Investigation of the Loss Angle and
Dielectric Constant of Cellulose

by Charles Richard Calkins

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AN INVESTIGATION OF THE LOSS ANGLE AND
DIELECTRIC CONSTANT OF CELLULOSE

A thesis submitted by

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INTRODUCTION

Paper has wide and varied uses in the electrical industry as an insulator. The properties that have made it desirable for such uses are its low power factor, its easily controlled dielectric constant, its desirable physical properties, and its relative economy. Although the physical properties of paper account for much of its usefulness in the electrical industry, the electrical properties are of greater scientific interest for two reasons. First, the physical specifications (often rigorous) can be met by the manufacturer by conventional means. Second, widespread advances in the use of paper in the electrical field have been limited by the present properties of paper dielectrics. Further advances, therefore, are to be anticipated through the improvement of the paper.

The chief constituent of electrical papers is cellulose, ranging from linen and alpha papers, which are almost pure cellulose, to unbleached kraft papers, which are perhaps 80% cellulose. Much research has been carried out upon commercial papers but comparatively little attention has been focused upon an understanding of the dielectric properties of the constituents of these papers. Furthermore, dielectric properties are intimately related to physical and chemical structure and might prove useful in increasing our knowledge of the physical chemistry of cellulose.

For these reasons, an investigation of the dielectric properties of cellulose is timely and desirable, both from a scientific and a practical viewpoint.

THEORETICAL BACKGROUND

All materials may be classified as conductors or as dielectrics. The former contain free electrons which move in an electrical field and cause a current flow. Such conducting electrons are not present in dielectrics, in which all electrons are bound into a space lattice framework. In an electrical field, a distortion of the positive and negative centers of charge occurs. This is known as polarization and gives rise to an external field. A dielectric placed between the plates of a charged condenser becomes polarized and its field is opposed to the field of the condenser. Since the charge on the condenser is constant and the effective potential difference is decreased by the introduction of the dielectric, the capacitance of the system (ratio of charge to potential difference) is increased. This polarization is characteristic of the dielectric under any particular conditions and is commonly expressed as the ratio of the capacitance of a condenser filled with the dielectric to its vacuum capacitance. It is known as the specific inductive capacity or, more commonly, as the dielectric constant (ϵ). When the potential difference is removed, the positive and negative centers of the charge revert to their former position and return energy to the circuit. Therefore, the dielectric constant is a measure of the ability of a dielectric to store energy.

In an alternating field a similar polarization takes place, reversing with the applied field. The current is 90 degrees out of phase with the applied voltage in accordance with the classical theory. Although all types of polarization take place in a static field, various

types of polarization are affected differently at different frequencies and, consequently, the dielectric constant is dependent upon frequency.

At extremely high (visible) frequencies, only electrons are displaced (electronic polarization). It has been established on both theoretical and experimental grounds that, at these frequencies, the dielectric constant is equal to the square of the index of refraction. As the frequency is decreased to the infrared region, atoms are displaced (atomic polarization) and the dielectric constant increases. In general, this type of polarization is of small magnitude. These polarizations are relatively independent of temperature.

As the frequency is further lowered into the electrical range, dipole polarization may take place. A polar molecule which is free to rotate in an applied field causes an increase in the dielectric constant. Debye (1) derived the following type of relation for such polarization:

$$\underline{P} = \underline{A}(\underline{a} + \underline{b}/\underline{T}), \quad (1)$$

where \underline{P} is molar polarization, \underline{A} , \underline{a} , and \underline{b} are constants for a particular material, and \underline{T} is the absolute temperature. This relation is quantitative in those cases where the basic assumptions (that the molecule is free to rotate and no molecular interaction occurs) are valid, as in the case of gases or dilute solutions of polar molecules in non-polar solvents. In most dielectrics, however, the equation has only a qualitative significance.

In a heterogeneous material in which various components have different electrical properties, interfacial polarization may occur. A charge builds up at the interfaces between the different components.

These charges may become oriented in the applied field, resulting in a higher dielectric constant. In general, interfacial polarization takes place at lower frequencies than other types of polarization because of the larger mass of the particles involved, and decreases at higher temperatures because of thermal agitation.

It is well known that the polarizability of a nonpolar dielectric is given by

$$\underline{P} = [(\epsilon - 1)/(\epsilon + 2)] (\underline{M}/\underline{D}), \quad (2)$$

where \underline{P} is molar polarizability, \underline{M} is molecular weight, and \underline{D} is density. If polarizability is considered a constant characteristic of the molecule independent of density, the dielectric constant may be related to density.

$$(\epsilon - 1)/(\epsilon + 2) \propto \underline{D} \quad (3)$$

This is one form of the classical Clausius-Mosotti relation. It has been found to hold approximately for many dielectrics in which the basic assumptions used in its derivation are not strictly true.

Thus far, an idealized dielectric has been considered. In a real dielectric, impurities, conducting surface loss paths, and lattice irregularities cause direct conduction. However, most dielectrics, when dry, have direct current resistances of the order of 10^8 to 10^{12} ohm-cm., and energy losses attributable to this cause are generally negligible.

It has been assumed that the centers of charge alternate with the applied alternating field without energy absorption. In a real dielectric this is not true. Because of this energy loss, a condenser with

A real dielectric may be represented as a perfect condenser $[C_p]$ in parallel with a resistance $[R_p]$. Then, if V is the impressed voltage and ω is the angular velocity or 2π times the frequency f , θ is the phase angle and δ is the loss angle as sketched in Figure 1.



FIGURE 1

In a circuit with voltage V and current I , the power dissipated may be represented as

$$\text{Power} = VI \cos \theta, \quad (1)$$

Therefore, the relative power loss of a dielectric in a condenser is given by $\cos \theta$ of the circuit element. Here θ is large and δ is small, the power factor, $\cos \theta$, may be related to the loss angle:

$$\cos \theta \approx \tan \delta = 1/\epsilon' \omega C_p \approx \epsilon''. \quad (2)$$

When power factor is low (as in most dry dielectrics) the power factor and the loss angle are very nearly equal.

The loss factor of a dielectric is defined as the product of its dielectric constant and the tangent of its dielectric loss angle.

The power loss per unit volume of a material is proportional to its loss factor. Therefore, this quantity is a measure of the energy loss of the dielectric in a particular use.

This dielectric loss may readily be explained by the concept of the relaxation time phenomenon. Each particle when displaced by the applied field requires time to return to its original position (because of internal resistance and inertia), and such time is characterized by the "relaxation time." If the period of oscillation of the applied field is of the same order as the relaxation time, there will be a phase difference between the oscillations of the field and the particle, and energy will be absorbed and converted to heat.

Lennig and Sell (2) have derived the following fundamental general equations for dielectric constant and loss angle, assuming only that this concept of "relaxation time" is correct.

$$\epsilon - \epsilon_{\infty} = \int_0^{\infty} \cos(\omega\theta) \phi(\theta) d\theta \quad (6)$$

$$\epsilon' = \int_0^{\infty} \sin(\omega\theta) \phi(\theta) d\theta \quad (7)$$

where $\epsilon_{\infty} = \epsilon$ at infinite frequency, and

θ = a general term representative of "relaxation time."

These equations show that dielectric constant and the loss angle are fundamentally related to "relaxation time" and frequency. In order to solve these equations, a numerical value for the relaxation function $[\phi(\theta)]$ must be assumed. Lennig and Sell make the following assumption:

$$\phi(\theta) = \underline{c} e^{-\underline{t}/\tau} \quad (8)$$

where \underline{c} = a constant,

τ = relaxation time, or the time for perfect condenser to discharge to $1/e$ of its original charge, and

\underline{t} = time

Integration of Equations (6) and (7) gives

$$\epsilon - \epsilon_{\infty} = \frac{Q\tau}{(1 + \omega^2 \tau^2)} \text{ and} \quad (9)$$

$$\epsilon' = \frac{Q\omega\tau}{(1 + \omega^2 \tau^2)}. \quad (10)$$

Murphy and Horan (3) interpreted dielectric loss with the aid of a mechanical analogy. They considered that a charged particle of a given mass displaced in an alternating field experiences a force \underline{F} which restores it to its equilibrium position and a frictional resistance \underline{r} to that restoration. By proper mathematical treatment, they derive the following equations:

$$\epsilon - \epsilon_{\infty} = (\epsilon_0 - \epsilon_{\infty}) / (1 + \omega^2 \tau^2) \text{ and} \quad (11)$$

$$\epsilon'' = [(\epsilon_0 - \epsilon_{\infty}) \omega \tau] / (1 + \omega^2 \tau^2), \quad (12)$$

where

$$\tau = (\epsilon_0 + 2) / (\epsilon_{\infty} + 2) \tau^0.$$

Comparison with Equations (9) and (10) shows the similarity between the relations derived from a fundamental basis and from a mechanical model. Assumptions of different relaxation functions may account for the differences.

Although such equations are often qualitatively correct, they do not agree exactly with experimental results. Yeager (4) assumed that a distribution of "relaxation times," rather than a single value, exists. He showed that, by proper selection of distribution functions, similar equations give results in accord with observed values.

Now, a dielectric may be pictured as being composed of a group of particles of varied mass and charge, restricted in their

equilibrium positions by internal forces. Depending upon their mass and charge, they are displaced at different frequencies. The dielectric loss of the material is the energy lost as heat when the movements of the particles become out of phase with the applied field, because of their mass and relaxation times. This loss increases at frequency bands where the dielectric constant is changing because this band is a region in which particles just begin to oscillate and, consequently, are not in phase with the applied field. This is known as a region of anomalous dispersion. A mechanical analogy considers that these particles encounter resistance in their movement in the applied field. The dielectric loss is the heat loss resulting from friction.

Cellulose is a linear polymer containing many polar groups. In general, such polymers exhibit increased dielectric constant and loss with increasing temperature and decreasing frequency. Fuoss (5-7) and Fuoss and Kirkwood (8) have shown that the observed dielectric behavior of other polymers of this type cannot be quantitatively explained by the previously discussed relations. They concluded that the observed effects are due largely to the motions of dipoles in what is effectively a medium of high viscosity. In a polymer of this type, the dipoles are restrained in their positions because of their attachment to the polymer chain. Secondary valence forces may be operative between the chains or portions of them. The motion of any dipole affects the motion of neighboring dipoles. Kirkwood and Fuoss (9) have modified Debye's original theory to apply to this case with semiquantitative agreement with observed results.

A definite relation between electrical and mechanical properties has been noted. Dielectric constant and loss vary inversely with the modulus of elasticity. Similarly, the presence of plasticizers affects dielectric properties. For example, Lewis, Miller, and Moore (10) found that the dielectric constant increased as the hardness of a series of plasticized polyvinyl chloride plastics decreased. Fisher and Taylor (11) showed that the dielectric constant and power factor were related to the interaction of the chains. In the case of polydecamethylene sebacide, they showed that decreased crystallinity and, hence, decreased hydrogen bonding increased the dielectric constant and power factor. The relative freedom of polar groups in a linear polymer is related to the observed dielectric properties.

Cellulose is a mixture of linear polymers with various degrees of polymerization, composed of anhydroglucose units connected by glucosidic linkages. There are three free secondary and one free primary hydroxyl groups for each unit. One carbonyl group may be present at the end of each chain and the possibility of the presence of carboxyl groups exists. The cellulose chains are arranged in a heterogeneous fashion. In some areas, the chains are oriented and show crystalline properties, including arrangement into unit cells of several possible modifications. The chains are held together by secondary valence forces, including hydrogen bonding. In other areas, the chains are free to move and are bound to other chains only infrequently. These areas give no x-ray diffraction and are designated as amorphous, although it is probable that there is some orientation. Water molecules can penetrate between the chains in the amorphous regions, whereas they can

be adsorbed only when the surface of the crystalline units. Finally, cationic impurities may be adsorbed or bonded to the cellulose.

When this system is placed in an alternating electrical field at "power frequencies," electronic polarizations will take place. By means of the relation, $\epsilon = n^2$, where n is the index of refraction, the contribution of this type of polarization to the dielectric constant is found to be about 2.5 or roughly a third of the accepted value of 8.1 for native cellulose. It is probable that little dielectric loss occurs.

Atomic polarizations also occur but, as these are generally of small magnitude, they will not be considered further.

Hydroxyl and other polar groups will be affected by the applied field. In accordance with the previously described concepts, these groups are restrained in their positions on the chains. It is probable that a substantial portion of the observed loss in cellulose is a consequence of its polar groups.

In the amorphous areas, portions of chains may be at least partially free to rotate.

Cellulose is heterogeneous and interfacial polarizations undoubtedly occur. Whether they make a substantial contribution to the observed loss and dielectric constant is not known.

Absorbed impurities, such as water and minerals, may contribute to both direct conduction and dielectric loss. There is abundant evidence that even small amounts of water cause disproportionate losses.

It is probable that, at low moisture content, water molecules are bound to the surface of the cellulose in such a manner as to behave like polar groups which are restrained in their oscillations in the field.

With this concept of cellulose as a dielectric, the literature and the results obtained in this investigation may be better evaluated and correlated with the present knowledge of the fundamental structure of cellulose.

EXPERIMENTAL METHOD

Only one investigation of the power factor of pure cellulose has been reported, although considerable work has been done upon linen and kraft papers. The dielectric constant has been more thoroughly investigated.

Stoops (12) measured the dielectric constant and power factor of cellulose in the form of cellophane over a wide range of frequencies and temperatures. He found the dielectric constant to be 7.6 at 25° C. at a frequency of 1000 cycles. It increased slightly at higher temperatures and decreased slightly at higher frequencies. The power factor reached a minimum value of 1.6% at temperatures from 20 to 50° C., the temperature of the minimum decreasing at lower frequencies. In accordance with the theory of anomalous dispersion, the power factor showed a maximum in the frequency range where the dielectric constant changed most rapidly. Tests upon pure cellulose triacetate showed that replacement of the hydroxyl groups in cellulose by acetate groups lowered the dielectric constant nearly 50% and the power factor slightly. Stoops attributed electrical loss to the rotation of the cellulose chains rather than to the rotation of hydroxyl groups, since the latter have a resonant frequency higher than the frequencies used. Furthermore, cellulose acetate had an appreciable power factor, although it contains no hydroxyl groups. Stoops dried his samples at 105° C. without evacuation. Heranno (13) has shown that under such conditions, a residual moisture content as high as 0.5% may remain. This could account for the relatively high power factor values of cellulose and for the lower values

for cellulose acetate, since the moisture absorption of the latter is considerably smaller under similar conditions.

According to International Critical Tables (14), the dielectric constant of cellulose varies from 3.9 to 7.5. Campbell (15) found a value of 6.7 for a regenerated cellulose. DeLuca, Campbell, and Marice (16) reported a value of 6.1 at 25° C. They measured the dielectric constant of cotton dispersed in hydrocarbon mixtures and found the mixture whose dielectric constant was not changed by the presence of cellulose.

Hansen (17) and Van den Akker (18) found that the dielectric constants of kraft and exploded fiber pulps were related to density by the classical Clausius-Mosotti relation. Endicott (19) considered paper to be a series of fiber resistances either in parallel or in series. He derived relations between the dielectric constant and the density for each assumption. For a particular kraft paper, the series representation fits quite accurately. However, further data (not given) indicated that a combination of series and parallel elements would be more accurate. Sample calculations with these equations reveal that such a combination would effectively give the same values as the Clausius-Mosotti relation. Over a wide density range, Endicott's equations lose validity.

Hansen assumed that the loss factor was proportional to density for a kraft paper. Endicott derived loss factor-density relationships from the forementioned assumptions. The parallel resistance case

is identical with Hansen's assumption. The series case differs only slightly over moderate density changes.

The relation between moisture content and the dielectric properties of papers and fibers has been investigated extensively. Murphy and collaborators (20-22) have shown that the presence of moisture causes increased direct conduction in cotton fibers.

Argue and Maass (23) measured the dielectric constant of cellulose at a series of moisture contents. They concluded that the water was increasingly tightly bound to cellulose. Only increments above 1% have dielectric constants approaching the value of pure water. Garton (24) also concluded that adsorbed water has a lower polarizability in cellulose than does free water. These results indicate that the presence of a small amount of water would have little effect upon the accuracy of the dielectric constant determination.

This was verified when Greenfield (25) measured the equilibrium dielectric constant of kraft paper at a series of vacuums. Reduction of the pressure from 400 to 0.25 mm. caused a decrease of only 3%. Under similar conditions, the power factor decreased 80%. Greenfield and Whithead (26) found that both values were related to the water present in the paper in an exponential fashion. Belevanti (27) was unable to definitely prove that drying kraft paper at 70° C. at a pressure of 8 microns eliminated dielectric loss resulting from moisture. Garton, on the other hand, claimed that paper could be completely dried at 60° C. with the circulation of dry air.

Greenfield (25) and Louts and Lohsen (26) concluded that water adsorption follows Freundlich's adsorption isotherm in the case of commercial kraft papers. However, the mechanism may be more complicated, particularly for the last traces of water. Lohsen and Fohman (29) pointed out that the fine capillary structure of paper introduces a new factor in drying. Purdy (30) analyzed the gases evolved during the drying of paper. He concluded that there was no final dry point, since the composition of the evolved gases reached a constant value. Dryness in all probability is a relative term when applied to a complex polymer like cellulose and it is difficult to judge by other than empirical methods if complete dryness has been attained.

Cellulose exhibits an affinity for cations and, in fact, can act as an ion exchanger (31). It is difficult to remove all cations and obtain an ash-free cellulose. The presence of these metallic contaminants in cellulose has been shown to lower the electrical resistance. Walker and Quill (32) noted that washing with distilled water raised the direct current resistance of cotton. Church (33) investigated the effect of a series of cations upon the direct current resistance of commercial condenser paper. Monovalent ions lowered resistance more than divalent ions. Adsorbed ions, as distinguished from bound ions, also lowered the resistance. Purdy and collaborators (20-22) have shown that both alternating and direct current conduction of cotton increases not only with increasing metallic ion content but also with increasing moisture content, the deleterious effect of metallic ions being enhanced by the presence of moisture. Hansen investigated the effect of the presence of calcium ions in well-desiccated

drift paper. He found that they had little effect at lower frequencies but caused some increase in the power factor at higher frequencies.

Vogel (34) found that the presence of electrolytes caused the power factor of commercial electrical papers to rise rapidly at higher temperatures. He attributed this to added water held by the electrolytes.

CELLULOSE CAPACITORS

Few reliable data have been reported for the electrical properties of pure cellulose. Little work has been done toward the correlation of the electrical behavior and the physical and chemical modifications of cellulose.

The problem, therefore, was to investigate the dielectric properties of native, regenerated, and degraded celluloses over as wide a temperature and frequency range as was practicable, and to explain the observed behavior on the basis of fundamental concepts.

As an adjunct to this major problem, a suitable test capacitor and auxiliary system was designed and constructed for use with the electrical equipment available at the Institute of Paper Chemistry in order that the range and reliability of the results could be enhanced.

APPENDIX FOR APPARATUS DESCRIPTIONS

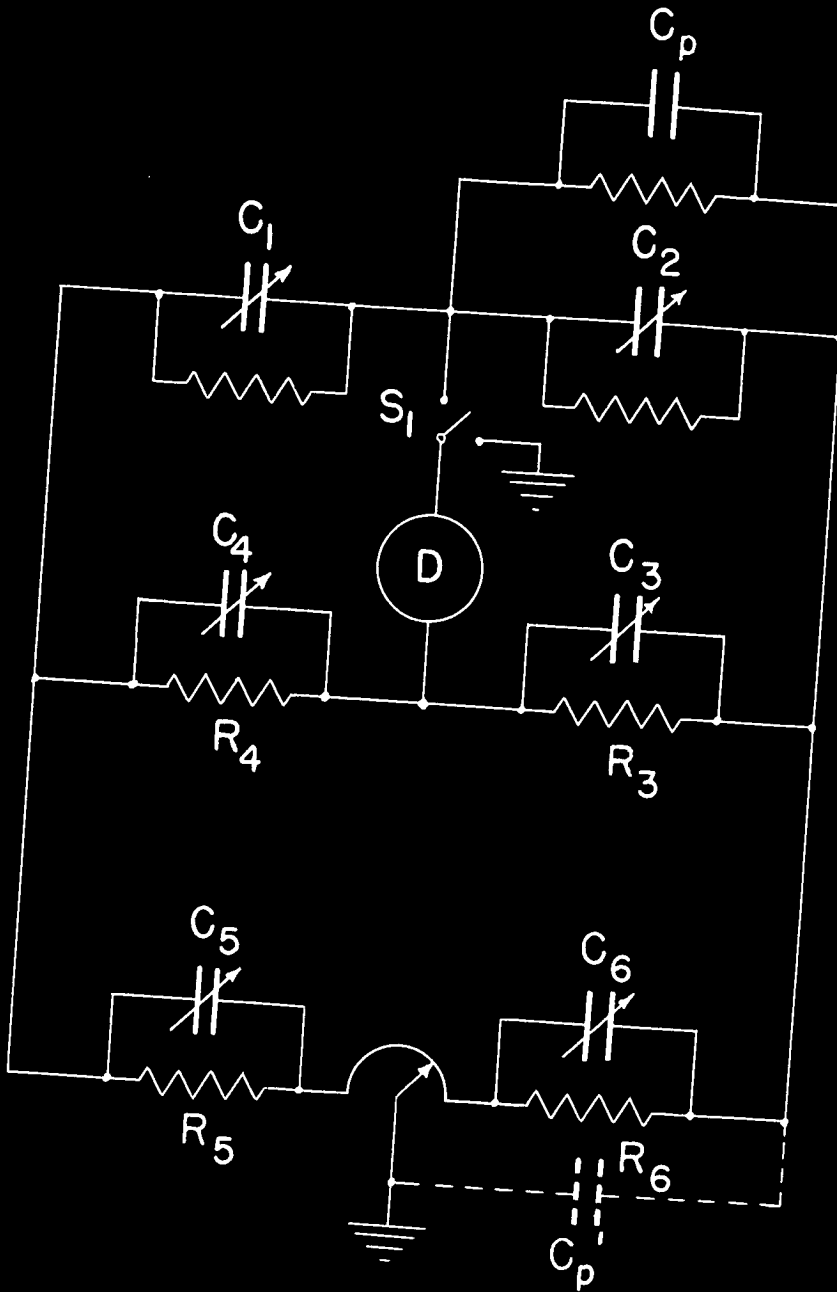
BRIDGE

A modified conjugate Schering bridge was used for most of the electrical measurements. The bridge is capable of measuring the equivalent parallel capacitance and loss angle of a test capacitor of suitable size over a wide frequency range. It was built as a table-top layout by Televenti (27) and was later mounted on a portable relay rack by the Physics Department of The Institute of Paper Chemistry. The design for the bridge was adopted from the American Society for Testing Materials' standard for the electrical testing of insulating materials (32).

Televenti described the bridge in detail and, therefore, only a schematic diagram of the circuit is shown in Figure 2. C_2 is a General Radio precision capacitor with negligible power factor. The others are air capacitors of suitable sizes. The resistors (R_3 , R_4 , R_5 , and R_6) are 10,000-ohm precision-matched noninductive resistors. S_2 is a shielded single-pole, double-throw, laminated wafer-type switch. The leads to the test capacitor are of shielded cable. The detector (D) is a high-gain vacuum-tube amplifier. The indicating device is a Weston Model 440 galvanometer, which measures the rectified alternating output of the amplifier.

OSCILLATOR AND MEASURING VOLTMETER

A transitron-type oscillator capable of delivering sinusoidal alternating voltages of frequencies ranging from 200 to 10,000 cycles per second was built by Jensen (17) from descriptions of Helwig (36) and Jordan (37) and is described in detail by him. This oscillator was used as a source of alternating current for the Schering bridge in this work.



Equivalent Electrical Circuit of Bridge

Figure 2.

In order to calibrate the transitron oscillator, it was necessary to have a primary frequency standard. A General Radio 1000-cycle tuning fork hummer was selected and adjusted by drillings in the ends of the fork to vibrate at 1000 cycles/sec.

The transitron oscillator was calibrated at a series of frequencies using an oscilloscope and the Lissajous' figure technique.

Calibrations were checked at regular intervals. It is estimated that the delivered frequency is within 0.5% of the desired value.

TEST CAPACITOR SYSTEM

A photograph of the test capacitor system, designed to eliminate spacing between the paper under investigation and the electrodes, is shown in Figure 3. It consists of a pair of electrodes of suitable size and design mounted in such a manner that considerable pressure can be exerted upon the sample while electrical measurements are being made. The system is equipped with a separation gage capable of measuring the electrode separation with an accuracy better than 0.0004 inch. The electrode and auxiliary equipment are encased in a bell jar connected to a vacuum system capable of evacuation to a pressure of 0.1 micron. A McLeod gage permits measurement of the pressure in the evacuated system. The entire apparatus is enclosed in a mounted insulated box whose temperature can be controlled with 1° C. from 25 to 110° C.

ELECTRODE SYSTEM

The photograph of the electrode mounting is shown in Figure 4, and a schematic diagram is given in Figure 5. The upper electrode and

Studies of Dielectric Properties of Chemical Pulps

III. Dielectric Properties of Cellulose

CHARLES R. CALKINS

A test capacitor embodying several desirable features has been designed and constructed for use with a Schering bridge. The loss angle and dielectric constant of native cellulose has been measured at frequencies from 500 to 4000 cycles per second at temperatures from 25 to 105°C., under conditions that assure no inaccuracy as a consequence of the presence of moisture. The observed behavior can be adequately explained if cellulose is regarded as a heterogeneous linear polymer with many polar groups. Similar measurements with regenerated celluloses showed significant increases in both loss angle and dielectric constant as compared with native cellulose. When these celluloses are subjected to moderate pressures, these values are reduced. A possible relationship between the observed dielectric constant and amorphous cellulose content (estimated by moisture regain) was found. However, the evidence is contradictory (a presumably amorphous cellophane was comparable with native cellulose), and no definite conclusions may yet be drawn.

PAPER HAS WIDE and varied uses as an insulator in the electrical industry, because of its low power factor, easily controlled dielectric constant, desirable physical properties, and its relative economy. Although much research has been carried out upon commercial papers, little attention has been focused upon an understanding of the dielectric properties of the constituents of these papers, and particularly cellulose. Such knowledge may lead to a better understanding of the dielectric behavior of electrical papers. Furthermore, dielectric properties are intimately related to physical structure, and might prove useful in elucidation of our knowledge of the physical chemistry of cellulose.

REVIEW OF PREVIOUS WORK

Delevanti and Hansen (1) have adequately reviewed the fundamental theories of dielectric behavior and the literature concerning electrical papers. Only investigations pertinent to this present work will be discussed here.

Stoops (2) measured the dielectric constant of cellulose in the form of cellophane over a wide range of frequencies and temperatures. He found the dielectric constant to be 7.6 at 1000 cycles at 25°C., which increased slightly at higher temperatures and lower frequencies. The power factor reached a minimum value of 1% at temperatures from 20 to 50°C., the temperature of the minimum decreasing at lower frequencies. Cellulose acetate had a lower dielectric constant and slightly lower power factor. Stoops attributed electrical loss to rotation of cellulose chains. His drying techniques are questionable in the light of more recent work.

Dielectric constant values for cellulose from 3.9 to 7.5 have been reported (3, 4). The most reliable value is that of De Luca, Campbell, and Maass (5), who found a value of 6.1 at 25°C.

Delevanti and Hansen (1) found that the dielectric constant of kraft paper was related to density by the classical Clausius-Mosotti relation, where ϵ is dielectric constant and D is density.

$$(\epsilon - 1)/(\epsilon + 2) \propto D \quad (1)$$

They found that loss factor and density bore a linear relationship. Endicott (6) derived several semiempirical relations that were adequate over moderate density ranges. Calculations showed that, over wide ranges, the relations failed.

The relation between moisture content and dielectric properties of cellulose-containing materials has been extensively investigated. The presence of moisture has been shown to cause increased conduction in cotton fibers (7-9). Argue and Maass (10) and Garton (11) both concluded that adsorbed water is increasingly tightly bound to cellulose as water is removed. Greenfield (12) showed that, although a small amount of water has little effect upon the dielectric constant, it contributes excessively to dielectric loss. He and Houtz and McLean (13) concluded that water adsorption follows Freundlich's adsorption isotherm. Others (14, 15) have shown that the mechanism may be more complicated and that dryness is a relative term in the case of a complex polymerlike cellulose.

Cellulose exhibits an affinity for cations. The presence of these metallic contaminants has been shown to lower electrical resistance (16, 17). Their deleterious effect is enhanced by the presence of moisture (9). Delevanti and Hansen (1) found that the presence of ash in kraft paper has little effect at low frequencies. Vogel (18) attributed increased loss of electrical papers at higher temperatures to the presence of electrolytes.

It is evident that the effect of moisture and ash must be eliminated in order to accurately measure the dielectric properties of cellulose.

EXPERIMENTAL PROCEDURES

Electrical Testing Equipment

A conjugate Schering bridge designed according to A.S.T.M. (19) and a transitron type oscillator were used for most of the electrical measurements. This equipment was built by Delevanti and Hansen (1) and is described by them.

The new test capacitor system is illustrated in Fig. 1. It consists of a pair of electrodes of suitable size mounted so that considerable pressure can be exerted upon the test specimen while electrical measurements are being made. The thickness gage is capable of the measurement of the electrode separation with an accu-



Fig. 1. Test capacitor system

acy of 0.0004 inch. A bell jar (not shown) encloses the electrode system and rests on the base plate. The system may be evacuated to a pressure of 0.1 mu. The apparatus is enclosed in a mounted shielded insulated box whose temperature can be controlled within 1°C. from 25 to 105°C.

A schematic diagram of the electrode system is shown in Fig. 2. The upper electrode and insulator are cemented to the upper plate. The lower electrode mount rides on a ball bearing on the upper shaft, whose movement, in turn, is controlled by a jack, mounted at the point indicated in the drawing. The upper electrode is therefore fixed in position, whereas the lower electrode may be raised or lowered. The syphon bellows permits this motion and, at the same time, preserves the vacuum. The base plate contains the electrical leads and connections to the vacuum system and McLeod gage. With this apparatus, pressures up to 1000 p.s.i. can be intermittently exerted upon the test specimen.

The electrode separation gage is a capacitor whose separation is directly related to the separation of the main electrodes as shown in Fig. 3. The upper electrodes of both the gage and test capacitor are stationary. The spacing of the test capacitor is determined by the position of the lower electrode. The lower electrode of the auxiliary capacitor is flexibly mounted with regard to vertical movement only and its position is determined by the main lower electrode, since the glass rod that acts as the support of the lower electrode of the gage extends through the center of the main upper electrode and rests upon the lower main electrode through a hole cut in the test specimen.

The capacitance of the gage capacitor is measured with a capacitance bridge. Standard shims of known thickness were placed between the electrodes and the bridge balanced at a series of electrode pressures and

temperatures. Suitable calibration charts prepared from these data were used to obtain electrode separations.

Method of Making Electrical Measurements

Several sheets of a particular cellulose were carefully selected for smoothness, good formation, and freedom from dirt specks. The specimens were inserted in place, and the apparatus assembled and heated to 105°C. After equilibrium (15 hours), the specimens were placed under 940 p.s.i. by the jack. The temperature and the vacuum were noted and the auxiliary bridge was balanced. The Schering bridge was balanced at 500, 1000, 2000, and 4000 cycles per second. The lower electrode was lowered, and the temperature allowed to drop to the next desired value, equilibrium established, and the procedure repeated. Measurements were made at approximately 105, 75, 50, and 25°C. The temperature was then raised and measurements made at these temperatures in a similar stepwise fashion. At the conclusion of the run, the vacuum was broken and the specimen was removed. The area of the specimen between the electrodes was carefully cut out, the area measured, and dried to constant weight at 105°C. The density was calculated as the mean mass per unit volume between the electrodes. Dielectric constant and loss angle were calculated using the approximation formulas given by A.S.T.M. (19). The dielectric

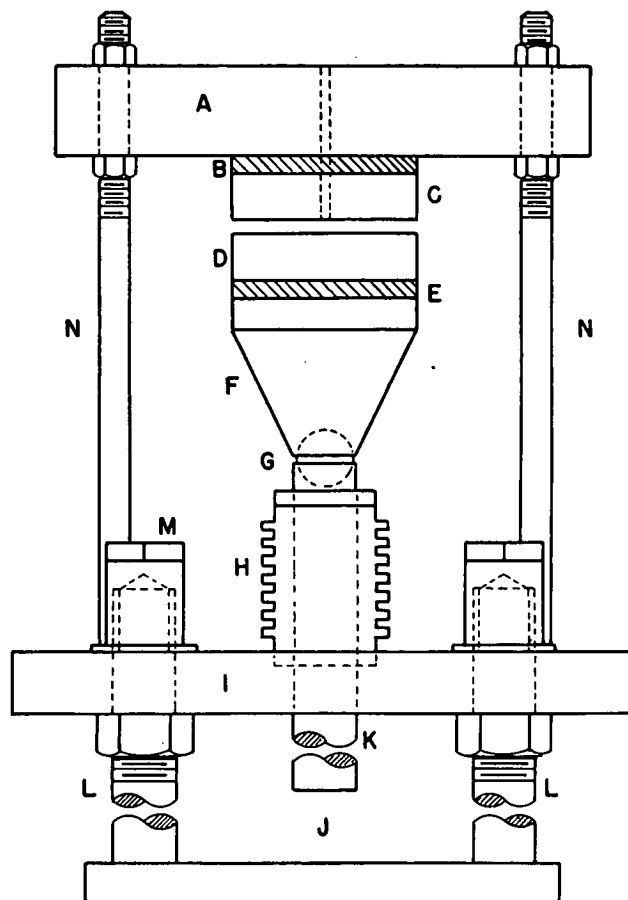


Fig. 2. Schematic diagram of electrode mounting system

A, Upper plate; B, upper main electrode insulator; C, upper main electrode; D, lower main electrode; E, lower main electrode insulator; F, lower main electrode mount; G, ball bearing; H, syphon bellows; I, base plate; J, hydraulic jack (not shown); K, main shaft; L, jack frame; M, cap nuts; and N, connecting shafts (only 2 shown).

constant was calculated to standard density (0.8 gram per cubic centimeter) by means of the Clausius-Mosotti relation. Loss angle was calculated to standard density by the method described by Delevanti and Hansen (1), assuming that loss factor and density bear a linear relationship. Dielectric constant and loss angle at standard density are designated $\epsilon_{0.8}$ and $\epsilon'_{0.8}$, respectively. At these low values, the loss angle and power factor are very nearly equal.

Sources of Error in the Measurements

The Schering bridge is inherently accurate, and the frequency of the transitron oscillator was stable and accurately known. Use of the approximation formulas was shown to introduce no appreciable error. The lead loss is small and was neglected. The new electrode system eliminates error due to spacing between the specimen and the electrodes. This was confirmed by measuring the loss angle of a specimen at a series of electrode pressures. At pressures of 800 p.s.i. or higher, observed values (corrected to standard density) became constant, indicating that spacing had been effectively eliminated. All measurements were made at a pressure of 940 p.s.i. upon the specimen. The

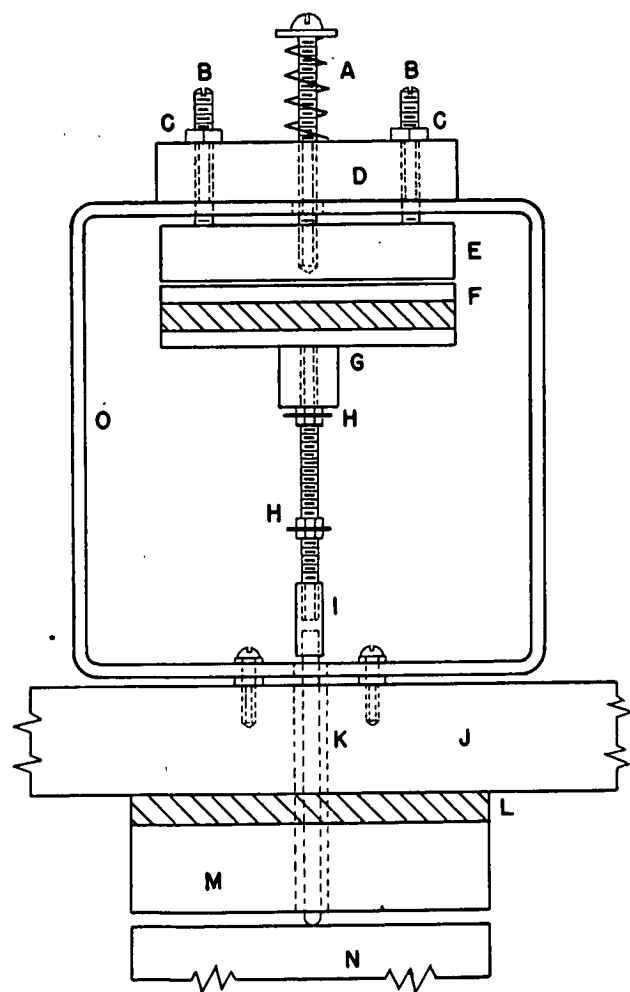


Fig. 3. Schematic diagram of electrode separation gage

A, Spring; B, set screws (only 2 shown); C, lock nuts; D, brass disk; E, upper electrode; F, lower electrode; G, lower electrode support; H, flexible support for lower electrode; I, glass rod holder; J, upper plate; K, glass rod; L, main upper electrode; M, main lower electrode; N, main lower electrode; and O, support frame for gage.

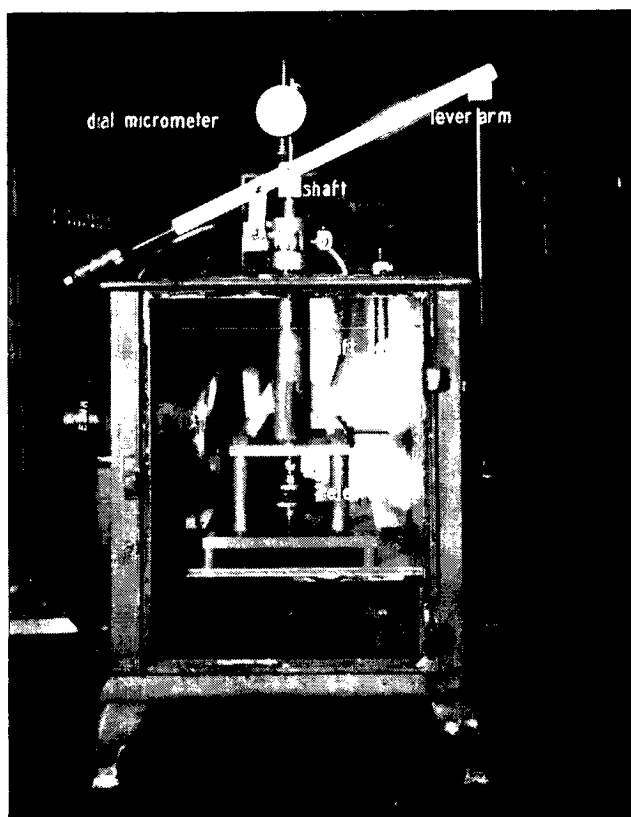


Fig. 4. Auxiliary dielectric constant apparatus

measurement of the dielectric constant of several specimens of native cellulose at different densities showed that the Clausius-Mosotti relation was applicable. Similar measurements of loss factor showed a slight deviation from linearity with density. The differences, however, were small and no appreciable error was introduced in the results by the assumption of linearity.

Equilibrium studies showed that 12 hours were sufficient for equilibrium loss angle measurements. The presence of moisture had no significant effect upon the results when the first stage of drying was at 105°C. This was shown in two ways. First, no hysteresis effect was observed in loss angle measurements, although it is known that, even at low gas pressures, hysteresis in moisture sorption does take place (13). Second, several tests were run at gas pressures up to 200 mu, rather than at 0.1 mu. No differences were noted in the loss angles at either pressure, except perhaps at 25°C., where the observed differences were within the experimental error. The dielectric constant was unaffected by the small changes in moisture content.

An estimation of the sources of error in the determination of dielectric constant indicated that the maximum error of a single measurement should be about 10%. Statistical analysis of some of the observed data in the case of native cellulose showed a standard deviation (for individual data) of less than 5%, in good agreement with the estimation. Similarly, the maximum error of a single loss angle measurement should be of the order of 10%. Standard deviations of the data varied from 4 to 6%.

The results show that both loss angle and dielectric constant determinations may be considered sufficiently accurate and precise for the purposes of this investigation.

As this investigation proceeded, the need for an auxiliary apparatus for the purpose of making independent and rapid dielectric constant determinations became apparent. A plastometer was modified for our purposes. A photograph of the completed apparatus is shown in Fig. 4. The upper electrode shaft is permitted vertical movement only by the shaft collar. The shaft is actuated by the lever arm. The lower electrode is stationary, and the electrode spacing is determined by the position of the upper electrode shaft. The foot piece of a dial micrometer rides upon the upper end of the shaft. The electrode separation is determined from the difference in the micrometer readings at zero and at the separation existing with a specimen in place. A moderate pressure can be exerted upon the specimens by loading the lever arm. The system is mounted in a laboratory oven equipped with a thermoregulator and a blower for the circulation of air. The capacitance is measured with a capacitance bridge connected to the electrodes through a rigid system of wires (to insure stable lead capacitance).

Desiccated air was bled into the oven to insure that all air flow was outward and that the specimens were conditioned in a dry atmosphere. [Previous investigations (10, 12) and preliminary experiments established that an extreme state of desiccation is not necessary for accurate determination of dielectric constant.]

Specimens were placed in the apparatus and conditioned at 65 to 70°C. until equilibrium was established. The door was opened, the specimen placed between the electrodes, the door closed, the bridge balanced, and the micrometer reading noted. The specimen was removed and the zero separation of the electrodes noted. Tests showed that this procedure did not produce error in the determination by permitting the specimen to adsorb significant amounts of moisture during the manipulation. The density was determined and the results were calculated to standard density in the manner previously described.

This equipment is probably not as accurate as the main apparatus. However, no significant differences could be noted between the results obtained in the two apparatuses for native cellulose.

DIELECTRIC PROPERTIES OF NATIVE CELLULOSE

Three native celluloses were tested. The first was a purified Hercules cotton linters (cellulose A), the second Whatman No. 50 quantitative filter paper (cellulose D), and the third bleached ramie fiber (cellulose K). Celluloses A and K were beaten in laboratory beaters,

Table I. Physical and Chemical Properties of Celluloses Tested

Cellulose	Description	Degree of polymerization	Carboxyl milli-equiv./100 g.	Copper No.	H ₂ O regain at 54% R. H. ^a	Ash, %
A	Cotton linters	1450	Neg.	...	6.1	0.07
D	Filter paper	930	Neg.	...	6.15	0.006
E	Regenerated	10.7	0.1
F	Regenerated	..	0.2	...	10.9	0.21
G	High carbonyl	360	1.6	4.5	6.05	0.12
H	High carboxyl	240	6.3	0.5	6.3	0.1
J	Regenerated	505	Neg.	...	11.65	0.13
K	Ramie	1055	6.2	0.15
L	Cellophane	11.6	...

^a Regain at 54% R. H. after 24 hours preconditioning at 25% R. H.

Table II. Dielectric Constant of Native Cellulose at Several Temperatures

Temp., °C.	$\epsilon_{0.8}$
25	2.42
50	2.36
75	2.41
100	2.50

screened, washed, and extracted with dilute acid as described by Delevanti and Hansen (1). Sheets were prepared by a method similar to the one described by them. Several experiments were carried out in the case of celluloses A and D. One short experiment was carried out with cellulose K. No significant differences existed between these native celluloses although cellulose K appeared to have a slightly lower loss angle at the lower temperatures. These results are not surprising, since each is pure cellulose, chemically speaking, as Table I shows. Only one difference is apparent in the analytical data; the ash contents vary from 0.006 to 0.15%. However, such differences have no significant effect upon loss angle under conditions of desiccation employed in the present work.

The mean loss angle curves at standard density are presented as a function of temperature in Fig. 5. The dielectric constant values at 1000 cycles are given in Table II. No significant differences were noted at other frequencies. Using the Clausius-Mosotti relation, a value of 6.0 is found for the dielectric constant of solid native cellulose at 25°C. in good agreement with the value of 6.1 reported by De Luca, Campbell, and Maass (5). The data show that the dielectric constant goes through a very slight minimum and then increases with increasing temperature. Other investigators have noted the rise in dielectric constant with increasing temperature, but the presence of a minimum has not been reported. After thorough consideration it is concluded that the dielectric constant of native cellulose shows a slight rise at higher temperatures, and that it is probable that it goes through a minimum in this temperature and frequency range.

Cellulose is a linear polymer with many polar groups. In general such polymers show increased dielectric constant and loss angle with increased temperature and decreased frequency (20, 21). Cellulose is also a heterogeneous material and interfacial polarization may occur. This type of polarization decreases with increasing temperature and increasing frequency, because of the relatively large masses of the particles involved (22).

If this concept of cellulose is correct, then the ob-

Table III. Increases in Loss Angle of Native Cellulose As a Result of Degradation

Cycles Temp., °C.	$\Delta\epsilon'_{0.8} \times 10^3$, radians			
	25	50	75	90
Carboxyl Groups ^a				
500	0.45	0.30	0.80	1.60
1000	0.35	0.35	0.55	1.25
2000	0.30	0.35	0.65	0.85
4000	0.15	0.20	0.35	0.80
Carbonyl Groups ^b				
500	0.05	0.10	0.30	0.25
1000	0.05	0.10	0.10	0.20
2000	0.05	0.15	0.15	0.20
4000	0.05	0.05	0.05	0.15

^a 1 carboxyl group per 100 anhydroglucose units.

^b 1 carbonyl group per 10 anhydroglucose units.

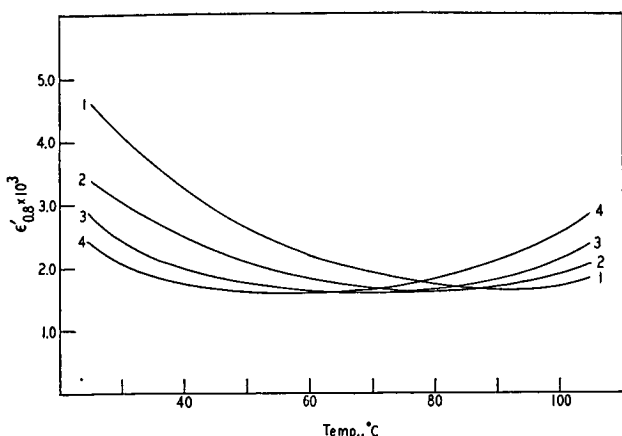


Fig. 5. Loss angle of native cellulose at several frequencies

Curve 1, 4000 cycles; Curve 2, 2000 cycles; Curve 3, 1000 cycles; and Curve 4, 500 cycles.

served loss angle-temperature relationship may be explained. If interfacial polarizations occur, the initial decrease may be the result of decreased loss as such polarizations decrease as a result of increased thermal agitation. However, the possibility of a low temperature region of anomalous dispersion cannot be ruled out. At higher temperatures, the loss attributable to polar groups increases, and a minimum is observed. This latter loss decreases with increasing frequency and, as a consequence, the minimum is shifted toward a higher temperature at higher frequencies.

The observed dielectric properties of cellulose are satisfactorily explained if cellulose is regarded as a heterogeneous linear polymer with many polar groups.

The dielectric behavior of native cellulose has been shown to be related to its polar character. In addition to the hydroxyl groups, carboxyl and carbonyl groups are found in cellulose. Their contribution to dielectric loss was ascertained by measurements carried out upon several oxycelluloses prepared from cotton linters according to the method of Birtwell, Clibbens, and Ridge (23). They were acid extracted, washed, and made into sheets in the same manner as the native celluloses. Analytical data indicating the content of carboxyl and carbonyl groups in celluloses G and H are presented in Table I. The copper number was used as a measure of carboxyl groups. Two experiments were carried out on each cellulose. In both cases higher loss angle values, as compared with native cellulose, were observed, particularly at higher temperatures.

The relative contribution of each group to the dielectric loss was estimated in the following manner. The increase observed in the case of cellulose H was assumed to be entirely due to the carboxyl groups present since the cellulose has a low copper number. The net increase at each frequency, as compared with native cellulose, was determined graphically, and is presented in Table III, together with similar data from cellulose G, which have been corrected for carboxyl content, using the results obtained with cellulose H.

The contribution of carbonyl groups to dielectric loss is negligible, except possibly at higher temperatures. Since this oxycellulose has a very high copper number, it may be concluded that carbonyl groups are not a source of appreciable dielectric loss in cellulose.

The contribution of carboxyl groups to dielectric loss is extremely high at higher temperatures, increasing

with decreasing frequency. Since analysis shows only one carboxyl group for each 100 anhydroglucose units, the effect is considerable. It is possible that cellulose contains carboxyl groups not revealed by present analytical methods. However, the possibility that such groups are responsible for the observed rise in the case of native cellulose must be discarded, since the magnitude of the effect is not so large that one or two carboxyl groups per 1000 anhydroglucose units could be the cause.

No significant changes in dielectric constant as compared with native cellulose were noted. This is not unexpected, since the differences, as compared with native cellulose, although drastic chemically speaking, have affected physical structure only slightly.

Several interesting deductions may be made from these observations in conjunction with other data. Delevanti and Hansen (1) have reported loss angle values at standard densities at 1000 cycles for kraft pulps of 2.1 to 2.4×10^{-3} radians at 80°C . Native cellulose under the same conditions has a loss angle of 1.7×10^{-3} radians. If it is assumed that the pulp is 80% cellulose and that its contribution to dielectric loss is proportional to its weight fraction, the contribution of the remaining components is found to be more than one third of the observed loss, even in the case of the best kraft pulp. Delevanti and Hansen (1) found that the loss angle of a bleached kraft pulp was only slightly lower than that of an unbleached kraft. The source of excessive loss is evidently in the noncellulosic constituents of the pulp with both lignin and hemicelluloses contributing to the dielectric loss. The behavior of the latter can be explained readily, since it is generally accepted that most of the carboxyl groups present in pulps are found in the hemicellulose fraction. Delevanti and Hansen have shown that lignin contributes excessively to dielectric loss.

These views are substantiated by the work of Miller and Hopkins (24). They found that the removal of lignin and associated materials from kraft electrical paper reduced the power factor. Alkaline extraction of the delignified residue with the removal of 4% of the hemicelluloses (based upon original paper) caused considerable reduction in the power factor. A limited extraction of this type would remove the carboxylic fraction of the hemicelluloses and, as the results of this investigation show, reduce the dielectric loss. Further extraction caused large increases in power factor. Such

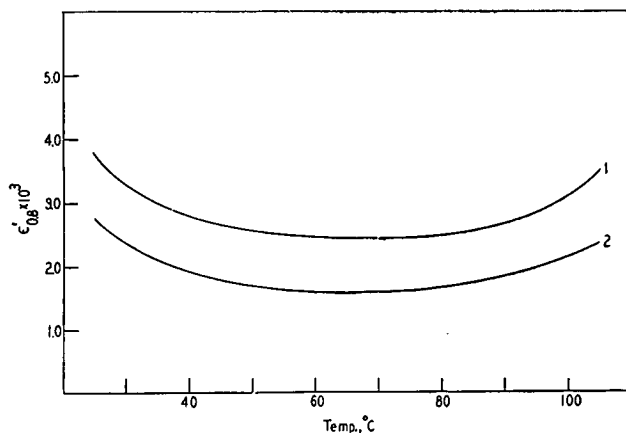


Fig. 6. Loss angle of regenerated cellulose at 1000 cycles

Curve 1, cellulose J and Curve 2, native cellulose.

extended treatment would not leave a pure native cellulose residue but rather might introduce considerable degradation which would account for the increase. Unfortunately, no analytical data of the residues were given.

It is believed that the following statement can be made. Improvements in the dielectric characteristics of present-day electrical papers are to be looked for in the elimination of those fractions of the noncellulosic constituents which contribute excessively to dielectric loss and, particularly, in the elimination of carboxyl groups.

DIELECTRIC PROPERTIES OF REGENERATED CELLULOSE

The previous section of this paper has been concerned with native celluloses which possess the normal crystal lattice (cellulose I) and are largely crystalline. Regenerated celluloses differ in two respects. The cellulose exists in a different crystal lattice and is largely amorphous as a consequence of the regeneration, according to Hermans (25). Most regenerated celluloses exist in the hydrate cellulose lattice (cellulose II). The terms crystalline and amorphous are used in the qualitative sense of indicating regular ordered arrangement and disordered random arrangement of cellulose chains, respectively.

Changes in the dielectric properties in comparison with native cellulose are possible as a consequence of these differences. In particular, if the amorphous content were related to the dielectric behavior, a valuable analytical tool might be developed.

Celluloses E, F, and J were prepared by regeneration from viscose according to the method of Jayme and Wellm (26). The viscose was precipitated into a turbulent regenerated bath and the cellulose obtained in a fibrous form. It was acid extracted, purified in the same manner as native cellulose, and stored in water. The moisture regain of these celluloses was almost twice that of native cellulose. Hermans has reported that amorphous cellulose has a much higher moisture regain than crystalline cellulose and, on the basis of his results, these celluloses must be considered amorphous. All exhibited plastic flow at low pressures, a property of amorphous materials.

The shrinkage of sheets prepared from these fibers was so great they invariably split upon drying. Splitting was avoided by slowly drying between stacks of blotters, but the sheets were somewhat wrinkled and, with few exceptions, were unsatisfactory for testing. Smooth soft sheets were prepared by drying these celluloses by solvent replacement, using methyl alcohol, ethyl ether, and cyclohexane in that order.

Two experiments were made with sheets of cellulose J prepared in this manner. The calculated loss angle values at 1000 cycles at standard density are presented as a function of temperature in Fig. 6. A similar curve for native cellulose is included for purposes of comparison. The dielectric constants at various temperatures, calculated to standard density at 1000 cycles, are presented in Table IV, together with similar data for native cellulose.

Similar results were found at all frequencies tested. Both loss angle and dielectric constant values are substantially higher than comparative values for native

Table IV. Dielectric Constant of Regenerated Cellulose at 1000 Cycles

Temp., °C.	Cellulose J $\epsilon_{0.8}$	Native cellulose $\epsilon_{0.8}$
25	3.5	2.42
50	3.6	2.36
75	3.8	2.41
100	3.9	2.50

cellulose at all frequencies. Before the cause and significance of these results is discussed, it is necessary to be assured that these differences are characteristic of the celluloses.

The solvent treatment had no effect upon the results. Methoxyl analysis revealed only a trace of methyl alcohol. Ether is not retained by cellulose (27). No cyclohexane was retained by the regenerated cellulose, although native cellulose after similar treatment retained 2 to 5% [based upon gain in weight method after Staudinger and Dohle (28)]. Tests upon a specimen of native cellulose dried by solvent replacement showed no differences as compared with air-dried native cellulose.

The auxiliary dielectric constant apparatus was utilized to make a series of dielectric constant determinations upon celluloses E and J, which had been dried in several ways. The condensed results are presented in Table V. In all cases a definite increase in dielectric constant is found. The regenerated cellulose specimens are of substantially lower density than the native celluloses. The results are calculated to standard density by means of the Clausius-Mosotti relation. If this is not applicable to regenerated cellulose, the apparent increase could be a result of the calculation. In Table V the dielectric constant of native cellulose has been calculated to the apparent density of each regenerated cellulose sample and comparisons made. Significant differences still exist. Therefore, the observed increases are not caused by an error in calculation.

The regenerated celluloses exist in the cellulose hydrate lattice (cellulose II). It is conceivable that the observed effects are a consequence of this change. A specimen of cellulose J was heated in glycerin at 240°C. for 40 minutes [according to Kubo (29) this largely shifts the lattice to cellulose I, although Hermans states the shift is to cellulose IV]. No significant change was observed in the dielectric constant, although the moisture regain dropped from 11.6 to 9.6% apparently because of the shift in lattice. It may be concluded that the lattice form has no effect upon dielectric constant. (The influence of this change in lattice on loss angle was not investigated.)

During the measurements with cellulose J in the main apparatus, it was noted that the specimens adsorbed diffusion pump oil from the atmosphere even at 0.1

Table V. Dielectric Constant of Several Regenerated Cellulose Sheets

Cellulose	Density	ϵ	$\epsilon_{0.8}$	$\epsilon_{0.8}/2.4$	ϵ/ϵ_N^a
J (solvent)	0.368	1.75	3.31	1.38	1.15
J (solvent)	0.538	2.30	3.45	1.44	1.26
J (solvent)	0.553	2.55	3.90	1.63	1.38
E (air dried)	0.518	2.08	3.09	1.29	1.17
J (ether) ^b	0.329	1.94	5.20	2.16	1.34
J (ether) ^b	0.335	1.85	4.37	2.36	1.27

^a ϵ_N is ϵ of native cellulose sheet at the density of regenerated cellulose sheet.

^b Dried by solvent replacement through ether.

Table VI. Dielectric Constant of Cellulose L

Specimen	Density, g/cc.	ϵ	$\epsilon_{0.8}$
L-1	1.50	4.27	2.16
L-2	1.43	3.37	1.99

mu pressure, a phenomenon not observed with any other cellulose. The oil could be easily removed with ether. Although it is possible that the presence of this oil could affect the loss angle determination, it is unlikely since oils generally possess low power factor and the amount present was negligible on a weight basis. Whether the surface activity demonstrated by these celluloses is the result of their high amorphous cellulose content or of their high specific surface is not known. They are definitely better absorbents than native cellulose.

It would appear that the cause of increased loss angle and dielectric constant of these celluloses is the increased content of amorphous cellulose. Examination of the loss angle curves shows that their shapes are similar to those of native cellulose. The increased values, as compared with native cellulose, might be explained by the fact that more hydroxyl groups are free to oscillate because they are no longer bound in a crystalline region, where the groups are close enough to permit hydrogen bonding to take place. Possibly portions of chains in the amorphous areas are free to oscillate. The observed increase in dielectric constant may be similarly explained. A similar increase in dielectric loss and dielectric constant with increasing amorphous content has been observed in the case of another linear polymer (polydecamethylene sebacamide) by Baker and Yager (30).

If these deductions are correct the dielectric constant of cellulose L, a cellophane having the same moisture regain as cellulose J and, presumably, a similar amorphous content, should show a similar increase. The results of two tests are presented in Table VI. Cellulose L does not show the expected increase in dielectric constant. It has been stored in formaldehyde solution. Formaldehyde is known to cause cross linkages in cellulose and it is possible that these linkages could cause a lowered dielectric constant. Stoops (2) found a dielectric constant of 7.9 for cellophane at 1000 cycles at 65°C. If a density of 1.5 gram per cubic centimeter is assumed, a value of 3.0 at standard density may be calculated, definitely higher than native cellulose.

These celluloses possessed thermoplastic properties. Under moderate pressures they flowed and showed substantial increases in apparent density. This pressing caused definite changes in the electrical properties. A specimen of cellulose F was pressed at 2000 p.s.i. for 10 minutes at 110°C., and tested. The loss angles at standard density at 1000 cycles are presented in Table VII together with comparative values for native cellulose and unpressed cellulose J.

Table VII. Loss Angle of Hot-Pressed Regenerated Cellulose at 1000 Cycles

Temp., °C.	$\epsilon''_{0.8} \times 10^3$, radians		
	Cellulose F (pressed)	Native cellulose	Cellulose J (unpressed)
25	2.60	2.80	4.78
50	1.55	1.70	2.60
75	1.90	1.62	2.45
100	3.75	2.13	3.08

Table VIII. Dielectric Constant of Hot-Pressed Regenerated Celluloses

Cellulose	Description	ϵ	Density, g/cc.	$\epsilon_{0.8}$	Moisture regain at 54% R. H.
J	Solvent dried, unpressed	1.75	0.37	3.31	11.6
J	Solvent dried, pressed	2.51	0.83	2.44	10.3
E	Water dried, unpressed	2.08	0.52	3.09	10.8
E	Water dried, pressed	1.86	0.68	2.07	10.0
J	Solvent dried, glycerin heated, unpressed	2.57	0.55	4.00	9.6
J	Solvent dried, glycerin heated, pressed	4.03	1.19	2.52	..
F	Air dried, pressed	2.54	0.98	2.15	10.0

Similar comparative results are found at other frequencies. The loss angle at lower temperatures is similar to that of native cellulose, but rises at higher temperatures. This rise may be partially explained by the presence of carboxyl groups in this cellulose. The dielectric constant is similar to that of native cellulose. The pressing has thus caused significant changes in dielectric properties.

The effect in the case of dielectric constant was confirmed by measurements in the auxiliary dielectric constant apparatus. Results of several experiments are reported in Table VIII. The pressing in each case has reduced the calculated dielectric constant to values similar to native cellulose.

It is possible that this treatment caused a partial reversion of amorphous regions to crystalline regions. This would account for the changes if the amorphous regions are responsible for the increase in loss angle and dielectric constant. Cold pressing of a specimen of cellulose J induced similar changes in the observed dielectric constant, as shown in Table IX. Even the short duration of the first pressing significantly reduced both the dielectric constant and the moisture regain.

Values of the dielectric constant computed to standard densities obtained in both apparatuses are presented as a function of moisture regain in Fig. 7. The mean value from Table IV at 65°C. has been taken as the value for the main apparatus determinations. A direct relation between the two quantities is indicated. If Hermans is correct in correlating moisture regain and amorphous content, the dielectric constant may be regarded as a measure of the amorphous content.

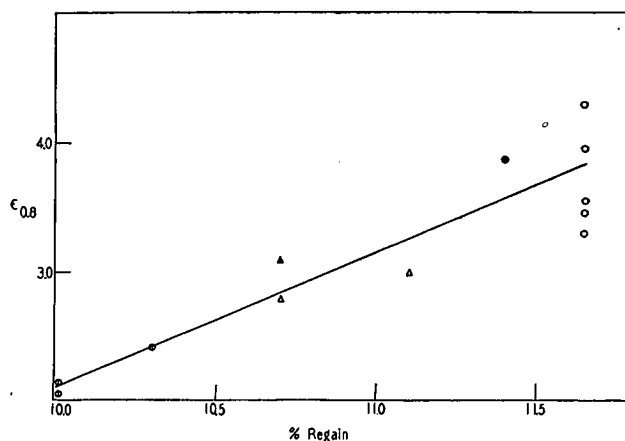


Fig. 7. Dielectric constant of regenerated cellulose as a function of moisture regain

○ J (unpressed); ● J (main apparatus); ⊙ E, F, J (hot pressed); △ J (cold pressed); and ▲ E (unpressed).

Table IX. Dielectric Constant of Cold-Pressed Solvent Dried Cellulose J

Treatment	ϵ	Density, g./cc.	$\epsilon_{0.8}$	Moisture regain at 54% R. H.
Unpressed	2.39	0.537	3.57	11.7
Pressed 15 sec. at 2000 p.s.i.	2.67	0.712	3.01	11.1
Pressed 10 min. at 2000 p.s.i.	2.74	0.785	2.79	10.9

However, the data obtained with cellulose L (cellophane) are contradictory since, on the basis of its moisture regain, it is amorphous and yet it has a low dielectric constant.

The regenerated celluloses are of low density in general, whereas cellophane approaches the density of pure cellulose. It is possible that both the dielectric properties and the moisture regain are related in some way to the apparent density differences. These celluloses are probably filled with submicroscopic small voids. This concept readily explains the low density, the ease of compressibility, and the escape of cyclohexane. If the surfaces of these voids (e.g., individual molecular chains) contribute to the dielectric constant and loss by the presence of free hydroxyl groups, as previously discussed, the observed differences can be accounted for. In a high-density cellulose, like cellophane, the relatively close packing might prevent the oscillations of hydroxyl groups. However, this explanation would not explain the lowered moisture regain observed upon pressing. The moisture regain test has not yet been applied over wide humidity ranges and its exact meaning is not clear. The possibilities of interference in the case of the cellophane test have been pointed out. In view of these facts, no definite conclusions can be drawn.

SUMMARY

A test capacitor system has been constructed for use with a conjugate Schering bridge, incorporating several desirable features. With this apparatus, measurements of loss angle and dielectric constant can be made at temperatures from 25 to 105°C. *in vacuo* of the order of 0.1 mu. Considerable pressure can be exerted upon the specimen during testing for the purposes of eliminating error resulting from incomplete filling of the test capacitor.

An auxiliary apparatus for the rapid and reasonably accurate measurement of dielectric constant has been constructed.

The applicability of the Clausius-Mosotti relation to native cellulose has been confirmed.

The loss angle and dielectric constant of several native celluloses have been measured at 500, 1000, 2000, and 4000 cycles per second at temperatures from 25 to 105°C. No significant differences between different native celluloses were noted. Loss angle-temperature curves exhibited a minimum, the temperature of the minimum increasing with increasing frequency. Dielectric constant-temperature curves showed a slight minimum and rose slightly at higher temperatures. No frequency effect was noted. These observations may be adequately explained if cellulose is regarded as a heterogeneous linear polymer with many polar groups.

Similar measurements upon degraded native celluloses confirmed these relationships. The presence of carboxyl groups caused increased dielectric loss at higher temperatures, whereas carbonyl groups had little effect. The dielectric constant was not affected.

The loss angle and the dielectric constant of specially prepared regenerated celluloses were higher than corresponding values for native cellulose at all frequencies. The dielectric constant of cellophane, however, was comparable with that of native cellulose. Pressing of the regenerated cellulose specimens at moderate pressures caused a lowering of these values. A possible correlation between amorphous cellulose content and dielectric properties was found, but the evidence is conflicting and no definite conclusions can be drawn.

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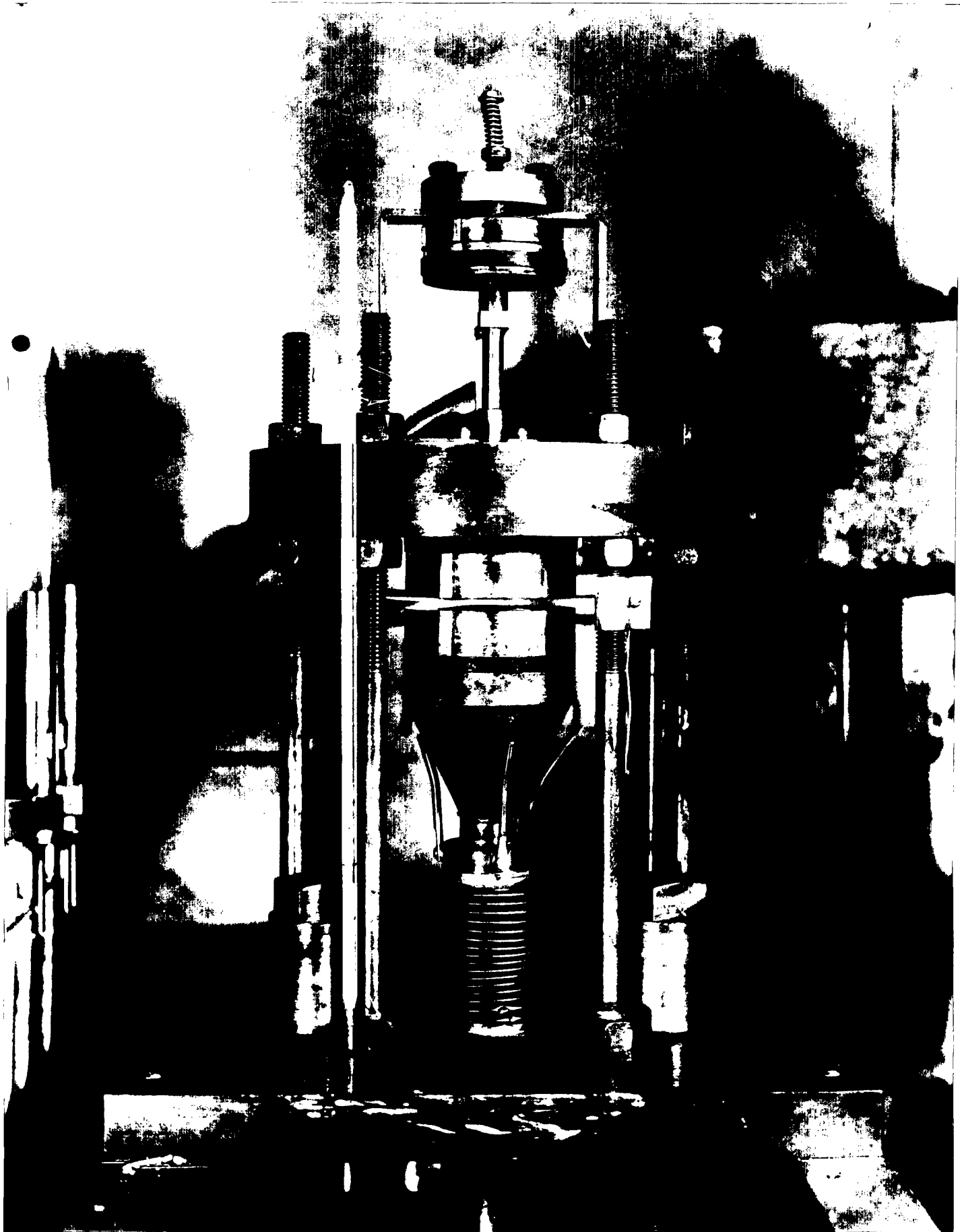
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jack

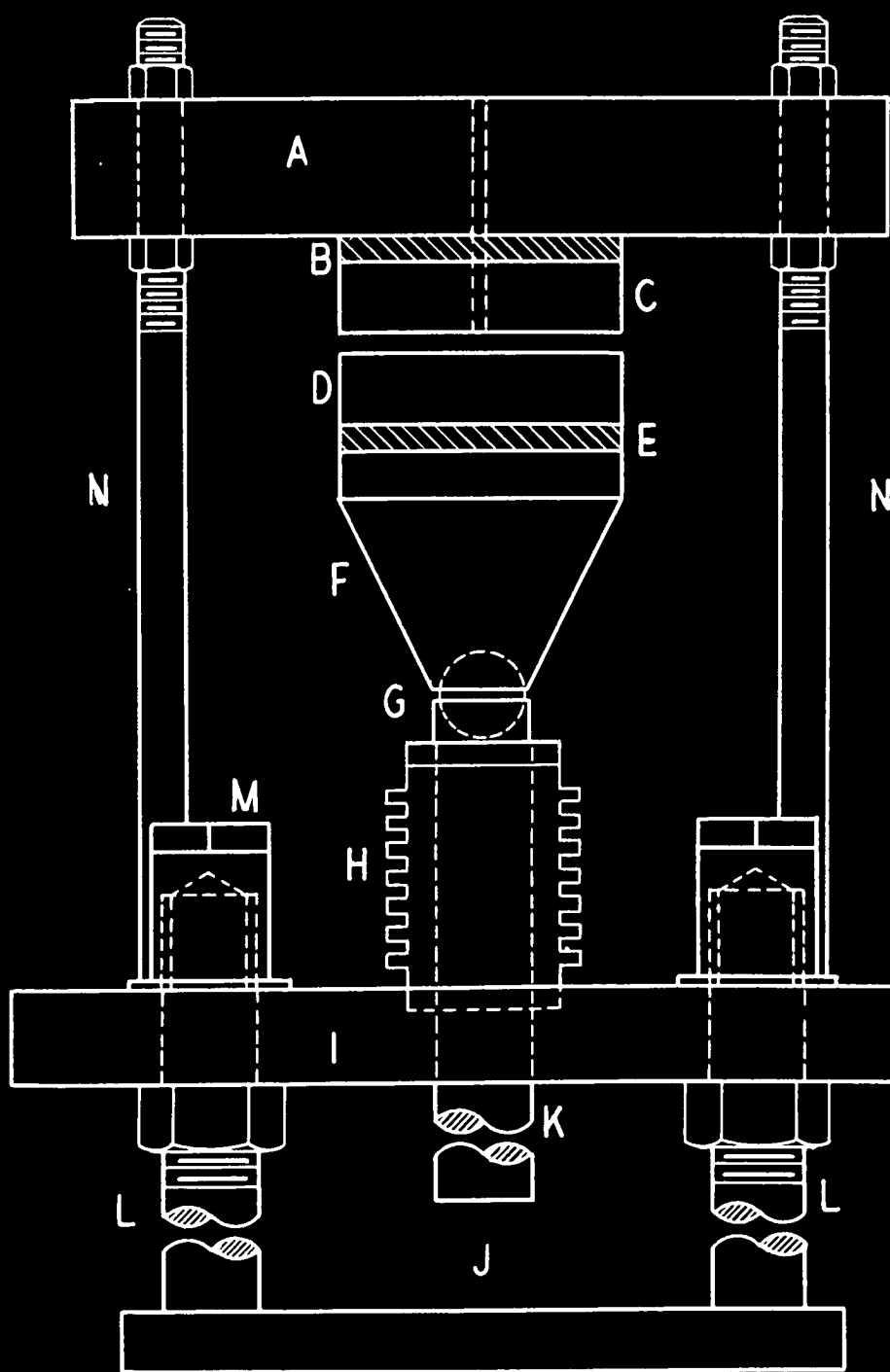
Test Capacitor System

Figure 3



Electrode Mounting System

Figure 4



Electrode System

Figure 5.

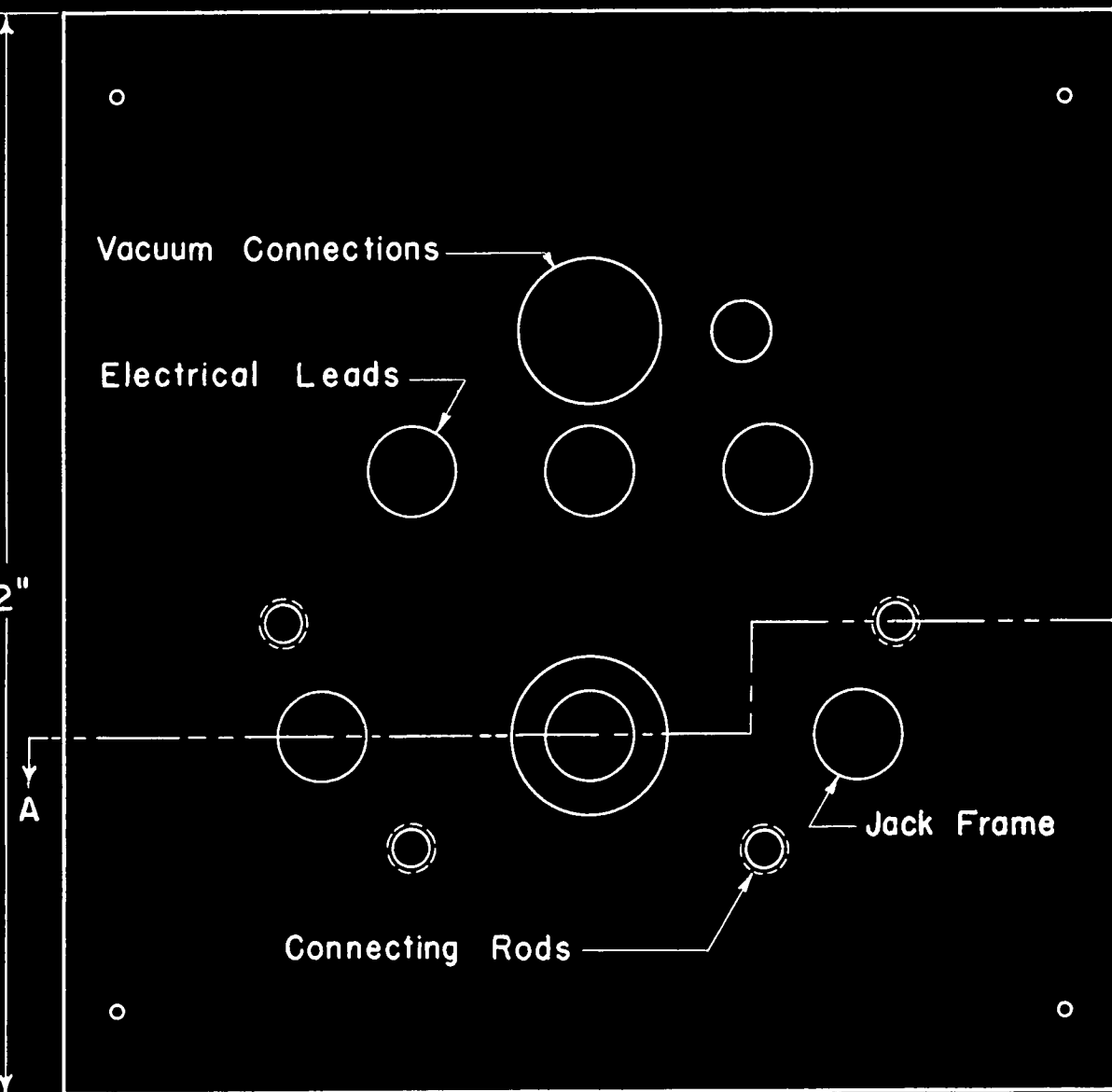
Legend for Figure 5

- A Upper plate
- B Upper electrode insulator (selected plastic)
- C Upper electrode
- D Lower electrode
- E Lower electrode insulator (selected plastic)
- F Lower electrode mount
- G Ball bearing
- H Cyphon bellows
- I Base plate
- J Hydraulic jack (not shown)
- K Main shaft
- L Jack frame
- M Cap nuts
- N Connecting shafts (only two shown)

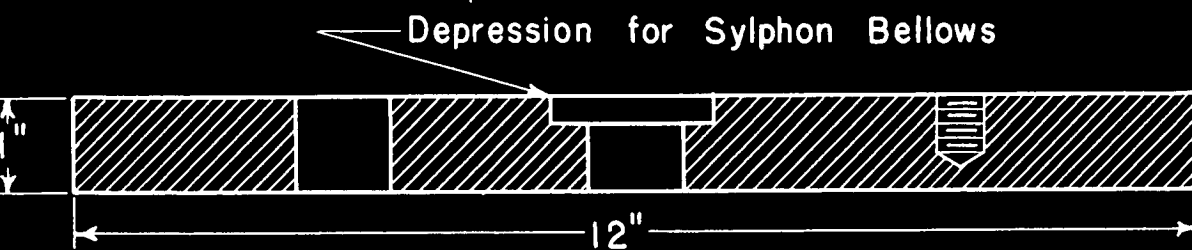
insulator are cemented to the upper plate which is fastened to the base plate by means of connecting shafts. The lower electrode and its insulator are cemented to the lower electrode mount. This piece, through a ball bearing, rides on the main shaft, whose movement, in turn, is controlled by a hydraulic jack. The jack is mounted in a frame which is bolted to the base plate as illustrated. The upper electrode is thus fixed in position, whereas the lower electrode is raised or lowered with the jack. The syphon bellows preserves a vacuum seal while permitting this motion. The base plate also contains the electrical leads and connections to the vacuum pump and the McLeod gage. With this apparatus pressures up to 1000 p.s.i. can be intermittently exerted upon the sample between the electrodes without affecting the vacuum. The component parts and the construction are discussed in detail below.

Base Plate

The base plate was drilled with a series of holes for the main shaft, the jack frame, electrical leads, and vacuum connections as illustrated in Figure 6. The main shaft was carefully fitted to its bearing. Other holes were drilled in the customary manner. The four 0.5-inch threaded holes are for connecting rods to support the upper plate. They do not extend through the base plate (in order to avoid vacuum leaks). The depression around the main shaft permitted the syphon bellows to be soldered to the base plate. Four one-fourth inch holes were drilled at the corners to bolt the base plate to angle-iron supports in the insulated box.



Top View



Section A-A

Base Plate

Figure 6.

Main Shaft

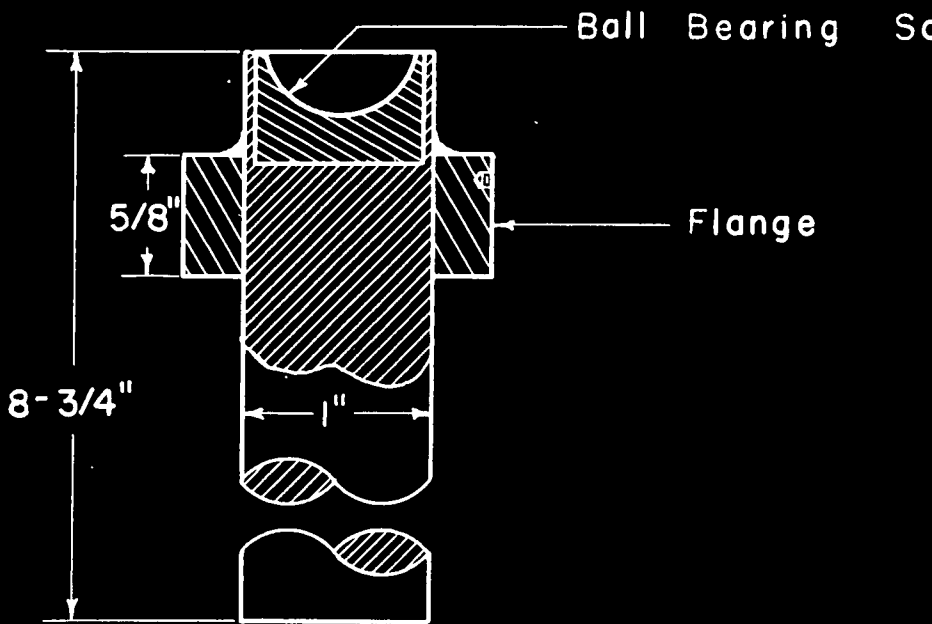
The main shaft was manufactured from one-inch drill rod stock; the dimensions are given in Figure 7. The lower end was given a slight curvature in order to provide a centered surface to ride upon the jock plate. The upper end was drilled out, filled with Babbitt metal, and cast into a socket for a ball bearing by pressing a steel ball in place and allowing the bearing metal to harden. The shaft was carefully fitted to the base plate bearing. A brass flange was braised to the shaft as illustrated. The upper end of the siphon bellows was soldered to its lower edge. Supports to hold the lower electrode mount in position are fastened by bolts to its upper part.

Upper Plate and Connecting Rods

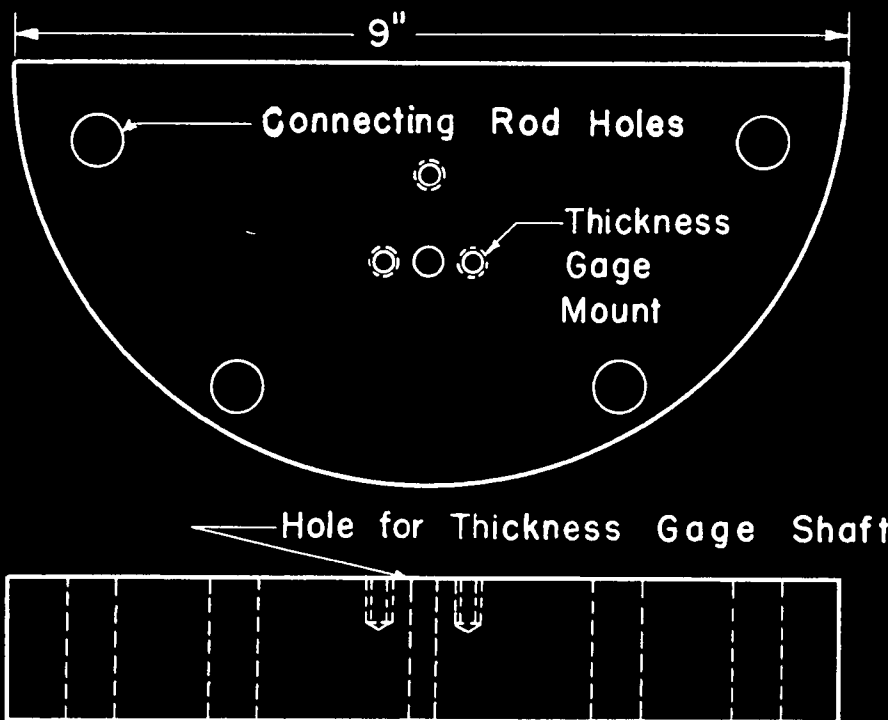
The upper plate was cut from 1.5-inch steel; the dimensions are shown in Figure 7. Calculations indicated that this plate was deflected less than 0.0002 inch when subjected to the loads contemplated. This is important since the thickness gage was mounted above the upper plate and a deflection of the plate could affect its reading.

The connecting shafts pass through the five-sixteenth inch holes, whose size allows manipulation of the upper plate in order to align the upper electrode exactly over the lower electrode. The one-fourth inch hole in the center permits the thickness gage shaft (described later) to reach the lower electrode. The threaded holes on top serve to mount the thickness gage.

The connecting shafts are made of 0.5-inch drill rod threaded at the bottom to screw into the base plate and at the top to hold the



Main Shaft (Full Scale)



Upper Plate (Half Scale)

Figure 7.

upper plate between nuts. Nuts were braised onto the lower threads for two purposes: first, to screw the threads to the proper depth and, second, to insure that the connecting shafts would be perpendicular when in place. This was accomplished by facing the lower surfaces of the nuts in a lathe; when tightened down against the base plate, the shafts were vertical.

Electrical Connections to the Schering Bridge

Two leads through the base plate are needed for the connections between the electrodes and the Schering bridge and one is needed for the electrode separation gage. Such leads have to be electrically insulated and vacuum tight. Vacuum tubes of the proper type have a well-insulated lead through a glass seal on top of a metal body which could be soldered in place. Type 6J7 tubes were found to be satisfactory. The bottom was sawed off with a hacksaw and the internal connections (with the exception of the upper lead) were removed. A section near the bottom of the cutoff tube was "spun" on a lathe to insure a tight fit in the baseplate hole. The protector over the glass seal on top was removed and a base plate lead was obtained (Figure 8). These

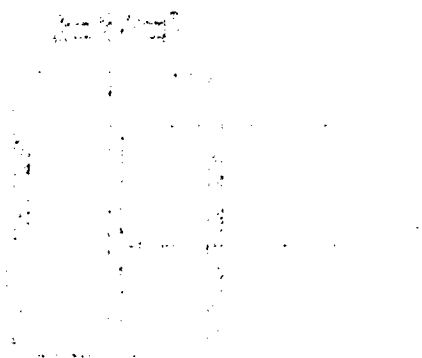


FIGURE 8

were soldered in position in the base plate. Shielded cable connections lead to the Schering bridge and the auxiliary bridge. The connections to the respective capacitors are unshielded copper wires.

Diffusion Pump and McLeod Gage Connections

A brass pipe, 1.5 inches in diameter and 30 inches long, was soldered into the base plate as a lead to the diffusion pump. The lower end was turned to fit evenly into the lip of the diffusion pump.

A one-inch brass pipe 14 inches long was soldered in the base plate to serve as a lead to the McLeod gage. The lower end was machined to fit into a 24 x 36 female ground-glass joint. A glass tube leads to the gage.

Jack and Jack Frame

The jack frame schematically illustrated in Figure 5 was a part of a used Butler plastic press. The jack is a Hein-Warner five-ton auto jack, tapped for a pressure gage. The pressure gage and jack were calibrated in the following manner. The jack was placed in a Baldwin-Southwark tester and a series of known loads was applied. The gage reading at each pressure was noted and a calibration curve was prepared.

The jack frame is bolted to the base plate as shown. The cap nuts at the tops of the jack frame shafts were a source of leakage, and various gasketing materials were tried including lead, neoprene rubber, silicone rubber, and copper. In use these gaskets are subjected to intermittent heavy loads, under which most gasketing materials (such

as lead) failed to remain vacuum tight. The only satisfactory seal proved to be copper gaskets which had been softened by heating to redness. These were placed in position, greased with silicone high-vacuum grease, and brought up as tightly as possible. In addition, the placing of heavy lock washers between the base plate and the lower nuts exerted a constant pressure on the gaskets.

Electrodes

The electrodes had to meet several requirements. They had to be of proper size so that their capacitance at the separations desired would be within the range of the Schering bridge. Calculation showed that, if the separation varied from 0.0002 to 0.010 inch, three-inch diameter electrodes would be satisfactory. They had to have sufficient mechanical strength to prevent distortion at stresses up to 1000 p.s.i. Edge effects had to be small, because construction of a guard ring capable of withstanding the large forces to be encountered would entail many difficulties. Scott and Curtis (38) have prepared an empirical edge correction equation which, although designed for thinner electrodes than those employed in this work, is applicable. A simplified form of this relation (35) is given below:

$$C_e = [0.147 \log 0.59/t + 0.047 \epsilon] P, \quad (13)$$

where

t = electrode separation, in.,

ϵ = dielectric constant of material,

P = perimeter, in., and

C_e = edge correction in micro-microfarad.

The following corrections were calculated by the use of this formula.

TABLE I

ELECTRODE EDGE CORRECTIONS
AT SEVERAL SEPARATIONS

Separation, in.	$\frac{C}{\mu\mu f}$	$\frac{C_e}{\mu\mu f}$	Edge Correction Error, %
0.002			
0.022	1000	4.5	0.45
0.010	200	2.8	1.40

The correction is small and, in any case, would not affect comparative measurements. Therefore, no guard rings were used.

The electrodes were manufactured from three-quarter inch surface-ground steel and were three inches in diameter. The upper electrode has a one-fourth inch hole through the center for the electrode separation gage. A third electrode was prepared as a grinding surface.

The electrodes were made flat in the following manner. The three surfaces were polished against one another in regular order with reversals of the up-down positions. The electrodes were designated A, B, and C. The order is given in Table II.

TABLE II

ELECTRODE POLISHING ORDER

Step	Electrode Positions	
	Down	Up
1	A	B
2	B	C
3	C	A
4	B	A
5	C	B
6	A	C

The polishing technique for each step was as follows. The appropriate polishing compound was placed on the surface of the bottom electrode. Twenty short strokes were made. The upper electrode was turned 45 degrees, and the operation repeated. This was continued until the upper electrode had returned to its original position.

The electrodes were ground with a slurry of No. 80 carborundum and water until no further improvement of the surface was noted (by inspection under a microscope) after additional polishing. This was repeated with No. 400 carborundum and, finally, with a dispersion of alumina in water.

The electrodes were then chromium plated by the Wisconsin Chromium Company, Appleton, Wisconsin. A final polishing was given with a water dispersion of alumina.

Tests with an accurate steel straight edge revealed no curvature (indicative of flatness to less than 0.0001 inch). In addition, the electrodes adhered to each other, again indicating an extremely flat surface.

A small bolt was placed in the side of each electrode, midway between the surfaces, to serve as an electrical connection.

Electrode Insulators

Several samples of electrical insulation plastics of the phenolic type were obtained, and tested for electrical loss. Samples one-fourth inch thick and having an a.c. parallel resistance of the order

of 10^7 ohms were selected and lathe cut to the dimensions of the corresponding electrodes. Although this is not a particularly high insulation resistance, it is large in comparison with the resistance of 10^4 ohms through the Schering bridge to ground. As the American Society for Testing Materials' method (35) points out, the only purpose of a high resistance at this point is to increase sensitivity and, in practice, the bridge was satisfactory.

Electrode Mounting

The lower electrode, together with its insulator, is mounted as shown in Figures 4 and 5. The ball-joint socket was made in the same manner as that in the main shaft. It permits the lower electrode to become parallel to the upper electrode under pressure. The upper electrode is attached to the upper plate.

The electrodes and their insulators were cemented to their respective supports with "Redux," a commercial metal-binding plastic. Each piece was carefully cleaned. The Redux was applied and allowed to air dry one hour. The pieces were assembled and pressed in a plastic press at 500 p.s.i. and 300° F. for 30 minutes, after which the excess plastic was removed. The insulators were tested in situ and an electrical resistance of the same order of magnitude as before was obtained.

Assembly of Electrode System

The first step was the soldering of the electrical leads, the vacuum system pipes, and the sylvan bellows to the base plate. The

soldered joints had to be vacuum tight, in addition to having mechanical strength. The base plate was large and it would be difficult to heat a localized spot to soldering temperature without causing distortion. The base plate was placed upon a brass plate of similar size heated by a gasoline torch and were slowly brought to the desired temperature. The various components (which had been cleaned and tinned) were placed in position and soldered in place. The main shaft, to which the sylvphon had been previously soldered, was slipped into place and the lower lip of the sylvphon was soldered.

After the assembly had cooled, it was mounted in the insulated box, leveled, and bolted in place.

The supporting rods were then screwed in place. The lower electrode mount was set in position on the ball bearing of the main shaft. The four nuts which support the upper plate were placed upon the upper threaded ends of the supporting rods. The upper plate and electrode were set on these nuts and were adjusted until level and exactly over the lower electrode. Leveling was accomplished by changing the positions of the supporting nuts. Positioning of the upper electrode was accomplished by moving the upper plate, since holes in the upper plate were one-sixteenth of an inch larger than the diameter of the supporting rod. When positioning was exact, the upper plate was bolted securely into position.

The lower electrode mount was prevented from tipping from position by three adjustable supports (see Figure 9) made from one-eighth inch steel rod.

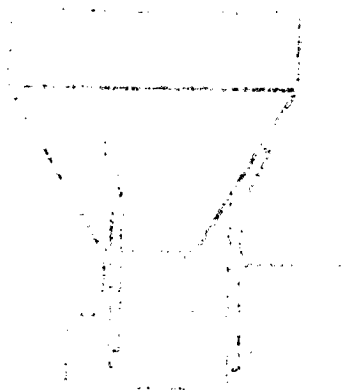


FIGURE 9

Each support is held in place by a bolt in the brass flange on the main shaft, and was bent and fitted until the lower electrode mount was held substantially in proper orientation.

SPECIMEN HOLDER

The cellulose specimens were held between the pair of aluminum rings shown in Figure 10. The rings are pivoted in such a manner

FIGURE 10

that they swing the specimen in and out between the electrodes, when a magnet outside the bell jar attracts the balance weight. In this manner the specimen could be moved without breaking the vacuum. Specimens were cut with a special die so that, when the holder was moved against a forward stop, the hole in the center of the sample coincided with the hole in the upper electrode.

CONTROLLED TEMPERATURE BOX

The electrode system is mounted in a large insulated box, equipped with a heating unit and circulating fan. The jack and jack frame extend below the box and are not heated.

The box frame (see Figure 3) is welded from 1.5-inch angle iron. The box itself is built up of 1/4-inch Transite, 1/2-inch Celotex, 0.010-inch copper sheeting, and 1/2-inch Celotex bolted to the frame. The Transite provides insulation and mechanical strength, the Celotex thermal insulation, and the copper electrical shielding.

The top and front of the box are removable to permit access to the apparatus.

The heating unit consists of Nichrome heating wire strung over Transite mounts around three sides of the box. A Powerstat voltage controller outside the box provides regulation.

A six-inch fan is mounted upon a vertical shaft extending through the bottom of the box. It is driven by a fractional horsepower motor, connected to the shaft by means of a belt. The fan provides adequate circulation to insure that all parts of the apparatus are at approximately the same temperature.

A light in the back of the box provides illumination and a small window arranged in the box front permits examination of tests in progress. Switch controls, the auxiliary bridge, the cold trap, and other adjuncts of the system are mounted upon the lower frame of the box.

HIGH VACUUM SYSTEM

Pressures as low as 0.1 micron are obtained by means of a diffusion pump and a Cenco HiVac pump. The pressure is measured by a McLeod gage with a range from 0.01 to 200 microns. The line to the gage includes a large U which passes through a cold trap in order to prevent mercury vapor from the McLeod gage entering the apparatus and affecting the tests and the soldered joints. The trap is a large Thermos bottle kept at -7°C . by a mixture of ethyl alcohol and "dry ice."

The soldered joints were painted with Elyptal (a resin-type paint) to insure vacuum tightness.

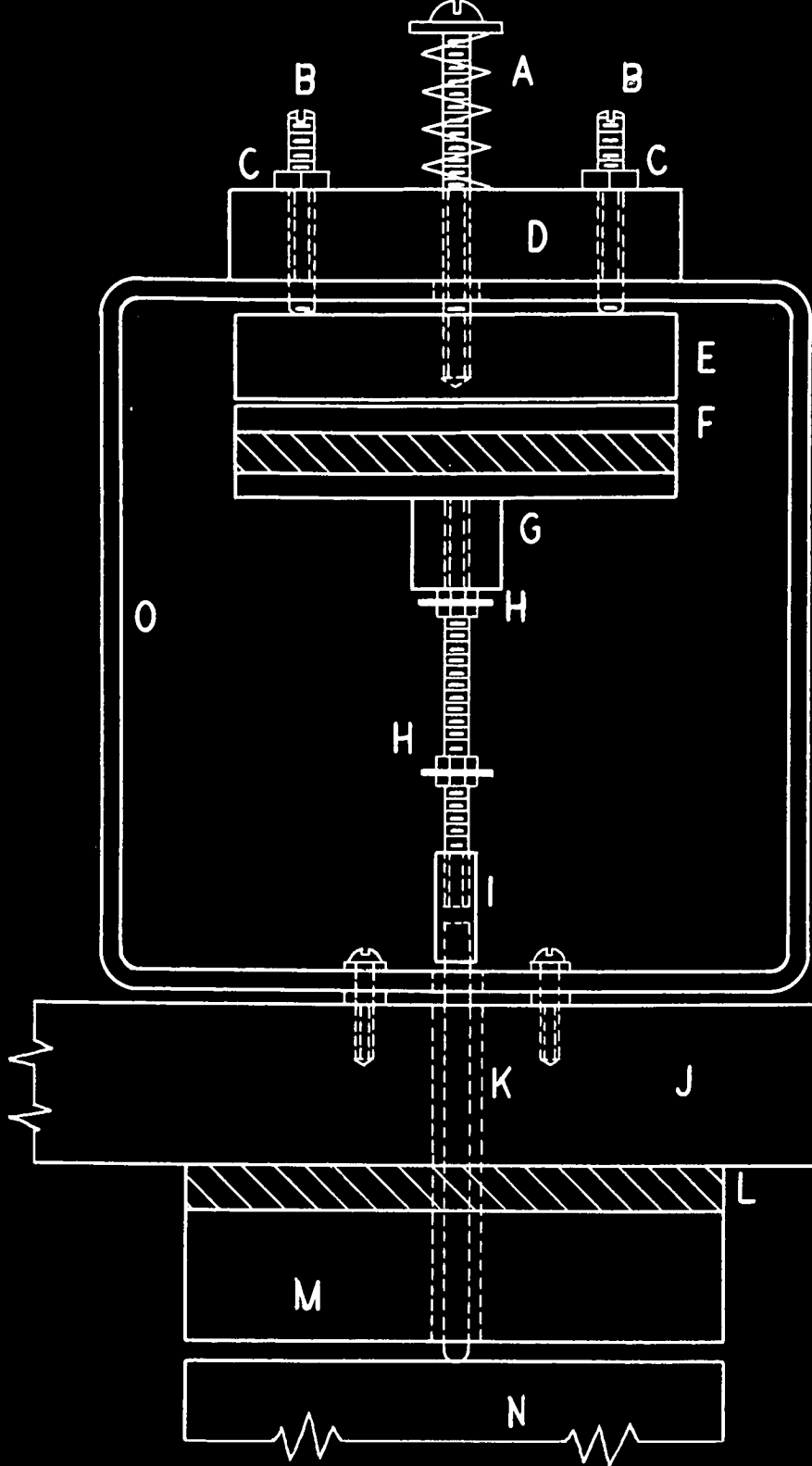
The bell jar-base plate seal presented a serious problem. Ordinary vacuum grease or modeling clay was inadequate at high temperatures. In the earlier experimental work, a seal was made with silicone high-vacuum grease backed by modeling clay; however, it was often unsatisfactory for longer runs. A smooth Butyl rubber gasket greased with silicone high-vacuum grease proved to be the most satisfactory seal and was used in later experimental work.

ELECTRODE SEPARATION GAGE

The accuracy of loss angle and dielectric constant measurements is dependent upon the accurate determination of the electrode separation. After some deliberation, a system was designed in which the spacing of an auxiliary capacitor was directly related to the main electrode separation. The capacitance of this auxiliary condenser was measured by a capacitance bridge, and a curve of the balancing condenser dial readings against electrode separation at various temperatures and pressures was drawn.

The auxiliary condenser is illustrated in Figure 11. The upper electrodes of both the auxiliary condenser and the test capacitor are stationary. The electrode separation of the test capacitor is determined by the position of the lower electrode. The lower electrode of the auxiliary condenser is flexibly mounted and its position is determined by the main lower electrode position since the glass rod that acts as a support extends through the center of the main upper electrode and rests upon the lower main electrode.

The lower auxiliary electrode is a disk 2-1/2 inches in diameter, machined from 1/8-inch stainless steel plate (to prevent possible corrosion at higher temperatures). Each face is surface ground to insure flatness. This electrode and a 1/4-inch plastic insulator are cemented with Redux to the lower auxiliary electrode mount (of similar dimensions) which, in turn, is mounted upon a 1/8-inch threaded shaft. The lower end of the shaft screws into the glass rod holder. The glass rod was cut to the proper length and cemented into the holder.



Electrode Separation Gage

Legend for Figure 11

- A Spring
- B Set screws (only two shown)
- C Lock nuts
- D Brass disk
- E Upper electrode
- F Lower electrode
- G Lower electrode support
- H Flexible supports for lower electrode assembly
- I Glass rod holder
- J Upper plate
- K Glass rod
- L Main upper electrode insulator
- M Main upper electrode
- N Main lower electrode
- O Supporting frame for gage

The lower auxiliary electrode system is mounted in a manner which permits vertical but not lateral movement (since the latter would change the capacitance). This was accomplished by holding the supporting shaft with two supports made from flexible spring steel as shown in Figure 12.

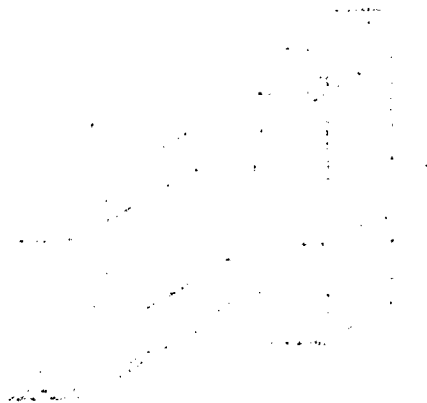


FIGURE 12

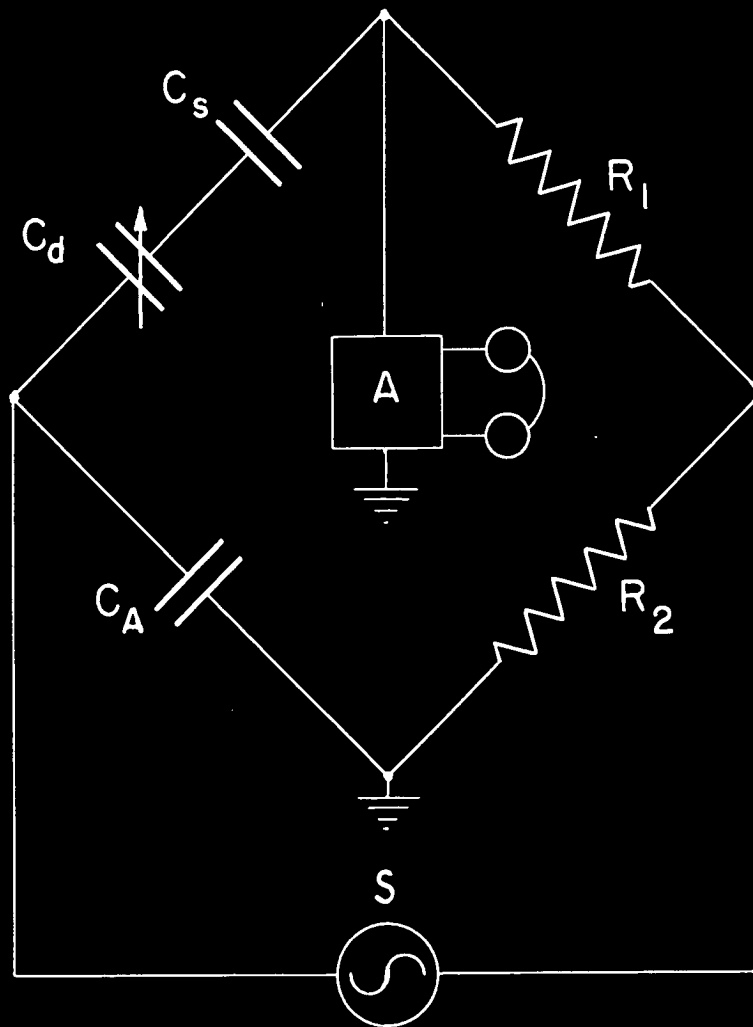
Lateral motion is impossible because of the stiffness of the strips in the horizontal direction, whereas vertical motion is freely permitted. The spring steel supports are held rigidly between brass blocks which are bolted to the upper main plate.

In order to obtain the proper range of capacitance for this variable auxiliary condenser, it was necessary to have extremely small electrode separations. Furthermore, the electrodes had to be parallel. Fine vertical or parallel adjustment would be rather difficult with the arrangement described for the lower auxiliary electrode. Therefore, the arrangement illustrated in Figure 11 was built. The upper auxiliary electrode has a centered bolt which extends up through a hole in the

supporting frame. Spring A exerts an upward force on the upper auxiliary electrode. Above it, a disk of 1/2-inch brass is fastened to the supporting frame. This disk has three set screws arranged 120 degrees apart near the perimeter. By adjustment of the set screws the vertical position and levelness of the upper auxiliary electrode could be controlled with a high degree of accuracy. After final adjustment had been made, the lock nuts on the set screws above the brass disk were tightened. The supporting frame was bent from the one-inch flat steel. The bolts holding it to the upper plate were placed close to the shaft so that movement of the supporting frame resulting from the deflection of the upper plate under load would be similar to the deflection of the main upper electrode, thus preserving their relative positions. The relative expansion and contraction of the various elements with changing temperature was compensated for by the calibration procedure, which is described later.

AUXILIARY CAPACITANCE BRIDGE

The capacitance of the auxiliary capacitor was measured by means of the capacitance bridge shown in Figure 13. The values of R_1 , R_2 , and C_0 were varied until experiment showed a proper range and sensitivity for the desired separations. R_1 and R_2 are wire-wound resistances. The entire bridge is shielded. The lead to the insulated side of C_A is a shielded cable to the bottom of the main box.



C_d	0 to 600 μF . Variable Air Capacitor with Ver
C_s	500 μF . Mica Capacitor
R_1	22,000 Ohm Wire Wound Resistor
R_2	10,000 Ohm Wire Wound Resistor
C_A	Auxiliary Capacitor
A	General Radio Amplifier Type 514A
S	General Radio 1000 Cycle Tuning Fork Hummer

Auxiliary Capacitance Bridge

Figure 13

CALIBRATION OF ELECTRODE SEPARATION GAGE

Thickness Standards for Calibration

Thickness standards were prepared from commercial brass shim stock. Brass was selected rather than steel because it is more compressible and a small high spot would be more readily flattened. Samples with a nominal thickness of 0.002, 0.004, 0.007, and 0.010 inch were obtained and cut to approximately 3-1/4-inch squares (a size slightly larger than the main electrodes). Their thickness was measured by means of a Federal compressibility gage, which is considered precise to 0.00002 inch. Its accuracy is affected by difficulties in obtaining a true zero and the possible bending of its shaft under load.

These difficulties were overcome by means of a comparison method of thickness measurement. A set of feeler gages, which had been calibrated by the National Bureau of Standards and may be considered accurate to within 0.00003 inch, was available. After approximating a zero adjustment with the Federal gage, a measurement was made of the feeler gage of the same nominal thickness as the shim being tested. The correction was applied to similar measurements upon the shim. Each shim was divided in 1/4-inch rows. Thickness measurements were made every 1/4 inch along these rows (approximately 150 separate thickness readings were obtained for each shim). At the end of each row, a check was made upon the feeler gage to insure that the right correction factor was being used.

After the shim had been measured, it was necessary to cut a small hole in the center for the glass rod of the electrode separation

gage. Since ordinary methods of cutting might burr or scratch the shims, the holes were etched by means of a technique designed to protect the surfaces from the acid. It is probable that the data on the thickness of the shims are accurate to 0.00004 inch. Shim values are given in Table III.

TABLE III

THICKNESS OF STANDARD SHIMS

Nominal Thickness, 0.001 in.	Actual Thickness, 0.001 in.
2.0	2.21
4.0	4.44
7.0	6.86
10.0	10.24

Errors of the standards resulting from compression and thermal expansion may be disregarded, since they are of the order of magnitude of 0.1%.

Method of Calibration

The gage was calibrated in the following manner. The electrodes, a standard shim, and the auxiliary electrodes were carefully cleaned. The shim was inserted in its proper position between the main electrodes. The bell jar was placed over the apparatus and the vacuum pump turned on. After vacuum and temperature equilibrium had been obtained, the auxiliary capacitance bridge was balanced at a series of pressures on the shim. The temperature was raised stepwise and observations were made at 25, 50, 75, and 105° C., after which the temperature was decreased stepwise, with observations at the foregoing temperatures. The

first calibration runs revealed that the effect of the vacuum was small, although there was a preliminary adjustment, probably as a result of mechanical stressing. These runs further revealed that it required 12 to 15 hours to obtain temperature equilibrium, because of the large heat capacity of the apparatus and the poor heat transfer through the evacuated space. A series of calibration runs were made. A graph at each pressure was made for each shim, plotting dial reading as the ordinate and temperature as the abscissa. The best curve was drawn and the data were used to prepare calibration charts as described below.

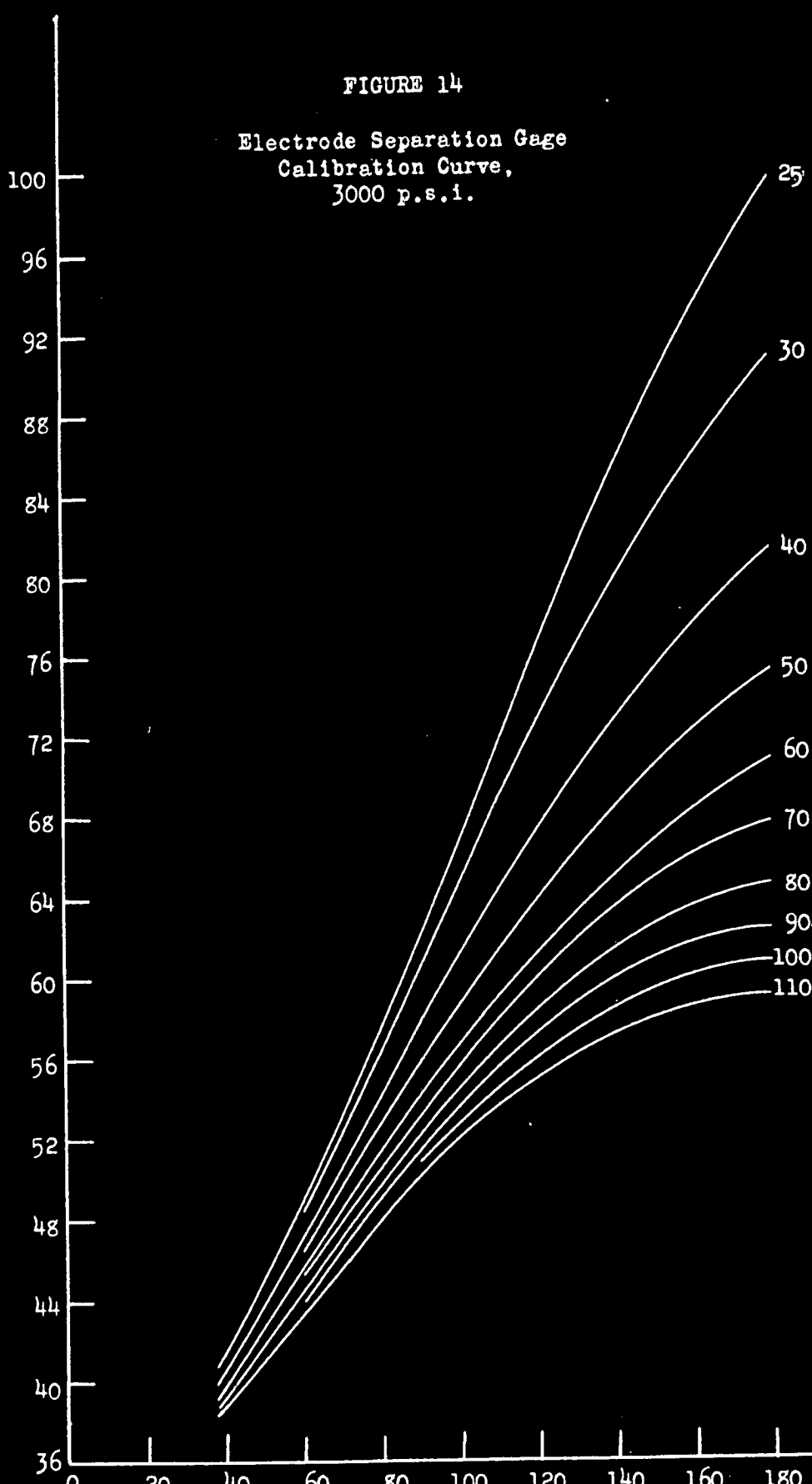
Preparation and Use of Calibration Charts

The ultimate measurement desired from the dial reading is the separation of the main electrodes. The independent variables are temperature and gage pressure. The pressure is constant for each chart. The reciprocal electrode separation (in reciprocal centimeters) is the abscissa and the dial reading is the ordinate. A separate curve was drawn for each 10° of temperature, giving rise to the family of curves in Figure 14.

From these charts it was hoped that the electrode separation could be found simply by balancing the auxiliary bridge and noting the temperature and gage pressure. However, after the calibration was completed it was found that checks upon individual shims differed slightly but significantly from the calibration chart. After careful elimination of other possibilities, it was assumed that discrepancies could be caused only by slight changes in the auxiliary electrode system, produced perhaps by a gradual change in the mechanical system, an

FIGURE 14

Electrode Separation Gage
Calibration Curve,
3000 p.s.i.



unforeseen jar or, less likely, by some change of the resistance or capacitance ratios in the auxiliary bridge. Since the drift was slow, it was felt that recalibration (which might have to be repeated regularly) was a needless sacrifice of time. Instead, a shim could be tested at the end of each run and a correction obtained to be applied to all thickness readings for the run. Two questions then arose. First, would the correction obtained be directly applicable to the dial reading or one applied through some mathematical formula and, second, could it correct from one temperature to another, or would a complete calibration run have to be made at the end of each run? A mechanical strain in the gage or electrode system would be reflected as the equivalent of a change in the separation of the electrodes. Since the chief effect of a temperature variation was a change in the spacing of the auxiliary capacitor because of the unequal coefficients of expansion of the component parts, it may also be regarded as a change in separation. If that assumption is made, a correction formula can be derived in the following manner. Let p_1 be the apparent separation with paper specimens in place, $p_{cor.}$ the actual separation, p_2 the apparent separation with a standard shim in place, and p_s the actual thickness of the shim, all expressed in reciprocal centimeters. If x represents the appropriate separation in centimeters, then

$$\underline{x} = 1/p_s, \underline{x}_1 = 1/p_1, \underline{x}_2 = 1/p_2, \underline{x}_{cor.} = 1/p_{cor.} \quad (14)$$

and

$$\Delta \underline{x} = \underline{x}_s - \underline{x}_2 = \underline{x}_{cor.} - \underline{x}_1 \quad (15)$$

Substituting in Equation (15) above and rearranging:

$$(p_2 - p_s)/p_s p_2 = (p_1 - p_{cor.})/p_1 p_{cor.} \quad (16)$$

Defining $\Delta p_{cor.}$ as the correction to be added to p_1 , and Δp as the difference between p_1 and p_2 , the following relation is obtained by substitution and rearrangement of Equation (16):

$$\Delta p_{cor.} = \Delta p (p_1 p_{cor.} / p_2 p_1). \quad (17)$$

This equation must be solved by a method of successive approximations and, consequently, a simpler expression was desired. Such an equation may be derived from the previous assumptions by means of calculus.

$$p = 1/x \quad (18)$$

$$\delta p = -1/x^2 \delta x \quad (19)$$

$$\delta x = -x^2 \delta p = -1/p^2 \delta p \quad (20)$$

$$\delta x_1 = \delta x_2 = -1/p_1^2 \delta p_{cor.} = -1/p_2^2 \delta p \quad (21)$$

Rearranging, and replacing δp with Δp .

$$\Delta p_{cor.} = (p_1^2 / p_2^2) \Delta p \quad (22)$$

Comparison with Equation (17) shows that, if the corrections are relatively small, the equations are similar. Equation (22) was used after it was found that, even with the largest deviations noted, the results were very nearly the same.

PROBABLE ERROR OF THE THICKNESS MEASUREMENT

The error of the separation measurement depends upon several factors. The auxiliary bridge variable condenser can be balanced accurately to 0.2 dial unit. This corresponds to a percentage error varying from 1.0 to 3%, depending upon the separation. The dial error in testing the standard shim results in a similar error in the final cor-

rected separation value. The assumptions used in deriving the thickness correction are not exact but, in most cases, the standard shim differs in thickness no more than 0.001 inch from the specimen, so that corrections are applied over small changes in thickness. The magnitude of differences between the observed values of the standard shims and the calibration chart values was usually less than three reciprocal centimeters.

For example, a sample was found to have a p value of 50 reciprocal centimeters. The appropriate standard shim ($p = 57.2$) gave a value of 54.2 reciprocal centimeters. Therefore, Δp was +3.0 units. Applying the correction formula, $\Delta p_{\text{cor.}}$ was found to be 2.5 units. Even large errors in $\Delta p_{\text{cor.}}$ will result in small percentage errors in $p_{\text{cor.}}$

Temperature can be estimated within 1°C. , which corresponds to an error of less than 1% in thickness. The calibration charts may be considered accurate, since on y the correct shape and relations of the curves are required.

The final electrode separation value in most cases is probably within 5% of the true value, if the preceding estimates of error are correct.

This was indirectly confirmed by statistical analysis of the data obtained in the dielectric constant measurements upon Celluloses A and D. The measurement of electrode separation is the major source of error in this determination. In Table IV the error calculated from

the dielectric constant data obtained with Celluloses A and B at 1000 cycles is presented, together with an estimate of the electrode separation gage error responsible for the deviation.

TABLE IV

ESTIMATION OF STANDARD DEVIATION OF ELECTRODE SEPARATION GAGE
FROM STANDARD DEVIATION OF DIELECTRIC CONSTANT DETERMINATION

Observations of Celluloses A and B at 1000 Cycles

Cellulose	σ of ϵ 0.8. ^a	σ of Gage. ^b
B	4.1	2.4
A	4.15	2.4
A ^c	3.1	1.7

^aFrom Table VI

^bEstimated

^cOne value, obviously in error, discarded

In several experiments the vacuum was broken with desiccated air, the specimen removed immediately, and its thickness measured with the Federal compressibility gage. This procedure would tend to give high results (lowered value in reciprocal centimeters) because of lowered pressure upon the specimen during measurement and the expansion of the specimen with moisture regain. Table V presents some of the values obtained in this manner and similar values measured with the electrode separation gage.

These data fail to reveal any gross error in the measured electrode separation.

With the evidence deduced from statistical treatment of some of the data, the estimation of the sources of error, and the comparison

TABLE V

COMPARISON OF ELECTRODE SEPARATION MEASUREMENTS
WITH MEASURED THICKNESS OF SPECIMENS

Sample	$R_{cor.}$ reciprocal cm.	ρ of Specimen, reciprocal cm.
J	26.7	25.4
F	57.0	59.7
G	42.9	42.0
G	53.6	47.9

with direct measurement, it may be concluded that the possible error of a single measurement with the electrode separation gage is approximately 5%.

MEASUREMENT AND CALCULATION OF LOSS ANGLE AND DIELECTRIC CONSTANT

PROCEDURE USED IN MAKING ELECTRICAL MEASUREMENTS

Two sheets of a particular cellulose were carefully selected for smoothness, good formation, and freedom from dirt specks. The use of double sheets prevented the possibility of conducting particles interfering with the measurement, since the chance of forming a conducting path across both sheets is vanishingly small. The samples were die cut to fit the sample holder and electrode separation gage. The apparatus was assembled and the system evacuated and heated to 105° C. After equilibrium had been reached (15 hours), the specimens were placed under 940 p.s.i. pressure by the jack. The temperature and vacuum were noted, the auxiliary bridge was balanced, and the reading was ascertained. This procedure was repeated after the Schering bridge was balanced at each frequency. Measurements were made at 500, 1000, 2000, and 4000

cycles per second, after preliminary experiments had shown that the Schering bridge could not be balanced at lower frequencies at the electrode separation used and that measurements at higher frequencies were inaccurate.

The Schering bridge was balanced in the following manner. With switch S_2 (see Figure 2) to ground, the bridge was balanced by successive adjustments of capacitors C_2 and C_4 , alternating with adjustments of the Warner ground (the latter being with S_1 to ground), and the values of C_2 in micro-microfarads and C_4 in dial units recorded. With switch S_2 connecting the test capacitor C_p to the circuit, new values for capacitors C_2 and C_4 were obtained. Ten readings were taken of capacitor C_4 at each setting.

The temperature was allowed to drop to the next desired value, equilibrium was established, and the procedure repeated. Measurements were made at approximately 105, 75, 50, and 25° C. The temperature was then raised and measurements made at these temperatures in a similar stepwise fashion.

At the conclusion of the run, the vacuum was broken and the specimens were removed. In later runs, the vacuum was broken with desiccated air, specimens were removed immediately, and their thicknesses were measured with a Federal compressibility gage. The thickness gage correction was obtained as described previously. The area of the specimen between the electrodes was carefully cut out and measured, and the specimen was dried to constant weight at 105° C. From these data, the

values of loss angle and dielectric constant were calculated as described below.

CALCULATION OF DIELECTRIC CONSTANT AND LOSS ANGLE AT STANDARD DENSITY

The simplified equations given by the American Society for Testing Materials (35) were used for calculation of the loss angle and the capacitance of the test capacitor.

$$\underline{C_p} = \underline{C_2} - \underline{C_2'} \quad (23)$$

$$\epsilon' = (\underline{C_2}/\underline{C_p}) 2\pi f R_4 (\underline{C_4'} - \underline{C_4})/10^{12} \quad (24)$$

where

$\underline{C_p}$ = the equivalent parallel capacitance of the test capacitor, in micro-microfarad,

$\underline{C_2'}$ = the capacitance of condenser $\underline{C_2}$ when the test capacitor is in the circuit, in micro-microfarad,

$\underline{C_2}$ = the capacitance of the condenser $\underline{C_2}$ when the test capacitor is disconnected from the circuit, in micro-microfarad,

$\underline{C_4'}$ = the capacitance of condenser $\underline{C_4}$ when the test capacitor is in the circuit, in micro-microfarad,

$\underline{C_4}$ = the capacitance of condenser $\underline{C_4}$ when the test capacitor is disconnected from the circuit, in micro-microfarad,

f = the frequency in cycles/sec., and

$\underline{R_4}$ = the resistance of resistor $\underline{R_4}$ in ohms.

Since $\underline{R_4}$ is 10,000 ohms, and Belevanti has shown that $(\underline{C_4'} - \underline{C_4})$ in micro-microfarads is equal to $\Delta \underline{C_4} \times 1.14$, where $\Delta \underline{C_4}$ is the change in dial reading of condenser $\underline{C_4}$, Equation (24) may be simplified to

$$\epsilon' = (\underline{C_2}/\underline{C_p}) f \Delta \underline{C_4} \times 7.16 \times 10^{-8}. \quad (25)$$

The dielectric constant of the test capacitor was determined from the ratio of the observed capacitance (C_p) to the calculated vacuum capacitance (C_v) of the test capacitor.

$$\epsilon = C_p / C_v. \quad (26)$$

Since C_v may be calculated from the equation

$$C_v = 1.11A / 4\pi d, \quad (27)$$

$d_{cor.}$ is defined as $1/d$ and A , the electrode area, is 43.7 sq. cm.; by substitution in Equations (26) and (27) and rearrangement, the following equation, which gives dielectric constant in terms of experimental data, is obtained.

$$\epsilon = 0.259 C_p / d_{cor.} \quad (28)$$

It is assumed that the specimen completely fills the space between the electrodes so that density (D) is defined as grams of specimen per unit volume between the electrodes.

$$D = W / dA, \quad (29)$$

where W is the oven-dry weight of material between the electrodes. By substitution of numerical values, a simplified form is obtained:

$$D = (W)(d_{cor.})(0.0229). \quad (30)$$

These equations enable the calculation of dielectric constant and loss angle at a given density. However, both properties vary with density. Since it was not feasible to make the density of all specimens equal, the method of calculation to a standard density described below was used.

The dielectric constant of a dielectric in which molecular interaction is not present may be related to density by Equation (31), one statement of the classical Clausius-Mosotti relation.

$$(\epsilon - 1)/(\epsilon + 2) \propto \rho \quad (31)$$

Similarly, the loss factor of such a dielectric may be shown to be directly proportional to the density. If the assumption is made that these relations are applicable to cellulose, then the dielectric constant and loss factor may be calculated from the following equations (using 0.8 as standard density and indicating the density used as a subscript).

$$(\epsilon_{0.8} - 1)/(\epsilon_{0.8} + 2) = [0.8/\rho](\epsilon - 1)/(\epsilon + 2) \quad (32)$$

$$(\epsilon\epsilon')_{0.8} = 0.8(\epsilon\epsilon')/\rho \quad (33)$$

Finally, the loss angle at standard density may be calculated by the simple division operation

$$\epsilon'_{0.8} = (\epsilon\epsilon')_{0.8}/\epsilon_{0.8} \quad (34)$$

All data were placed upon a comparable basis by the methods just described.

SOURCES OF ERROR IN THE METHOD OF MEASUREMENT OF DIELECTRIC CONSTANT AND LOSS ANGLE

It will be of value to examine the fundamental accuracy of the methods of measurement and calculation. The inherent accuracy of the bridge and each of the assumptions used for calculation and simplification are discussed below.

The Schering bridge is capable of measurement of the loss angle and the dielectric constant of the test capacitor within less than 0.5%, if the exact bridge equations are used. Televanti, however, has shown that no appreciable error is introduced if the simplified forms of the equations are employed for the range of samples and values used in this work.

As noted previously it is probable that the frequency of the bridge source is accurate to within 0.5%.

The Schering bridge measures the loss angle not only of the specimen but also of the test capacitor and its leads. Televanti has shown that the loss angle of the specimen is given by the Equation (35).

$$\epsilon = \epsilon_{\text{comb.}} / (1 + \frac{R_s}{R_c}) \quad (35)$$

where

$\epsilon_{\text{comb.}}$ = loss angle of specimen and test capacitor,

R_s = equivalent parallel resistance of specimen, and

R_c = equivalent parallel resistance of test capacitor and leads.

Furthermore,

$$\epsilon = 1/R_s C_p \omega \text{ and } \epsilon_c = 1/R_c C_p \omega. \quad (36)$$

where ϵ_c is the measured loss angle of test capacitor alone. Typical observed low values of the loss angle are 2.0×10^{-3} radians at a capacitance of 600 micro-microfarads, whereas under no circumstances did the measured loss angle of the empty test capacitor exceed 0.2×10^{-3} radian at a capacitance of 100 micro-microfarads. At 1000 cycles the actual loss angle of the specimen is found to be equal to 95% of the

observed loss angle in this case. Since this is the maximum error, no serious error is introduced by neglecting this correction.

The error in measured capacitance introduced by a lack of guard rings has previously been shown to be negligible.

It has been assumed that the dielectric is uniform and completely fills the space between the electrodes. It is probable that the specimens are as uniform as it is possible to make in the laboratory, since great care was taken in sheet making and selection of test sheets. Delevanti has shown that, if the sample does not completely fill the electrodes, the loss angle and dielectric constant of the specimen are given by the following expressions:

$$\epsilon' = \epsilon'_1 \left[1 + \epsilon \left(\frac{d - t}{t} \right) \right] \text{ and} \quad (37)$$

$$\epsilon = \frac{1}{1 - \frac{d}{t} + 1/(\epsilon_1 t/d)} \quad (38)$$

where

ϵ'_1 = observed loss angle of test capacitor,

ϵ_1 = observed dielectric constant of test capacitor,

t = specimen thickness, and

d = electrode separation.

In a typical experiment ϵ'_1 is 2.00×10^{-3} radians, ϵ_1 is 2.4, d is 0.007 inch, and w is 0.62 mm. If it is assumed that the specimen completely fills the space between the electrodes, the calculated values of the loss angle and the dielectric constant will be 2.0×10^{-3} radians and 2.4, respectively. However, if t is actually 0.0065 inch, then the values of the dielectric constant and the loss angle of the specimen are

2.5 and 2.39×10^{-3} radians. The calculated loss angle value will be substantially lower than the actual value of the test specimen if the specimen does not completely fill the test capacitor, although the dielectric constant value will not be substantially changed for moderate differences. This could be a significant source of error, since such spacing could easily be caused by small irregularities or particles in the test sheets. However, it is possible in the present apparatus to place the specimen under considerable pressure during testing, for the purpose of eliminating such spacing. Results which will be presented later show that the test capacitor system adequately accomplished its designed purpose, and it may be assumed that no significant error in the final results is introduced by such spacing.

It has been assumed that the Clausius-Mosotti relation is applicable to cellulose. This was verified when the dielectric constant of native cellulose was measured at several densities as described in a later section.

It has been assumed also that the loss factor is directly proportional to density. Data obtained for native cellulose at several densities did not confirm this relation. Inspection of Figure 19 (in a later section) shows that the relation is not linear. However, the deviation is not large and, if the correction is applied over a small range of densities, no serious error should result. For example, Cellulose A has an apparent density of 0.73 g./cc. An observed loss factor of 3.35×10^{-3} radians at this density would give a calculated value of 3.67×10^{-3} ; the true value, according to the curve of Figure 17, is 3.82×10^{-3} radians. An error of less than 4% is introduced

by the assumption of a linear relation between loss factor and density. Specimens of lower than standard density would give low calculated results, whereas the reverse is true for those of higher than standard density. If a serious systematic error is being introduced, it should be evident in the calculated data. This investigation has established that the loss angle of Celluloses A and D are similar. The densities of sheets of Celluloses A and D are lower and higher, respectively, than the standard density. Therefore, the calculated loss angles of Cellulose A at standard density should be lower than those for Cellulose D. This could not be observed. It may be concluded, therefore, that the assumption of linearity between loss factor and density for the purpose of calculation of results to standard density is sufficiently accurate for our purposes.

It may be concluded from the previous discussion that the measurement of dielectric constant is inherently accurate. A small error, however, may be introduced in the measurement and calculation of loss angle by the assumption that loss factor and density bear a linear relation, and by the slight error due to lead loss. No evidence of the former could be found in the calculated data, and, for our purposes, the calculated loss angle may be regarded as accurate.

STATISTICAL EVALUATION OF THE PRECISION OF THE MEASUREMENT OF DIELECTRIC CONSTANT AND LOSS ANGLE

In the measurement of loss angle and dielectric constant, random errors are introduced by inexactness in the determination of the various experimental quantities. An inspection of the errors of these values will enable an estimation of the precision of the test.

It has previously been shown that a particular electrode separation measurement may be regarded as being with 5% of the true value.

The area of the specimen between the electrodes is cut out and dried at 105° C. The error incurred in cutting out the test area is low, since the samples are clearly marked by the electrodes. Furthermore, the area is determined and a correction is applied if it differs from the known electrode area. The oven-dried sample is weighed on an analytical balance. Hermans (13) has pointed out that a small amount of water is present in cellulose even at this temperature as a result of the laboratory humidity. This, however, was ignored since the maximum error would be less than 0.5%. It is estimated that the reported weight of material between the electrodes is within 1% of the true value.

The measurement of C_2 and C_2' is very accurate, since the capacitor C_2 is accurate to one micro-microfarad and an excellent capacitance balance may be obtained with the Schering bridge.

The accuracy of ΔC_4 is not as great. The balance is not as sharp and the Vernier dial of capacitor C_4 can be read only to 0.1 unit. However, ten readings were taken at each balance, and the average value could be considered accurate to within 0.1 dial unit. Thus, ΔC_4 could be considered to be within 0.2 dial unit of the true value. This corresponds to an error of 3% for most readings where ΔC_4 was 8 units or higher (at the highest frequency, some readings are lower and the error is higher).

The largest error associated with the measurement and calculation of dielectric constant is that of the electrode separation, since it enters the calculation twice. By combination and rearrangement of Equations (28), (30), and (32), Equation (39) is obtained,

$$\epsilon_{0.8} = (1 + 2\underline{x}) / (1 - \underline{x}), \quad (39)$$

where

$$\underline{x} = \left[\frac{0.259 \underline{C}_p - \underline{p}_{cor.}}{0.259 \underline{C}_p + 2\underline{p}_{cor.}} \right] \left[\frac{0.8}{0.0229 \underline{W} \underline{p}_{cor.}} \right]$$

A typical sample has a measured \underline{C}_p of 600 micro-microfarads, \underline{W} is 0.537 gram, and $\underline{p}_{cor.}$ is 65 reciprocal centimeters. The calculated dielectric constant at standard density is 2.39. If Equation (39) is differentiated with respect to $\underline{p}_{cor.}$ and these values are substituted, Equation (40) is obtained.

$$\underline{d} \epsilon_{0.8} / \underline{d} \underline{p}_{cor.} = -0.055. \quad (40)$$

An error of 5% in $\underline{p}_{cor.}$ will cause an error of 1.6% in $\epsilon_{0.8}$. Since the effect of other errors upon the determination is small, the estimated experimental error of a single measurement of dielectric constant should be somewhat greater than 2%.

The observed dielectric constants for Celluloses A and D at 1000 cycles were analyzed statistically to check the validity of these assumptions. Pertinent results and the calculated maximum probable error are given in Table VI. This is in agreement with the estimated error of the determination.

It can be shown, in a similar manner as in the case of the dielectric constant, that the error introduced in loss angle by an error

TABLE VI

STANDARD DEVIATION OF THE DIELECTRIC CONSTANT DETERMINATION
(FOR SINGLE OBSERVATIONS)

From Data on Native Cellulose at 1000 Cycles

Cellulose	Number of Observations	σ^a	σ for $\epsilon'_{0.8}{}^b$
D	20	0.098	4.1
A	20	0.104	4.15
A ^c	19	0.078	3.1

^a $= [\sum (\underline{x} - \underline{X})^2 / \underline{n}]^{1/2}$, where \underline{x} is the observed value, \underline{X} is the mean value, and \underline{n} is the number of observations

^b Based upon mean value of $\epsilon'_{0.8}$

^c One value, obviously an error, discarded

in $\rho_{\text{cor.}}$ of 5% is approximately 4%. The error caused by inaccuracy of ΔC_u has been shown, in most cases, to be about 3%. The error in the density estimation and other small errors is approximately 2%. The maximum possible error of a single loss angle measurement then should be of the order of 10%. The standard deviation of the loss angle measurements of native fibers at all frequencies are summarized in Table VII.

TABLE VII

STANDARD DEVIATION OF THE LOSS ANGLE DETERMINATION
(FOR SINGLE OBSERVATIONS)

From Data on Native Celluloses A and B

Frequency, Cycles/sec.	σ^a	σ for $\epsilon''_{0.8}{}^b$
500	0.092	4.4
1000	0.089	4.3
2000	0.139	6.2
4000	0.157	6.3

^a Radians $\times 10^3$

^b Based upon mean $\epsilon''_{0.8}$ values.

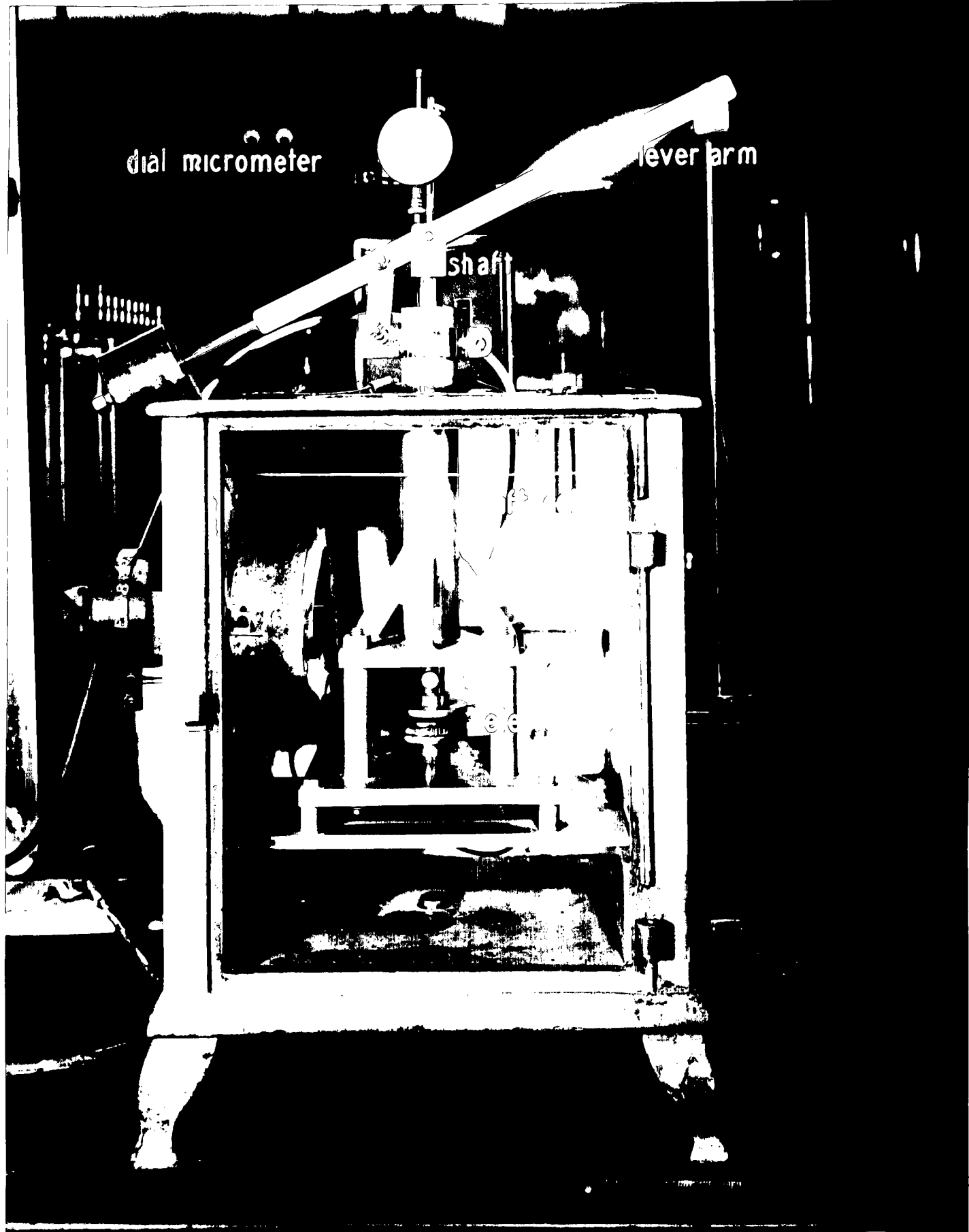
The calculated error is of the magnitude expected at lower frequencies. It increases somewhat at higher frequencies because of the greater inaccuracy in ΔC_u values.

These results show that both loss angle and dielectric constant measurements may be considered sufficiently precise for the purposes of this investigation. Since a number of observations were made in each case, the error of the means is considerably less.

AUXILIARY DIELECTRIC CONSTANT APPARATUS

As this investigation proceeded, the need of an auxiliary apparatus for the purpose of making independent and rapid dielectric constant determinations became apparent. Previous investigations (23, 25) and experiments which will be described later with the main test capacitor system and the Schering bridge have shown that an extreme state of desiccation is not necessary for the accurate measurement of dielectric constant. Therefore, a vacuum drying system is not necessary. A test capacitor system which could be heated to moderate temperatures and would permit an accurate determination of electrode separation would be satisfactory.

A plastometer, available at The Institute of Paper Chemistry, was modified for this purpose. A photograph of the completed apparatus is shown in Figure 15. The upper electrode shaft is permitted vertical movement only by the shaft collar. The shaft is actuated by the lever arm. The lower electrode is stationary and the electrode spacing is determined by the position of the upper electrode shaft. The foot piece of a dial micrometer rides upon the upper end of the



Plastometer

Figure 15

shaft. The electrode separation is determined from the difference in the micrometer readings at zero and the desired separation. A moderate pressure can be exerted upon samples between the electrodes by loading the lever arm. The system is mounted in a laboratory oven equipped with a thermoregulator and a blower for the circulation of air.

In the original plastometer the upper shaft abutted a shaft of similar size. Steel electrodes of the desired diameter were cemented over them. The upper electrode consists of a circular disk two inches in diameter, with a one-inch circular depression machined to fit over the upper shaft base as illustrated in Figure 16. The lower electrode

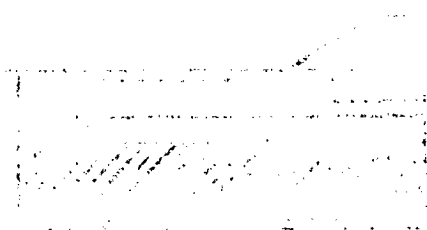


FIGURE 16

mount is a similar piece to which the lower electrode and its insulator are cemented with Redux. The depressions were painted with Glyptal and slipped over the original electrodes. The faces of the electrodes were held tightly together by loading the lever arm until the Glyptal was dry. This assured that the electrode faces would be parallel.

Electrical connections to the electrodes were made through a rigid system of wires (to insure stable lead capacitance) to bolts placed midway between the surfaces of the electrodes.

Compressed air, dried by passage through a copper coil immersed in a refrigerating bath at -35° C., was bled into the oven. By this means all air flow was outward through leaks in the oven and the samples were conditioned in a dry atmosphere.

The capacitance of the test capacitor and the leads was measured with a General Radio impedance bridge (Type 650A) connected to the system by a rigid series of wires. The lead capacitance was found by measuring the total capacitance at a series of electrode separations and subtracting the calculated test capacitor capacitance.

PROCEDURE FOR MAKING DIELECTRIC CONSTANT MEASUREMENTS WITH AUXILIARY EQUIPMENT

Specimens were placed in the oven and conditioned at 65 to 70° C. until equilibrium was established. This was found to occur in as short a time as two hours, although all measurements were checked at a minimum of 15 hours. The door was opened, the specimen placed between the electrodes, the door closed, the bridge balanced, and the micrometer reading noted.* The specimen was removed and the zero separation of the electrodes determined.

The dielectric constant was calculated from the ratio of the measured test capacitor capacitance to the calculated value.

$$\epsilon = (C_{\text{obs.}} - C_{\text{lead}}) / C_{\text{cal.}} \quad (41)$$

where $C_{\text{obs.}}$ = observed capacitance of test capacitor and leads, in micro-microfarad,

*Tests proved that this procedure, which permitted the specimen to absorb moisture during the manipulation, did not appreciably affect the accuracy of the dielectric constant determination.

C_{lead} = capacitance of leads, 38 micro-microfarad, and

$C_{cal.}$ = calculated vacuum capacitance of the test capacitor.

The value of $C_{cal.}$ was determined by use of Equation (27). Since λ is 20.34 sq. cm., and d is measured in inches, this may be reduced to the following.

$$C_{cal.} = 0.704/d \quad (42)$$

At the conclusion of a test, the specimen was removed, its area measured, dried to constant weight at 105° C., and W , the weight between the electrodes, found. Density is defined by Equation (29). By substitution of values in Equation (29), the following relation, where d is expressed in inches times 10^3 , was established:

$$\begin{aligned} D &= W/20.34(d \times 2.54) \text{ or} \\ D &= 19.45 W/d. \end{aligned} \quad (43)$$

The dielectric constant at standard density of 0.8 g./ml. was calculated as previously described.

ERROR OF THE AUXILIARY DIELECTRIC CONSTANT DETERMINATION

The method of measurement of the dielectric constant is similar to that used in the main apparatus, except that specimens are not placed under a high pressure and, therefore, a greater possibility exists that the sample does not fill the electrode spacing. However, as previously pointed out, little error is introduced at moderate spacings and it may be concluded that the method is accurate.

The error in the measurement of capacitance, including error of lead capacitance, is estimated to be less than 3 micro-microfarad,

since the bridge can be balanced with precision of one micro-microfarad. The accuracy of the dial micrometer was estimated by measurement of the standard shims previously described. The results indicated that the micrometer is accurate to 0.3×10^{-3} inch in all separations.

The errors involved in the determination of the density are slightly higher than in the main apparatus, since the specimen is smaller, and errors in the determination of the area will be higher.

It is estimated that the maximum error of a single determination is within 10% of the true value. This was confirmed by measuring the dielectric constant of several samples of Cellulose D. The results are given in Table VIII. These results indicate that the measurement

TABLE VIII

ERROR OF DIELECTRIC CONSTANT DETERMINATION
IN THE AUXILIARY APPARATUS

Cellulose	$\epsilon_{0.8}$	error ^a , %
D-1	2.57	7.1
D-1	2.29	-4.6
D-1	2.32	-3.3
D-2	2.40	0.0

^a based upon a value of 2.4 for Cellulose D

is at least as accurate as estimated. The precision of the determination is shown by the reproducibility of the values for the same specimen.

PREPARATION OF CELLULOSES FOR TESTING

Pertinent data for the different physical and chemical modifications of cellulose prepared for this work are given in Table X.

The raw material (with two exceptions) was specially purified cotton linters. The data in Table IX (from Hercules Powder Company) indicate that it may be considered a pure standard cellulose.

TABLE IX

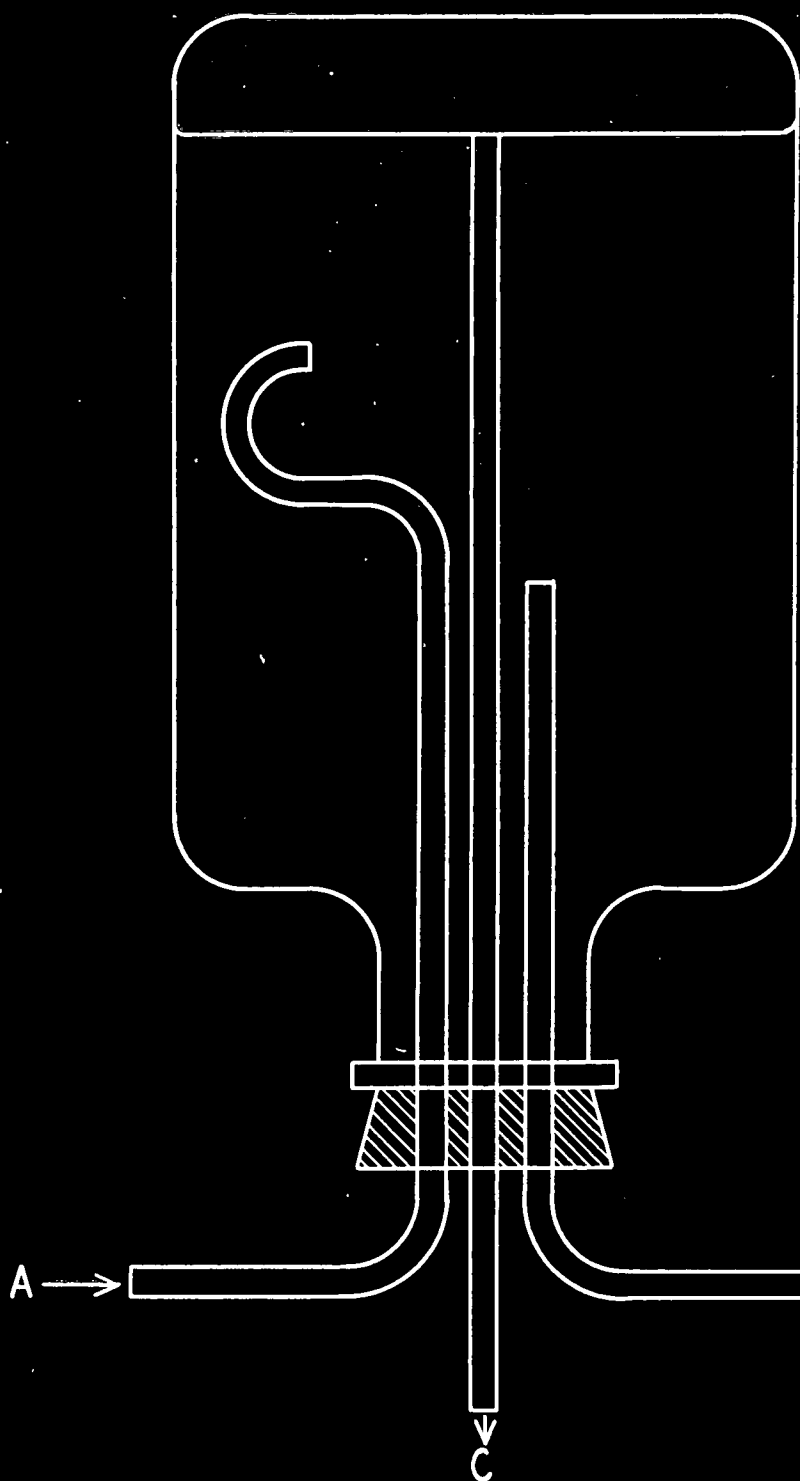
ANALYSIS OF HERCULES STANDARD CELLULOSE

D.P. (calculated from A.C.S. viscosity)	1600
Alpha-cellulose	99.4%
Ash	0.01%
Iron	0.0004%

The linters were used without treatment for the preparation of the regenerated fibers. However, their fiber length and papermaking properties precluded the preparation of suitable test sheets without further treatment. Therefore, they were beaten in a Valley one-pound beater to 440 cc. Schopper-Riegler freeness and screened with a laboratory screen. Dirt particles were largely removed by the dirt-settling device illustrated in Figure 17. The slurry at 0.3 to 0.5% consistency enters the lower part of the separator. Filtered water enters through a nozzle on the periphery and gives the system a slow upward circulatory movement toward the overflow. The fibers move upward and the dirt particles and fiber bundles settle. With proper regulation of the rate of flow, a clean linters cellulose in suitable form for sheet making was obtained.

TABLE X
PHYSICAL AND CHEMICAL PROPERTIES OF VARIOUS CELLULOSES

Cellulose	Description	Degree of Polymerization	Carboxyl Content, Milli-Equiv./ 100 g.	H ₂ O Regain at 54% R.H., %	Ash, %	Copper Number
A	Cotton linters	1450	Reg.	6.1	0.07	--
T	Filter paper	930	Reg.	6.15	0.006	--
B	Regenerated	--	--	10.7	0.1	--
F	Regenerated	--	0.2	10.9	0.21	--
G	High carbonyl	360	1.63	6.05	0.12	4.5
H	High carboxyl	240	6.32	6.3	0.10	0.5
J	Regenerated	505	Reg.	11.65	0.13	--
K	Ramie	1055	--	6.2	0.15	--
L	Cellophane	--	--	11.6	--	--



- A Filtered Water
- B Cellulose Slurry
- C Purified Cellulose

DIRT SETTLING APPARATUS

Figure 17

NATIVE CELLULOSE

The prepared cotton linters was extracted with 1% hydrochloric acid for one hour at room temperature and washed with distilled water until the washings showed no precipitate with silver nitrate. This was designated Cellulose A.

Whatman No. 50 quantitative filter paper was designated Cellulose B.

Blanched ramie fibers were beaten in a Dilts laboratory beater to a freeness of 250 cc. Schopper-Kiegler. The ramie was extracted with 1% hydrochloric acid to which approximately 0.1 gram of calcium hypochlorite had been added and washed in the same manner as the linters. It was designated Cellulose C.

REGENERATED CELLULOSE

A cellulose that possesses high reactivity and is presumably of high amorphous content was prepared by regeneration from cellulose xanthate according to the method of Jayne and Wellm (39). The cellulose was obtained in a fibrous form by precipitation into a turbulent bath. The material was further defibered in a British disintegrator. It was acid extracted, washed in the same manner as the native fibers, and kept in water suspension until preparation into sheets. Celluloses E, F, and J were prepared in this manner.

A cellophane manufactured for use in dialysis bags was obtained from the Cellulose Department of The Institute of Paper Chemistry. The sheets had been kept in a dilute formaldehyde solution. They were

washed and allowed to soak in distilled water overnight. The sheets were dried upon laboratory drying frames. This was designated Cellulose I.

CHEMICALLY MODIFIED CELLULOSE

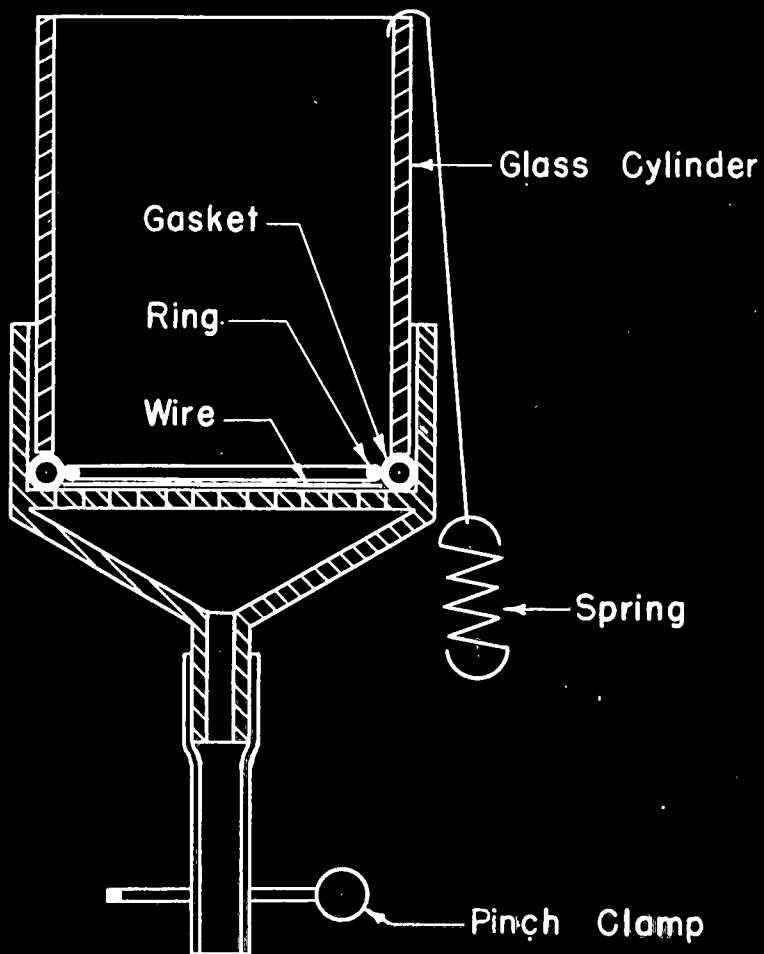
The most important types of cellulose degradation are hydrolysis of the chains and introduction of carboxyl groups. Birtwell, Clibbens, and Ridge (40) have shown that the type of degradation caused by hypochlorite solutions is dependent upon the pH of the oxidizing solution. Two oxycelluloses of different carboxyl and carbonyl content were prepared by slight modification of their methods. The high carbonyl content oxycellulose (Cellulose G) was prepared as follows: Fifty-five grams of air-dry prepared linters were mixed with 750 ml. of $\text{M}/5$ acetic acid and 35.6 ml. of sodium hypochlorite solution (49.9 grams available chlorine per liter) were added. After thorough mixing the pH was 3.5. The slurry was placed in a closed container in the dark at room temperature until the chlorine was exhausted (220 hours). The cellulose was extracted with dilute hydrochloric acid and washed in the usual manner.

The high carboxyl content oxycellulose (Cellulose H) was prepared as follows: Fifty-five grams of air-dry prepared linters were mixed with 750 ml. of $\text{M}/10$ sodium carbonate and 35.6 ml. of sodium hypochlorite (49.9 grams available chlorine per liter) were added. After mixing the pH was 11.2. The slurry was placed in a closed container in the dark at room temperature until exhaustion of the chlorine (650 hours). It was washed to neutrality, extracted with acid, and purified in the usual manner.

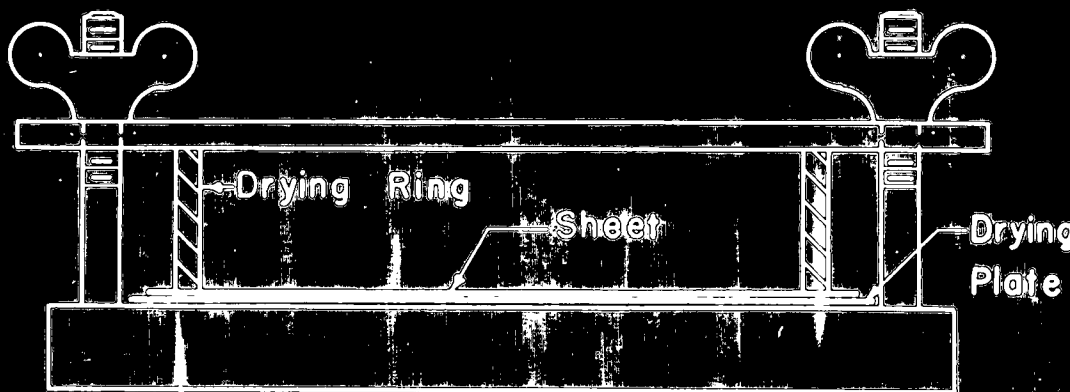
PREPARATION OF TEST SHEETS

In order to prevent contamination of the purified celluloses, a special sheet-making device (illustrated in Figure 18) was built. The base is a Büchner funnel mounted upon a ring stand. A tube of natural rubber is cemented around the inside as a gasket. The mold is a cylinder made by cutting the ends off a glass bottle of proper diameter. It rests upon the gasket and is held in place by three hooks connected by springs to a ring below. The hooks can be lifted and the cylinder removed for cleaning. A large mesh stainless steel wire is placed in the bottom of the funnel and the sheet is formed upon a fine bronze wire. Both wires are held in place by a stainless steel ring that fits snugly inside the rubber gasket.

The sheet-making technique was as follows. The wires and the stainless steel ring were positioned and the glass cylinder was secured in place. The mold was rinsed and then filled about three-quarters full with distilled water. The pulp was dispersed in a liter of water and added to the partially filled mold. The slurry was stirred, allowed to settle momentarily, and the water allowed to drain. After the sheet had drained, the cylinder was removed. The sheet, with the wire, was carefully removed and placed between new blotters. The stack was pressed several times with a heavy roller. The pressed sheet was removed from the wire by hand and placed upon a chromium-plated metal plate. New blotters were applied and the stack was pressed two minutes at 50 pounds (gauge) pressure in a Hermans hydraulic sheet press. Brass drying rings (four inches in diameter) were placed over the most desirable areas of the sheet. The rings were held tightly against the sheet



Sheet Mold



Drying Frame

Figure 18.

and drying plate by the device illustrated in cross section in Figure 18. It is a board, equipped with pairs of threaded shafts, on which the plates and rings are placed. A bar slipped over the two shafts holds the drying ring tightly against the sheet when wing nuts are tightened against the bar. The sheets were allowed to air dry in this manner.

This technique was satisfactory for all native fiber and oxycellulose pulps. However, the shrinkage of the regenerated fiber pulps was so great that the sheets invariably split upon drying. Splitting was avoided by slowly drying such sheets between stacks of blotters, but the sheets were somewhat wrinkled and, with few exceptions, were unsatisfactory for testing.

Staudinger and Dohle (41) removed water and obtained reactive celluloses by solvent replacement with methyl alcohol, ethyl ether, and cyclohexane in that order. A modification of this method was successfully used to prepare smooth soft handsheets. The handsheets, prepared and pressed as above, were placed between blotters in a bath of absolute methyl alcohol, which was changed twice during 24 hours. Ethyl ether was then substituted and changed five times over a period of two days. The sheets were then soaked in cyclohexane for one day, with one change of solvent. The sheets were then air dried between blotters.

Since the methoxyl analysis revealed a small amount of methyl or ethyl (from the ethyl ether) alcohol, the sheets were washed with low boiling petroleum ether. Miertelak and Garbaczówna (42) have shown that alcohol may be removed from cellulose by ethyl ether; presumably hydrocarbons, which are not adsorbed by cellulose, have a similar

action. This treatment was successful, since only a negligible methoxyl content (0.03%) was present after such washing.

It was found that 2 to 5% of cyclohexane was adsorbed by native cellulose dried by solvent replacement. Similar tests upon regenerated cellulose showed no adsorption. It is possible that the regenerated amorphous form permits escape of the cyclohexane. The significance of this point is considered in a later section.

ANALYTICAL PROCEDURES

Ash

Ash determinations were carried out according to Institute Method 610 except that, in some cases, the test samples were as small as 0.3 gram.

Carboxyl Content

The carboxyl content was determined by the calcium acetate method as described by Davidson and Nevell (43). The only modification was the substitution of a pH meter for the mixed indicator in the estimation of the end point.

Degree of Polymerization

The degree of polymerization was estimated from the intrinsic viscosity of the nitrated derivative in acetone by means of the modified Staudinger equation,

$$D.P. = (\eta)/\bar{K}_m. \quad (44)$$

where

(η) = intrinsic viscosity, and

$$\bar{K}_m = 11 \times 10^{-4}.$$

The samples were nitrated and the viscosities were measured according to the method described by Atchison (44).

Moisture Regain

The samples were preconditioned overnight at 25% R.H. and 90° F. The conditioned weight was determined at 54% R.H. and 76° F., using the technique and apparatus described by Wink (45). The oven-dry weight was determined by drying at 105° C. to constant weight.

The effect of preconditioning at 25% R.H. rather than at 0% R.H. was shown in the following manner. Several specimens were vacuum dried at 50° C. overnight and weighed. They were conditioned at 54% R.H. in the usual manner, oven dried, and weighed. Moisture regain results are given in Table XI, together with values determined by preconditioning at 25% R.H. The results obtained by preconditioning at

TABLE XI

EFFECT OF PRECONDITIONING UPON MOISTURE REGAIN

Cellulose	Regain at 54% R.H.	
	Preconditioned at 0% R.H., %	Preconditioned at 25% R.H., %
D	5.94	6.15
J	10.75	11.65
L	11.40	11.60

0% R.H. are slightly lower than those obtained by preconditioning at 25% R.H. However, the differences are not large. Furthermore, the results are low because of the moisture retained in the cellulose upon oven drying at 105° C. (13), and these errors will tend to cancel.

The test is a comparative one and, for this purpose, it may be regarded as satisfactory and comparable with moisture regain determinations carried out under more rigorous conditions.

Methoxyl

The methoxyl content was determined according to Institute Method 14.

Copper Number

Copper number was determined according to Institute Method 416.

Cyclohexane Retention

The retention of cyclohexane was determined by the general method of Staudinger and Bohle (41). The cellulose was vacuum dried at 50° C. overnight and weighed. It was soaked one hour in distilled water, dried by the solvent replacement technique, vacuum dried as before, and weighed. The observed gain in weight was reported as the cyclohexane retention of the cellulose.

PRELIMINARY EXPERIMENTS

In the method of calculation previously described, it has been assumed that the specimen completely fills the electrodes, that the Clausius-Mosotti relation is applicable to cellulose, and that loss factor and density bear a linear relation. These assumptions must be verified if the calculated results are to be considered valid.

The rate of attainment of equilibrium must be determined in order to assure that all measurements are made at equilibrium conditions.

The possible effect of the presence of moisture under the test conditions must be ascertained if the values obtained are to be considered representative of the cellulose being tested.

In the following sections the results obtained in the investigation of these problems are discussed and evaluated.

EFFECT OF PRESSURE UPON SPACING BETWEEN SPECIMEN AND ELECTRODES

It is possible to put the test specimen under considerable pressure during testing by means of the previously described test capacitor system. Its purpose is to eliminate localized high spots which are the chief cause of incomplete filling of the test capacitor. The effectiveness of the system was tested by measuring the dielectric properties of a specimen under a series of pressures. Reference to Equation (37) shows that the loss angle measurement is exceedingly sensitive to changes in the spacing, and any changes should be reflected in the calculated loss angle. The experimental data and calculations of

a test upon Cellulose D are given in Table XXIV*; the pertinent results are presented in Table XII.

TABLE XII

EFFECT OF PRESSURE UPON THE CALCULATED
DIELECTRIC PROPERTIES OF CELLULOSE D

Mean of Two Observations at 1000 Cycles

Pressure, p.s.i.	$\epsilon_{0.8}$ (105° C.)	$\epsilon'_{0.8}$ ^a (105° C.)	$\epsilon_{0.8}$ (75° C.)	$\epsilon'_{0.8}$ ^a (75° C.)	$\epsilon_{0.8}$ (50° C.)	$\epsilon'_{0.8}$ ^a (50° C.)	$\epsilon_{0.8}$ (27° C.)	$\epsilon'_{0.8}$ ^{a, b} (27° C.)
265	2.24	1.93	2.04	1.35	2.35	1.60	2.36	2.53
520	2.28	2.05	2.13	1.48	2.37	1.71	2.41	2.93
800	2.23	2.20	2.27	1.61	2.43	1.78	2.47	3.23
930	2.19	2.14	2.33	1.60	2.38	1.79	2.49	3.21

^aDensities $\times 10^3$

^bOne observation only

Even at low pressure, the spacing is low since there is no significant variation in the dielectric constant. However, the value of the loss angle increases with increasing pressure up to 800 p.s.i., indicating that the spacing is decreasing. A further increase in pressure has no effect. From this it may be concluded that the spacing has been effectively eliminated. At a pressure of 930 p.s.i. (used in all experiments), the assumption that the specimen completely fills the electrodes is valid.

RELATION BETWEEN ELECTRICAL PROPERTIES AND APPARENT DENSITY OF CELLULOSE D

The usefulness of the Clausius-Mosotti relation for the calculation of the dielectric constant to a standard density has been

*The detailed tables have been assembled in the Appendix.

noted. In order to confirm the applicability of this relation to native cellulose, the dielectric constant of several samples was measured at a series of densities. The specimens tested were Cellulose A, Cellulose B, and a high-density cellulose prepared by pressing several sheets of Cellulose B at 45,000 p.s.i. for ten minutes at room temperature. The dielectric constants reported for the lower density samples are average values obtained in the investigation of native cellulose discussed later. Those reported for the high-density cellulose represent one experiment reported in full in Table XXV. The results, calculated to a standard density of 0.8 g./cc. are given below. This is excellent agree-

TABLE XIII

DIELECTRIC CONSTANT OF NATIVE CELLULOSE AT STANDARD DENSITY
CALCULATED FROM MEASUREMENTS AT SEVERAL DENSITIES

Cellulose	Density ^a , g./cc.	$\epsilon_{0.8}$ (25° C.)	$\epsilon_{0.8}$ (50° C.)	$\epsilon_{0.8}$ (105° C.)
D	1.14	--	2.37	2.50
B	0.88	2.38	2.30	2.38
A ^b	0.73	2.45	2.40	2.70

^a Mean value

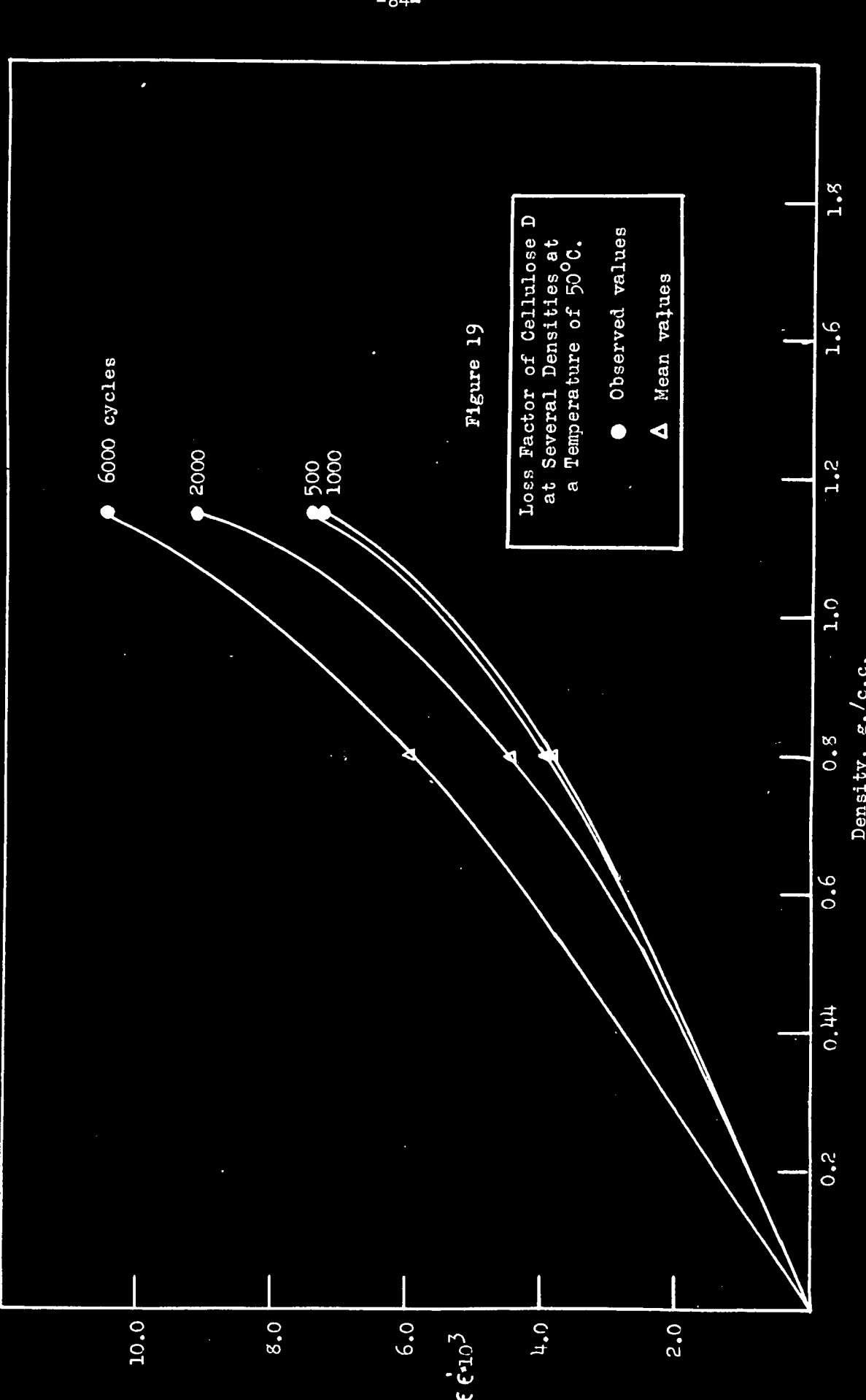
^b It is probable that Cellulose A has a higher dielectric constant than Cellulose B at 105° C.

ment, particularly since the measurement is not extremely precise. Data are reported for 1000 cycles only, since there is no apparent frequency effect. Corroborative evidence that the Clausius-Mosotti equation relates the dielectric constant and the density is obtained when the dielectric constant of solid cellulose is calculated from the observed values at 25° C. (using 1.57 as the ultimate density). A value of 6.0

is found, compared with the value of 6.1 experimentally determined by Campbell, Deluca, and Maass (16). The use of formulas derived by Endicott (19), on the assumption that paper fibers may be regarded as resistance elements, gives a value of 3.75 for the parallel case and a negative result for the series case. It can be concluded that the dielectric constant and the density of native cellulose are related by the Clausius-Mosotti equation.

The latter equation was originally derived upon the assumption that the polarizability of each molecule is independent of other molecules. This is probably not strictly true, since dielectric loss may be explained by the effects of internal forces which restrain the oscillation of polar groups in an alternating field, but it appears that such interference does not affect this displacement as the density is changed.

Delevanti showed that the loss factor of a dielectric is proportional to its density if the power loss is proportional to the mass of the material between the electrodes and to the square of the field strength. Hansen experimentally verified this relation for a kraft pulp. However, this could not be confirmed for native cellulose, although the deviations noted were not great, as shown in Figure 19. The high density values in Figure 19 are those observed with the specially pressed Cellulose D (the experimental data are given in Table XXV). The points at 0.8 density are the products of the mean observed loss angle and the mean dielectric constant value of native cellulose at 50° C. Similar results are found at other temperatures. The



observed relation is not linear but, over a small density range, could be considered so. Inspection of Hansen's data shows that a similar curve could be drawn through his experimental points, although all lie within the experimental error of the linear relationship.

STUDIES OF THE ATTAINMENT OF EQUILIBRIUM VALUES OF DIELECTRIC PROPERTIES

The time necessary to attain thermal and moisture equilibrium as reflected in loss angle measurements must be determined in order to be certain that the reported values are correct. Such observations may also be of value in determining the effect of moisture upon the dielectric properties.

In the normal procedure, the test specimen was heated to 105° C., allowed to come to equilibrium, and the electrical tests carried out. The temperature was allowed to fall to the next desired value and the procedure was repeated. After room temperature was reached, the temperature was raised in a similar stepwise manner. In a number of experiments, however, after the conditioning at 105° C., the temperature was held at a particular value and several measurements were taken over a period of hours. Some of the observed results are shown in Table XIV.

Equilibrium was reached within 15 hours at all temperatures, including the time necessary for heating and cooling. Since 12 hours is the minimum time necessary for attainment of the thermal equilibrium of the electrode separation gage, no investigations were made at shorter intervals of time. A minimum of 15 hours was allowed at each temperature for the attainment of equilibrium.

TABLE XIV

EQUILIBRIUM STUDIES AT VARIOUS TEMPERATURES

Cellulose	Temp., ° C.	Time, ^a hr.	$\epsilon_{0.8} \times 10^3$, radians
D	104	14	2.15
	105	21	2.10
D	105	20	2.39
	105	23	2.23
D	26	12	2.69
	26	22	2.64
D	54	16	1.74
	55	24	1.76
A	76	12	1.65
	74	24	1.63
A	48	17	1.79
	50	27	1.78
	48	53	1.78
A	26	21	2.84
	26	33	2.98
	25	47	2.87

^aTime from last equilibrium temperature

It was of interest to determine if equilibrium would be attained as rapidly without drying at 105° C. In a number of experiments a preliminary conditioning was carried out at a lower temperature, measurements were made at that temperature, the specimen was then conditioned at 105° C., and the experiment was carried out in the usual manner. The observed loss angles after the preliminary conditioning and the accepted value, determined from the mean curve of all the observed values with a particular cellulose, are presented in Table IV. Cellulose J reached equilibrium at 80° C. and Cellulose G at 56° C. However, in both cases, three out of four observed values are above

TABLE XV

LOSS ANGLE OF CELLULOSE AFTER DRYING
AT INTERMEDIATE TEMPERATURES

Cellulose	Drying Time, hr.	Drying Temp., ° C.	Frequency, cycles/ sec.	$\epsilon'' \times 10^3$, radians	Equilibrium $\epsilon'' \times 10^3$, radians
J	18	80	500	2.75	2.65
			1000	2.52	2.40
			2000	2.53	2.47
			4000	2.49	2.48
F	22	46	500	3.76	1.80
			1000	4.22	1.97
			2000	5.84	2.15
			4000	5.62	2.60
G	24	56	500	1.89	1.77
			1000	2.03	1.94
			2000	2.14	2.03
			4000	2.28	2.48

the accepted values. Cellulose F had not attained equilibrium at 46° C. Celluloses F and J are regenerated celluloses and, under given conditions, would presumably contain more moisture than a native fiber. The rate of water removal may be lower in the case of regenerated celluloses, since the difference in the conditioning temperature between Celluloses F and G is only 10° C. Specimens can be conditioned at lower temperatures in a reasonable time, but it is a safer practice to dry them at 105° C., as was done in these investigations.

It is possible to attain equilibrium even at room temperature. This is illustrated by the results obtained when a specimen of Cellulose E was conditioned at several gas pressures for an extended period at room temperature. The results are presented graphically in Figure 20 and the complete experimental data are given in Table XVI. Equilibrium

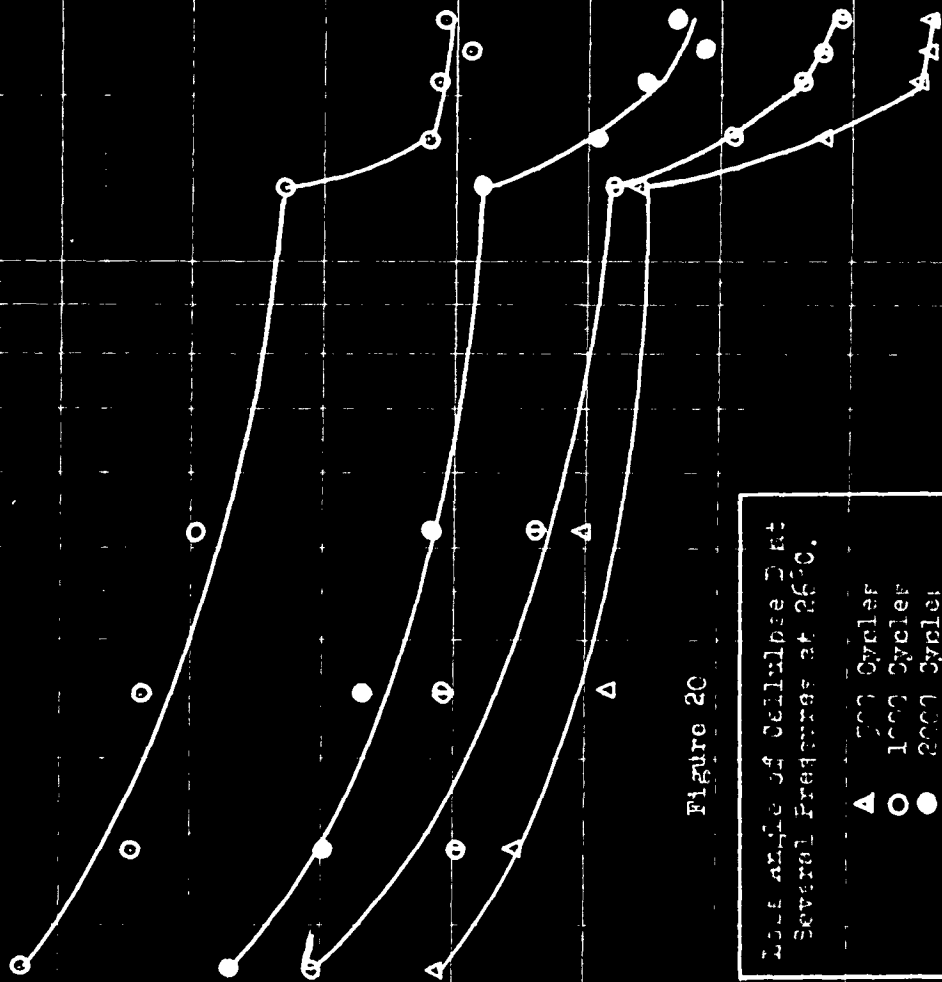


Figure 20

Angle of Cellulose vs
Several Frequencies at 26°C.

- ▲ 100 Cycles
- 1000 Cycles
- 2000 Cycles
- 5000 Cycles

100 microns — 250 microns — 500 microns

reached at almost exactly the mean values obtained from a series of measurements in the usual manner. This may be regarded as evidence that equilibrium has been attained at room temperature during the regular tests.

The effect of lowering the pressure in the system is illustrated by the rapid drop in loss angle values when the pressure is reduced from 200 to 0.1 micron. The magnitude is given in Table XVI.

TABLE XVI

CHANGE IN LOSS ANGLE OF CELLULOSE D
CAUSED BY LOWERING PRESSURE

Frequency, cycles/sec.	$\epsilon''_{0.8 \times 10^3}$ at 200 microns, radians	$\epsilon''_{0.1 \text{ micron}}$ at 0.1 micron, radians	$\Delta \epsilon''_{0.8 \times 10^3}$ radians
500	3.32	2.23	1.09
1000	3.43	2.53	0.90
2000	3.90	3.10	0.80
4000	4.65	4.00	0.65

The contribution of moisture to the dielectric loss decreases with increasing frequency.

Whether the same equilibrium loss angle values would be attained at the higher pressure, given sufficient time, cannot be answered definitely. However, if the portion of the curves at the higher pressure were extended, the accepted values would not be reached for nearly as long a time. Certainly, the relative humidity is higher at the higher pressure since the difference in total pressures alone could hardly account for the rapid drop induced by the lower pressure simply on the basis of the more rapid diffusion of water from the specimen. On the other

hand, the equilibrium moisture content, even at the higher pressure, might be low enough to have no significant effect upon the loss angle.

No change in dielectric constant was noted. Even the amount of moisture present early in the experiment caused no significant difference. This is in accord with the observations noted in the literature (23, 25) that a small amount of water makes no significant contribution to dielectric constant.

These investigations of equilibrium have established that 15 hours' conditioning at any temperature is sufficient, provided that the specimen was previously conditioned at 105° C. Equilibrium may be established at lower temperatures, including room temperature. It has been shown that the relative humidity at higher (gase) pressures is significantly greater than at 0.1 micron, but whether or not such differences affect the loss angle equilibrium has not been determined. The dielectric constant determination has been shown to be independent of the relatively small amounts of water present in the celluloses during these studies.

EFFECT OF PRESENCE OF MOISTURE UPON DIELECTRIC PROPERTIES OF CELLULOSE

The deleterious effect of the presence of moisture upon the loss angle of cellulose and similar materials is well known. Even a definition of dryness is difficult when one is dealing with a material which holds water as tenaciously as cellulose. The safest procedure is to estimate empirically that the dryness of the particular material being treated is satisfactory. This has been done in the present

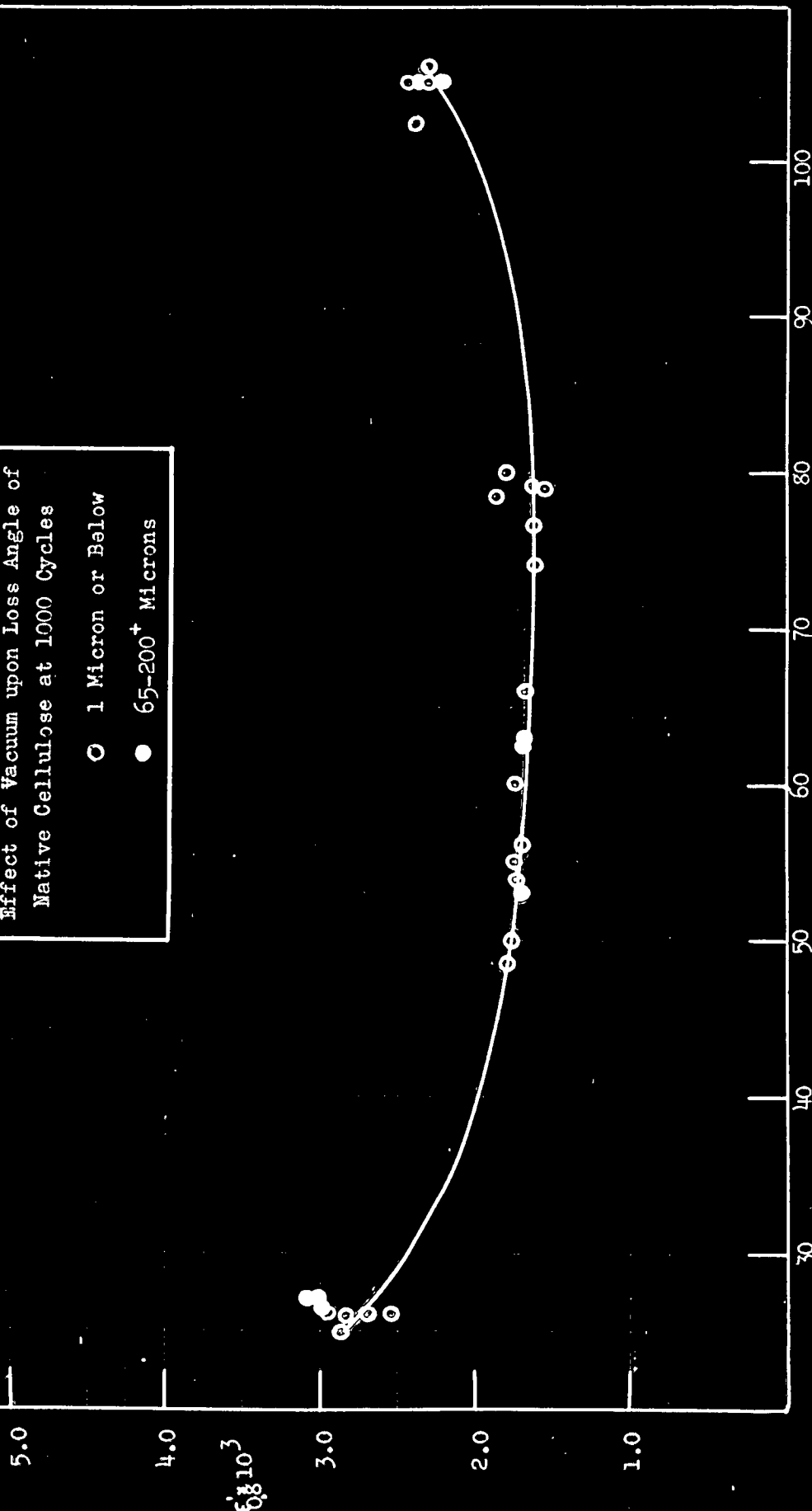
investigation by varying the moisture content in an indirect manner and ascertaining that this variation had no significant effect upon the measured dielectric properties of native cellulose.

Measurements of loss angle and dielectric constant were made upon samples of Cellulose II which had been conditioned and tested at two pressure ranges (1 micron or less and 65 to 200 microns). This is equivalent to varying the relative humidity of the conditioning atmosphere, as shown in the previous section but, it should be noted, not necessarily in the ratios of the observed pressures. This is evident if one considers a perfect vacuum system. The observed pressure in such a system might be completely due to water vapor, whereas a system with a leak permits entry of air which contains only a small portion of water vapor and the observed pressure would represent both water vapor and air. The measurements were made in the customary manner at the low pressure and then repeated at the higher pressures on the same specimen without breaking the vacuum. The results at 1000 cycles are presented graphically in Figure 21 (other frequencies give similar results). Above 50° C., it is evident that no differences are observed between the two series. Only at room temperature does there appear to be an increase in observed loss angle. However, these points are within the possible error of a single measurement and it cannot definitely be stated that the observed increase is real. In any case, the differences are of small magnitude. As a precaution, observations made at high pressures at room temperature were discarded. The loss angle measured at the higher temperatures may be regarded as the true loss angle of the cellulose being tested, since this experiment has shown that an

Figure 21

Effect of Vacuum upon Loss Angle of
Native Cellulose at 1000 Cycles

○ 1 Micron or Below
● 65-200⁺ Microns



increase in water content has no effect upon the observed values. At room temperature the possibility exists, however, that the observed drop with lower pressure is real, and that a still lower pressure would further decrease the loss angle. Greenfield and Whitehead (26) observed that the electrical loss of adsorbed water decreased rapidly as the total amount of water decreased. If this type of relation exists at these low water contents it is probable that no significant change would be observed by conditioning the specimens in the best available vacuum.

Cellulose exhibits a hysteresis effect upon adsorption and desorption of moisture. At normal humidities, the desorption equilibrium water content is sensibly higher than the adsorption value. Evidence (28) has been presented that hysteresis occurs even at extremely low humidities. If the presence of moisture were sensibly affecting the measurements, a hysteresis effect should be noticed in the loss angle values. Typical data at 1000 cycles are presented for two different celluloses in Figure 22. The curves were obtained by plotting the adsorption and desorption points for all the data secured for native Celluloses A and D, and for regenerated Cellulose J. No hysteresis effect is evident.

It seems reasonable to assume that the observed loss angle values of this investigation represent, within the error of determination, the loss angle of the test specimen without any significant contribution from the moisture content.

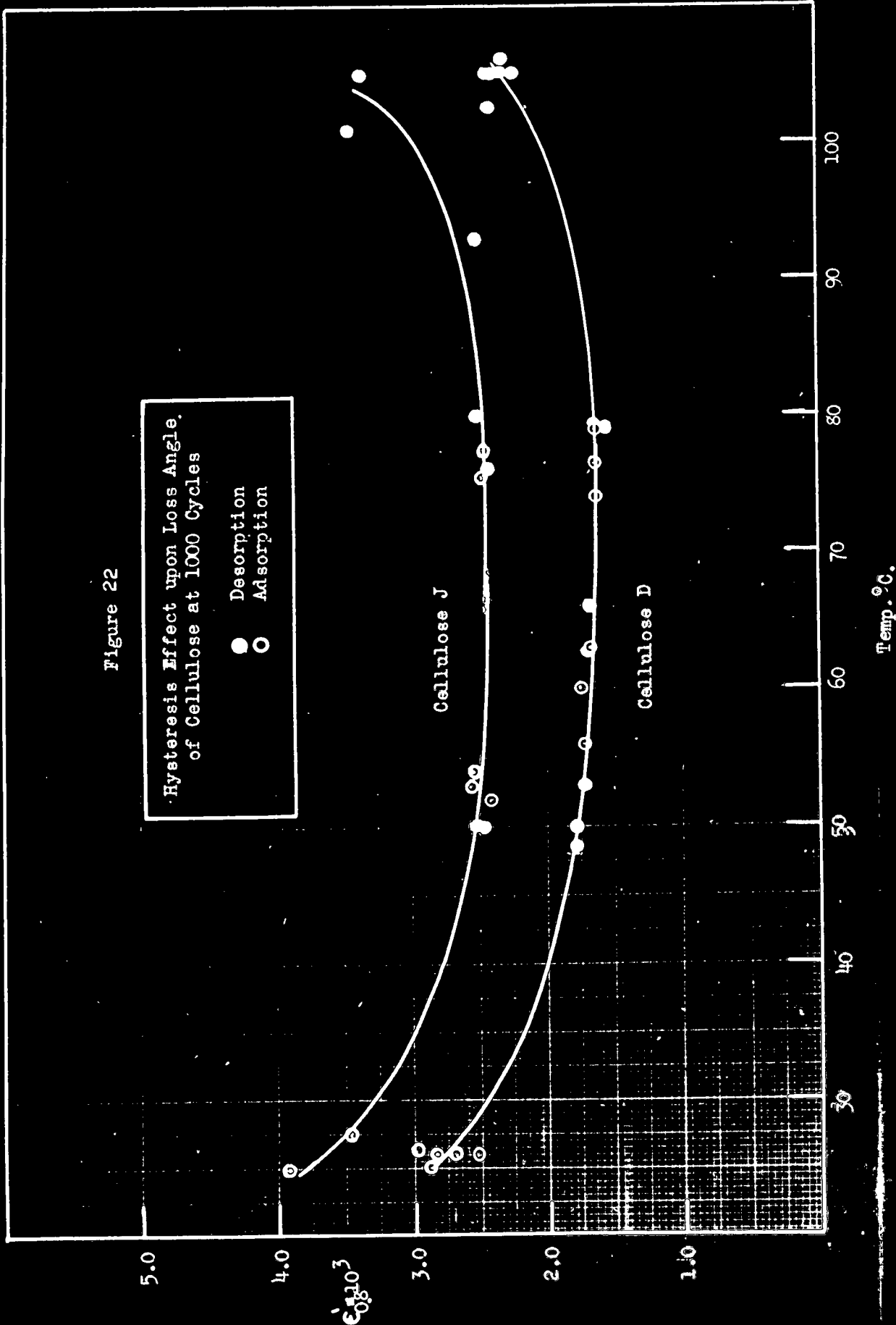
Figure 22

Hysteresis Effect upon Loss Angle,
of Cellulose at 1000 Cycles

- Desorption
- Adsorption

Cellulose J

Cellulose D



INVESTIGATIONS OF THE DIELECTRIC PROPERTIES OF NATIVE CELLULOSES

DIELECTRIC PROPERTIES OF PURIFIED NATIVE FIBERS

The loss angle and the dielectric constant of test specimens prepared from Cellulose A (cotton linters), Cellulose D (filter paper), and Cellulose K (ramie) have been measured at a series of frequencies from 500 to 4000 cycles and over a temperature range from 25 to 105° C. Two extensive experiments were carried out in the case of Celluloses A and D. The experimental data and results are presented in Tables XXVII-XXX. One experiment was made upon Cellulose K, the results of which are given in Table XXXI.

The observed values of the loss angle are plotted as a function of temperature at each frequency in Figures 23-26.

No significant differences can be noted between the loss angles of Celluloses A and D at any frequency or temperature. The loss angle of Cellulose K appears to be low at the lower temperatures but it is within the possible error of a single measurement. In view of the limited number of observations, it cannot be concluded that a significant difference exists.

The loss angle of native fibers is similar regardless of their source and purification treatment, at least in this frequency and temperature range. This is not surprising, since each is a pure cellulose, chemically speaking. Inspection of Table X shows that all possess a high degree of polymerization, and that their moisture regain under the conditions of this particular test is the same. This indicates that

Figure 23

Loss Angle of Native Cellulose
at 500 Cycles

- Cellulose A
- Cellulose D
- ⊙ Cellulose K

$\epsilon'' \cdot 10^3$

30 40 50 60 70 80 90 100

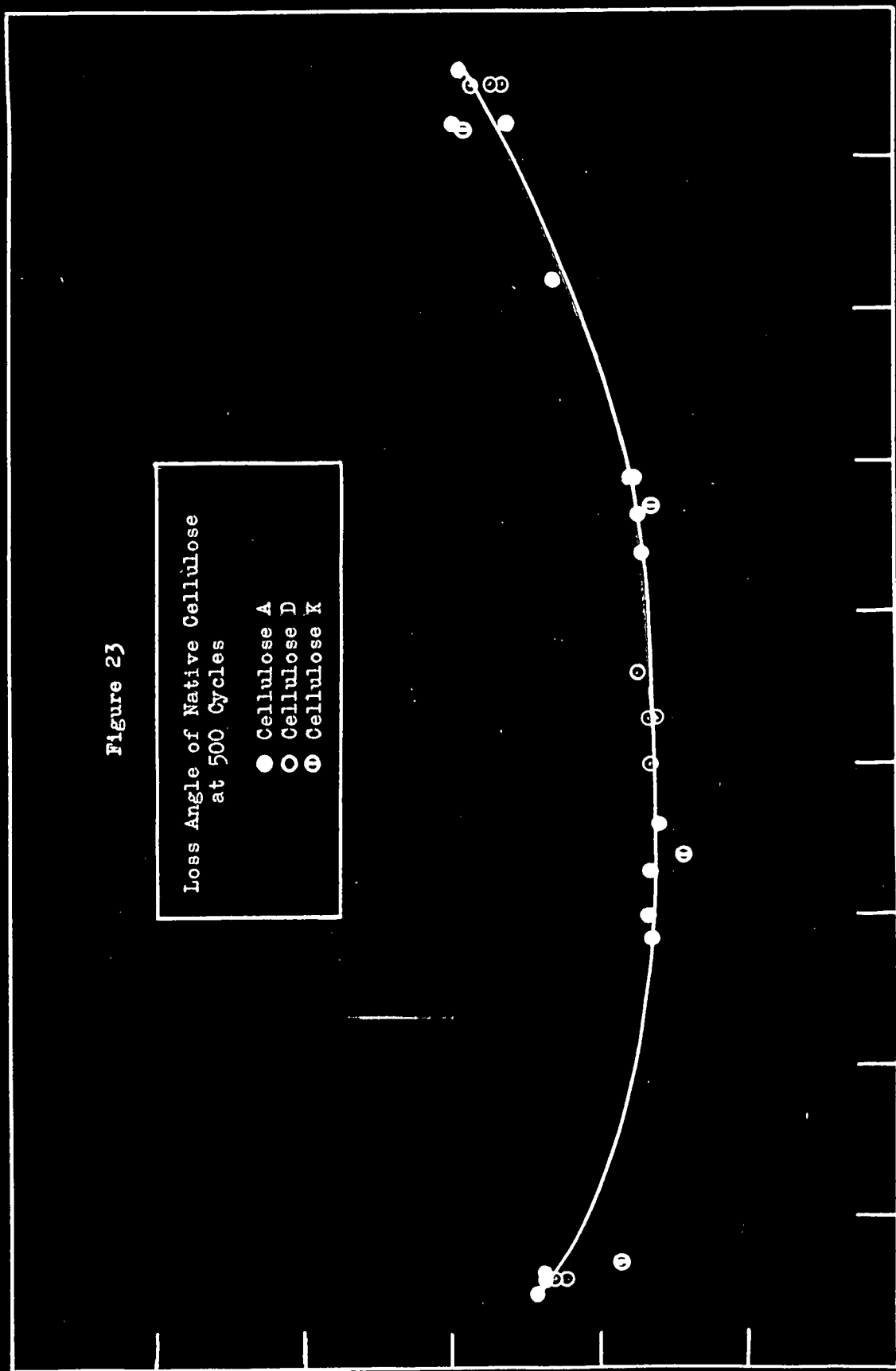


Figure 24

Loss Angle of Native Cellulose
at 1000 Cycles

- Cellulose A
- Cellulose D
- Cellulose K

5.0

4.0

3.0

2.0

1.0

$\epsilon'' \cdot 10^3$

30

40

50

60

70

80

90

100

Temp., °C.

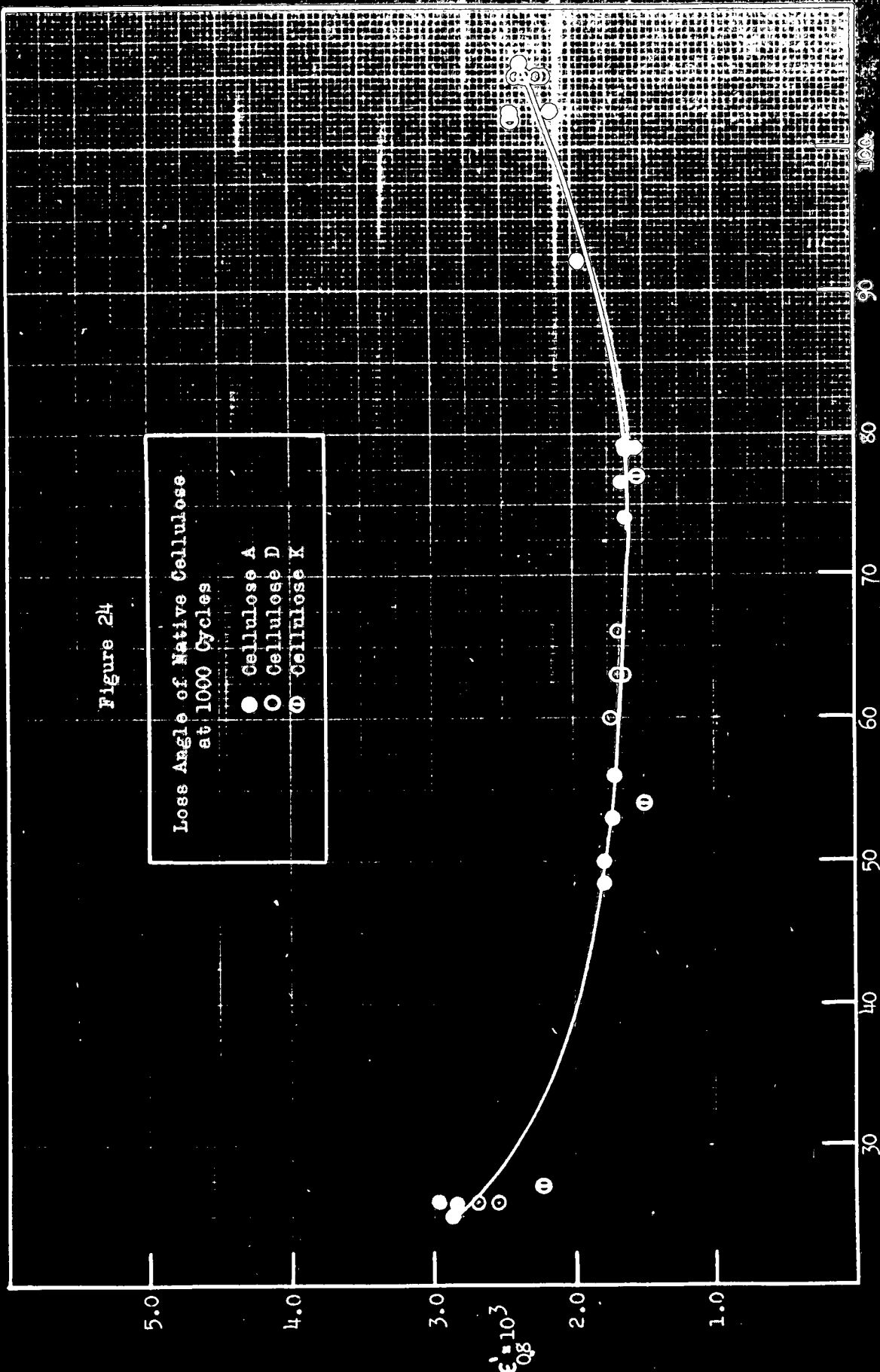


Figure 25.

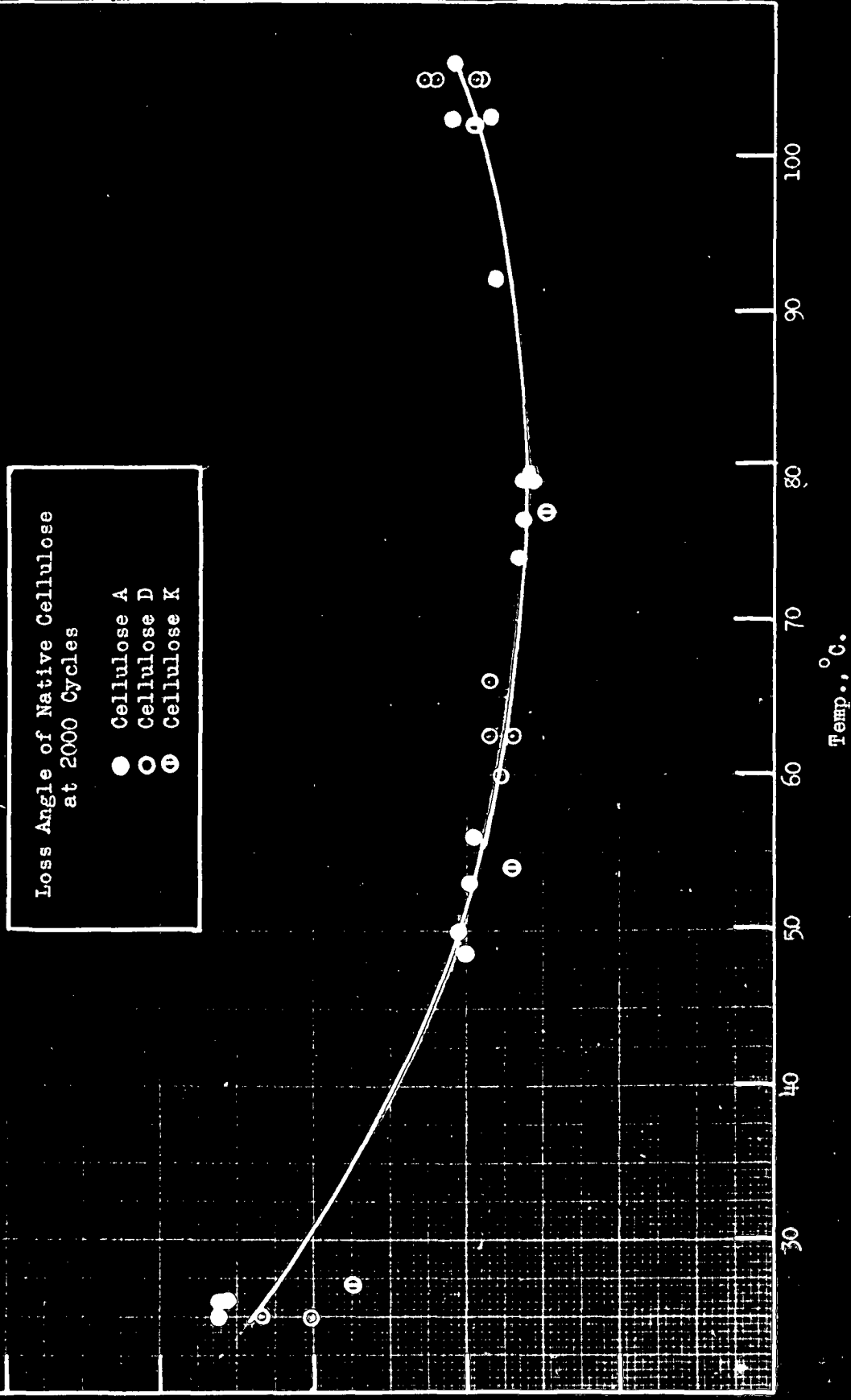
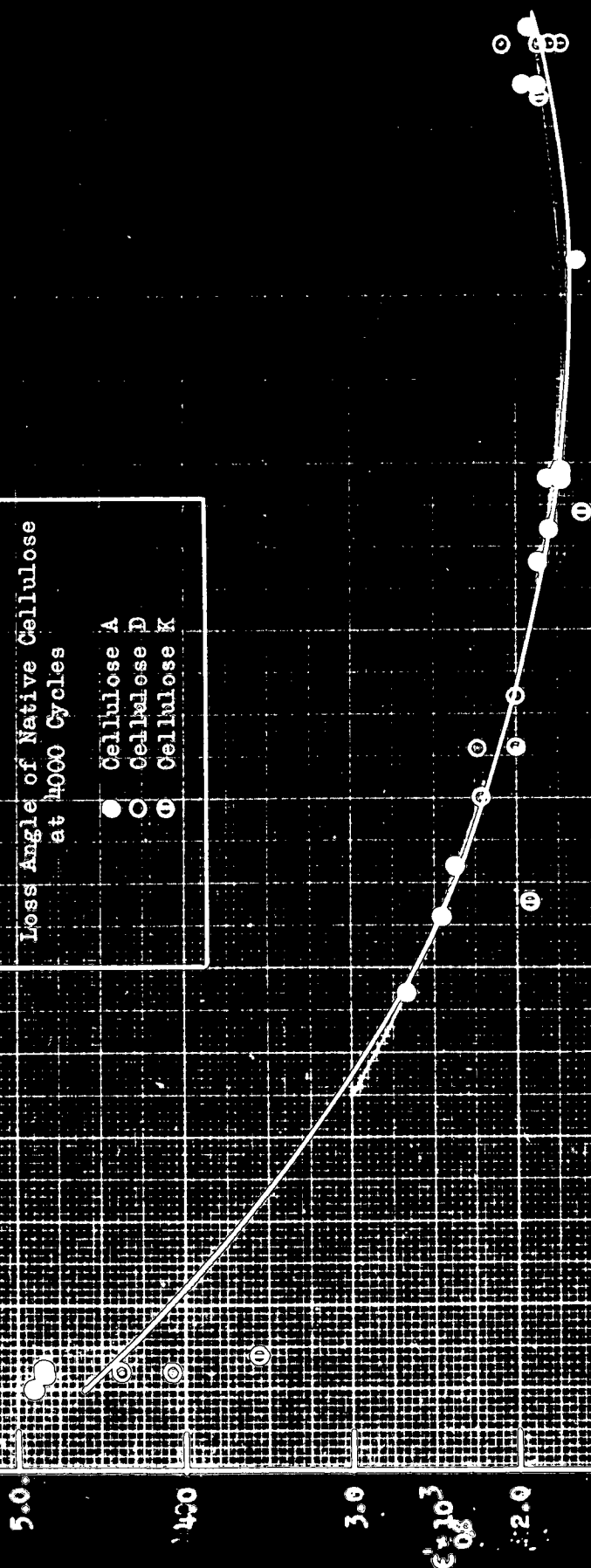
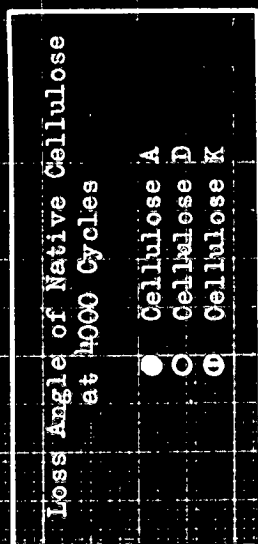


Figure 26



they possess the same modification of the native cellulose lattice (Cellulose I) and, possibly, that they are similar in their amorphous cellulose content. In a recent article Hermans (46) has confirmed these similarities in x-ray measurements.

Only one difference is apparent from the analytical data. The ash contents vary from 0.006 to 0.15%. It is well known that excessive amounts of ash cause an increased dielectric loss. These data, however, show that, at these low ash contents, the effect is negligible. It may be concluded that, if the ash of a specimen of native cellulose is reduced to 0.1%, no significant contribution to the dielectric loss will occur in this frequency range.

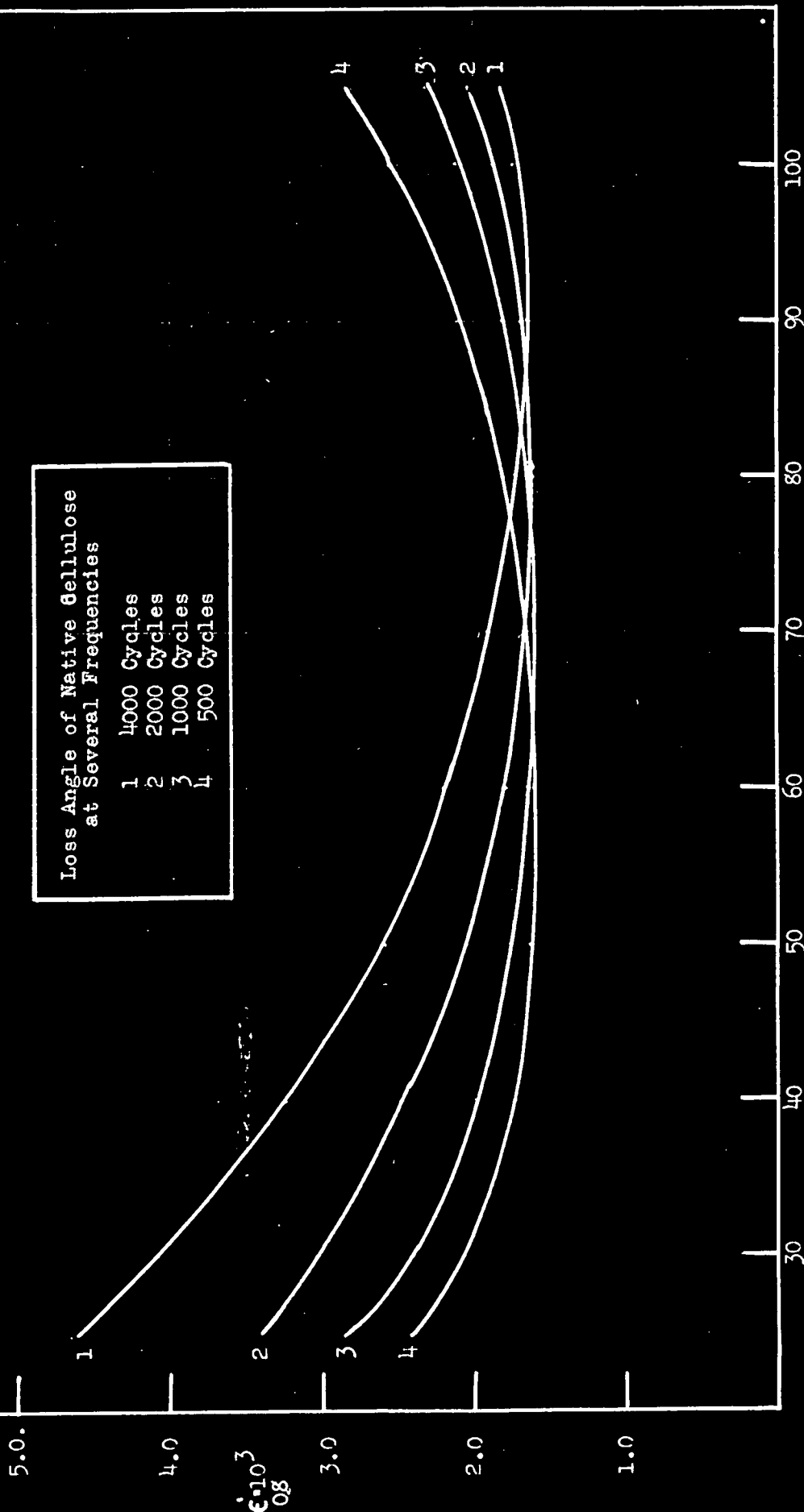
The loss angle-temperature curves at each frequency are collected in Figure 27. Each curve shows a minimum point. The temperature at which this minimum occurs increases with increasing frequency. This is similar to the behavior observed by Stoops (12), although his values were much higher (a result explained by poor desiccation).

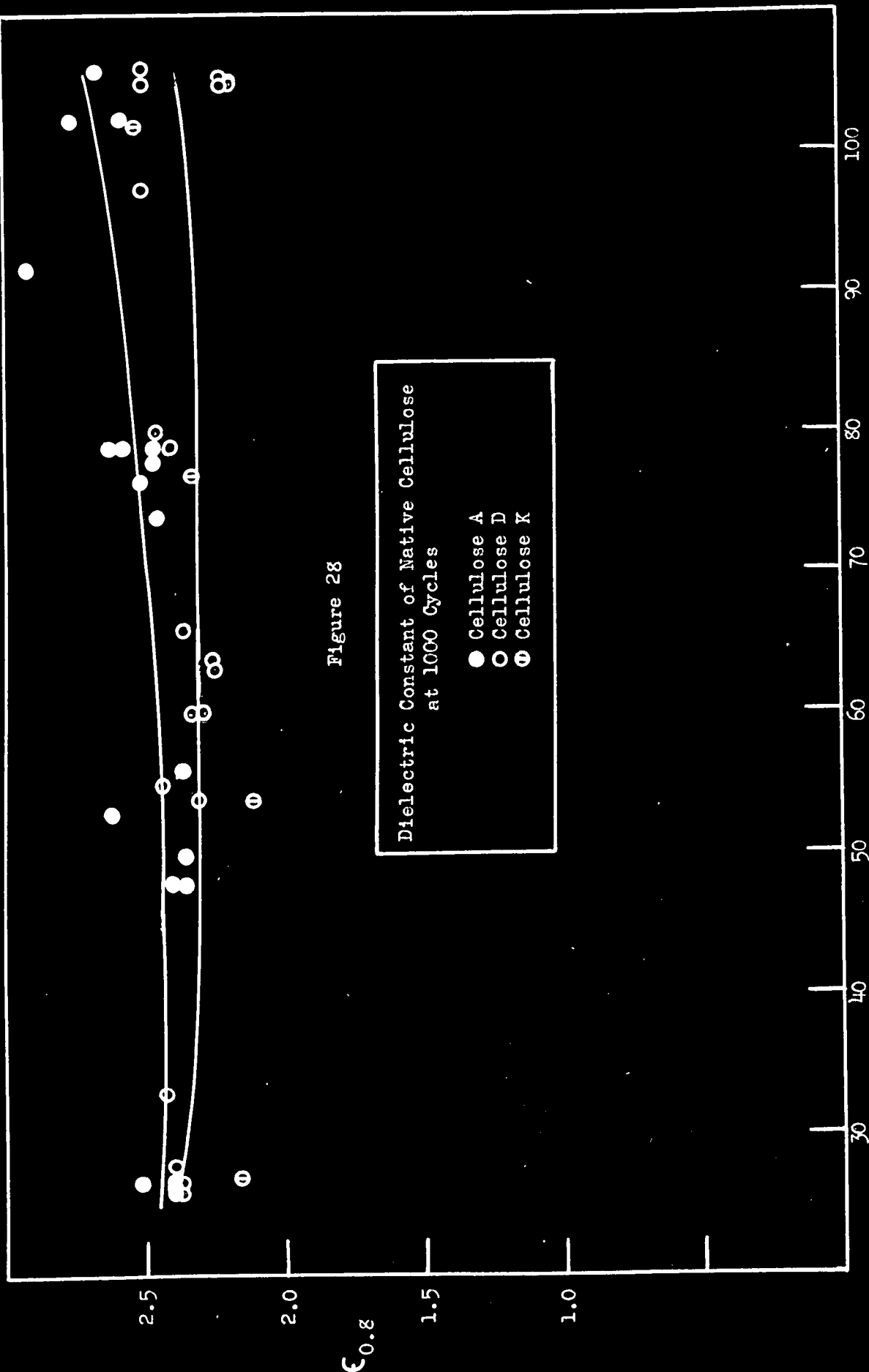
The dielectric constant values at 1000 cycles, calculated to standard density, are presented as a function of temperature in Figure 28. No significant differences were noted at other frequencies. A difference exists between Celluloses A and D. No reason for this is apparent. In both cases, it appears that the dielectric constant passes through a minimum and then increases with increasing temperature. Other investigators have noted the rise in dielectric constant with increasing temperature, but the presence of a minimum has not been reported. It is possible that a small systematic error in the deter-

Figure 27

Loss Angle of Native Cellulose
at Several Frequencies

- | | |
|---|-------------|
| 1 | 4000 Cycles |
| 2 | 2000 Cycles |
| 3 | 1000 Cycles |
| 4 | 500 Cycles |





mination of the electrode separation could account for the minimum. It is concluded that the dielectric constant of native cellulose shows a significant rise at higher temperatures, and that it is probable that it passes through a minimum in this temperature and frequency range.

The preliminary experiments have indicated that the contribution of adsorbed water to either dielectric constant or loss angle may be neglected. The effect of ash content has been shown to be negligible. Therefore, the explanation of the observed dielectric behavior will be found in the structure of the cellulose.

Contributions to dielectric loss and dielectric constant as a result of electronic and atomic polarizations will not be further considered since, as previously pointed out, they will be constant over this frequency and temperature range. Cellulose is a linear polymer with many polar groups. In general, such polymers show increased dielectric constant and loss with increased temperature and decreased frequency. Cellulose is also a heterogeneous material and interfacial polarizations occur. This type of polarization decreases with increasing temperature and increasing frequency, because of the relatively large masses of the particles involved (1).

If this concept of cellulose is correct, then the observed loss angle-temperature curves can be explained. The initial decrease may be the result of the decreased loss as the interfacial polarizations decrease because of the increased thermal agitation. At the same time, the loss attributable to polar groups increases and a minimum is observed. This loss decreases with increasing frequency and, as a con-

sequence, the minimum is shifted toward higher temperatures at the higher frequencies. The possibility of a low temperature region of anomalous dispersion however cannot be ruled out.

The observed behavior of the dielectric constant may be explained in a similar manner. It is evident that the observed minimum in the curve relating dielectric constant and temperature is real.

It may be concluded that the observed dielectric properties of cellulose are satisfactorily explained if cellulose is regarded as a heterogeneous linear polymer with attached polar groups.

DIELECTRIC PROPERTIES OF DEGRADED NATIVE CELLULOSES

The dielectric behavior of native cellulose has been shown to be related to its polar character. A knowledge of the contributions of substituent polar groups to the dielectric loss is desirable. With the exception of hydroxyl groups, carboxyl and carbonyl groups are most likely to be found in cellulose. Their contribution was ascertained by measurements carried out upon several oxycelluloses prepared from cotton linters, as previously described. Analytical data for the content of carboxyl and carbonyl groups in Celluloses G and H are presented in Table XVII taken from Table I. The copper number was used to estimate the carbonyl groups.

TABLE XVII
CARBOXYL AND CARBONYL CONTENTS OF CELLULOSES G AND H

Cellulose	Carboxyl Content, Milli-equiv./ 100 g.	Copper Number
G	1.6	4.8
H	6.3	0.5

An experiment was carried out with each cellulose in the customary manner. The observed data and the calculations are reported in Tables XXXII and XXXIII. The loss angle values at standard density are presented as a function of temperature at each frequency in Figures 29-32. In addition, the mean curve obtained at each frequency for native cellulose is included on each graph for comparison.

Both celluloses have significantly higher loss angle values than native cellulose at the higher temperatures. The observed values are higher than those for native cellulose at the lower temperatures, but the differences are less than at the higher temperatures and may not be significant. Cellulose H, the high carboxyl content cellulose, shows the greatest loss, particularly at higher temperatures and lower frequencies.

The relative contribution of each group was estimated in the following manner. As a first approximation, the increase observed in the case of Cellulose H was assumed to be due entirely to the carboxyl groups present, since the cellulose has a low copper number. The net increase at a series of temperatures was determined graphically and is presented as a function of temperature at each frequency in Figure 33, together with similar curves for Cellulose G, which have been corrected for the carboxyl content from the results obtained with Cellulose H.

The contribution of carbonyl groups to the dielectric loss is negligible, except possibly at the highest temperature. Since this oxycellulose has a very high copper number (corresponding to one carbonyl group for each ten anhydroglucose units), it may be concluded

Figure 29

Loss Angle of Degraded Celluloses
at 500 Cycles

○ Cellulose G
● Cellulose H
⊖ Native Cellulose

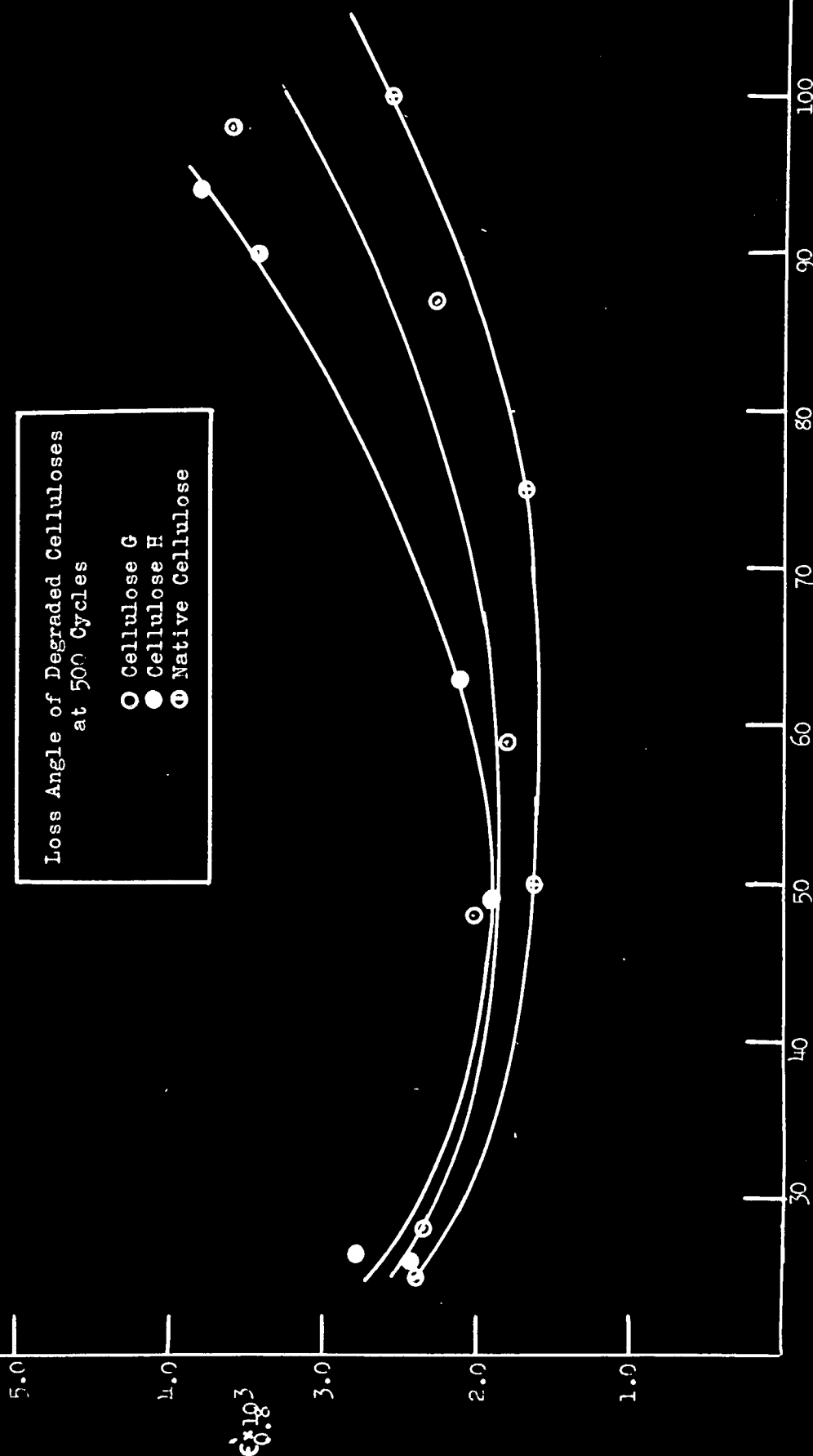


Figure 30

Loss Angle of Degraded Celluloses
at 1000 Cycles

- Cellulose G
- Cellulose H
- ⊙ Native Cellulose

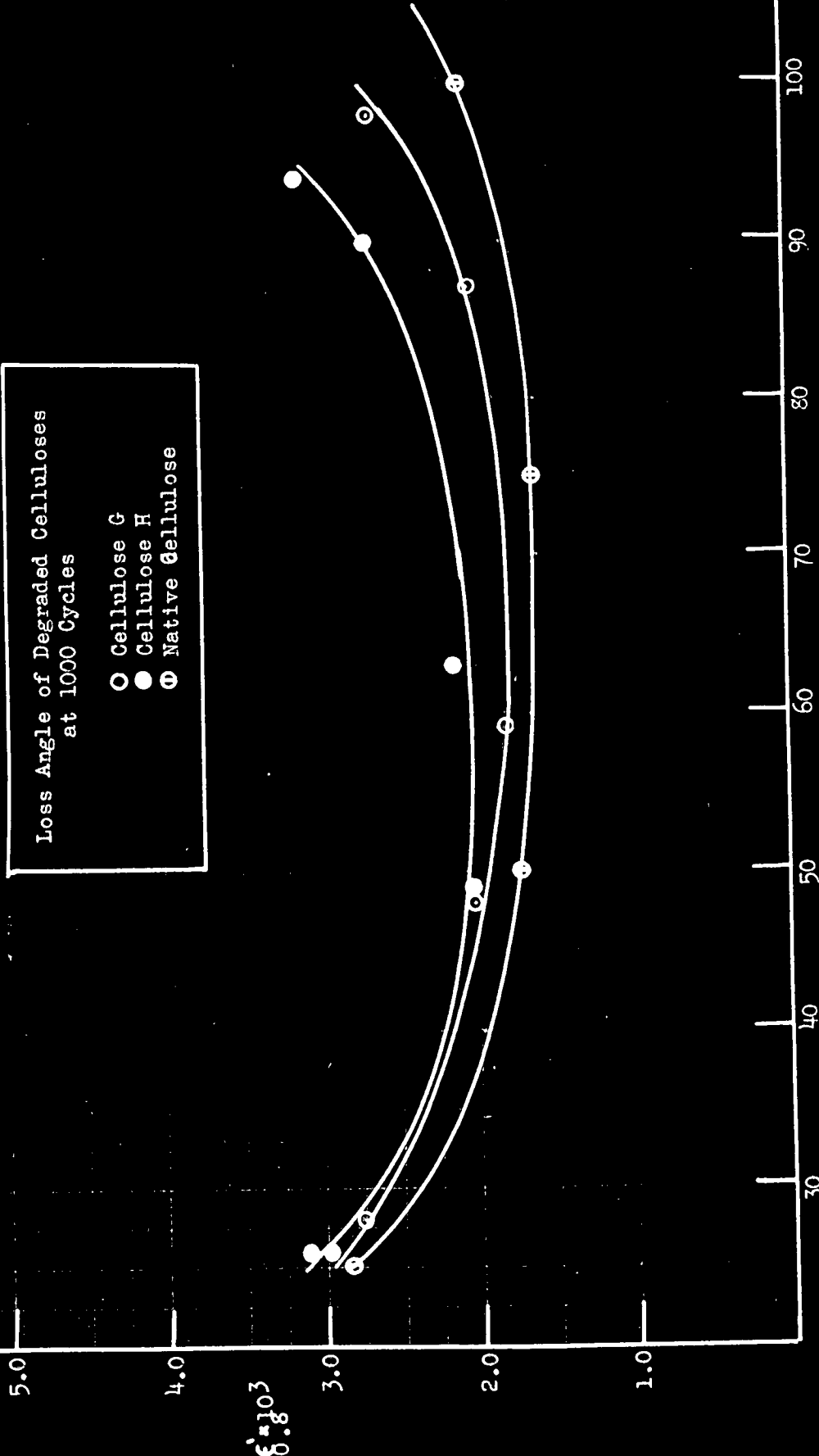


Figure 31

Loss Angle of Degraded Celluloses
at 2000 Cycles

- Cellulose G
- Cellulose H
- ⊙ Native cellulose

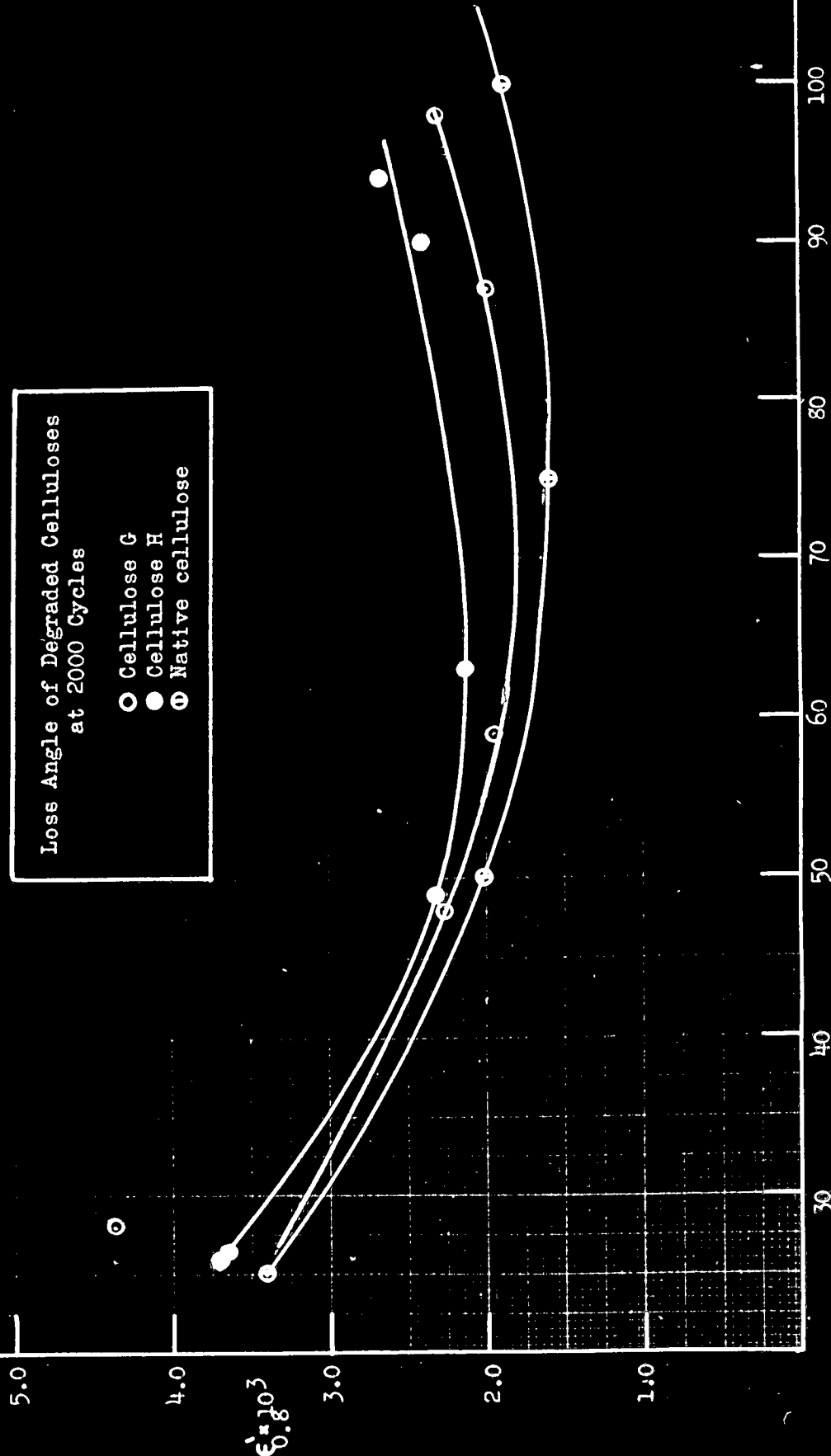
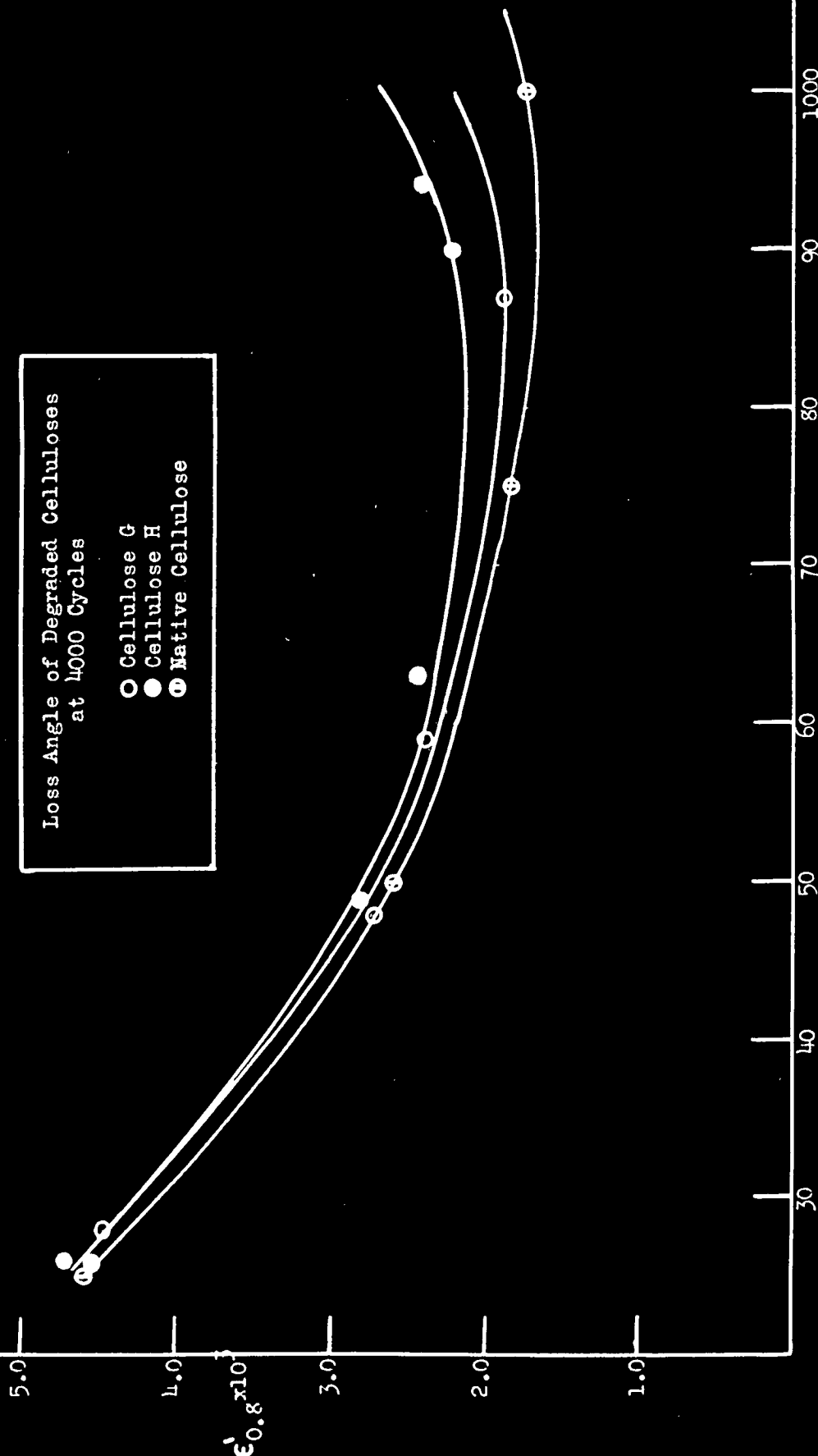
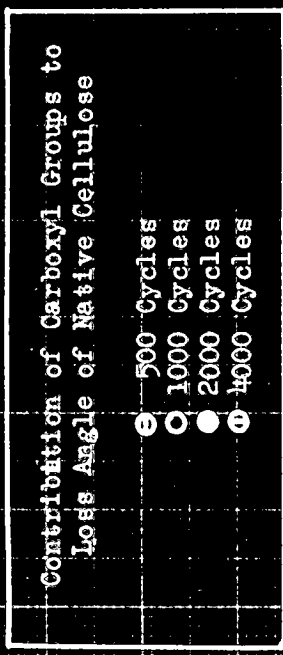
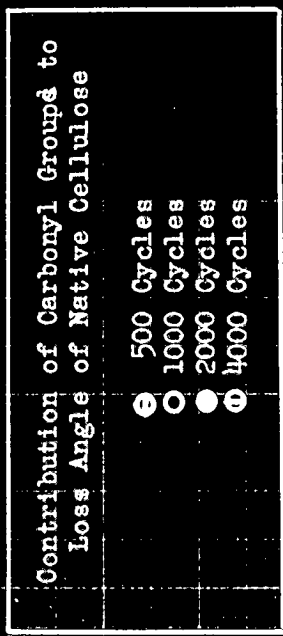


Figure 32

Loss Angle of Degraded Celluloses
at 4000 Cycles

- Cellulose G
- Cellulose H
- ⊙ Native Cellulose





that carbonyl groups are not a source of appreciable dielectric loss in cellulose.

The contribution of the carboxyl groups to the dielectric loss is extremely high at the higher temperatures, particularly since only one group is present per 100 anhydroglucose units. The shape and relation of the curves of Figure 33 are similar to the native cellulose curves at the higher temperatures. It is possible that cellulose contains carboxyl groups not revealed by present analytical methods. The possibility that such groups are responsible for the observed rise in the case of native cellulose must be discarded, since the magnitude of the effect is not large enough to be accounted for by the presence of one or two carboxyl groups per 1000 anhydroglucose units.

Cellulose II contains sufficient ash (0.1%) to provide cations for the carboxyl groups present. The results for an ash-free carboxyl cellulose cannot be predicted. Church (33) has shown that free carboxyl groups cause lower direct current resistivities in condenser paper than bonded ones. An interesting possibility would be that only part of the carboxyl groups are free and that these cause the observed increases.

No significant changes in the dielectric constant, as compared with that of native cellulose, were noted. This is not unexpected since the differences, as compared with native cellulose (although drastic, chemically speaking), have affected physical structure only slightly.

DISCUSSION OF RESULTS OF TESTS UPON NATIVE CELLULOSE

Several interesting deductions may be made from these observations and the published data. Hansen (17) has reported loss angle values at standard densities at 1000 cycles for kraft pulps of 2.1 to 2.4×10^{-3} radians at 80° C. Native cellulose under the same conditions has a loss angle of 1.7×10^{-3} radians. If it is assumed that the pulp is 80% cellulose and that its contribution to the dielectric loss is proportional to its weight fraction, the contribution of the remaining components is found to be more than one-third of the observed loss, even in the case of the best kraft pulp. A bleached kraft with an observed loss angle of 2.04×10^{-3} is only slightly better than an unbleached kraft. The source of excessive loss is evidently in the noncellulosic constituents of the pulp, with both lignin and the hemicelluloses contributing to the dielectric loss. The behavior of the latter can be explained readily, since it is generally accepted that most of the carboxyl groups present in pulps are found in the hemicellulosic fraction. Hansen has shown that lignin contributes excessively to dielectric loss.

These views are substantiated by the work of Miller and Hopkins (47). They found that the removal of lignin and associated materials from kraft electrical paper reduces the power factor. Alkaline extraction of the delignified residue, with the removal of 4% of the hemicelluloses (based upon the original paper), caused a considerable reduction in the power factor. A limited extraction of this type would remove the carboxylic fraction of the hemicelluloses and, as the results of this investigation show, reduce the dielectric loss. Further

extraction caused large increases in the power factor. Such extended treatment would not yield a pure native cellulose residue but rather might cause considerable degradation which would account for the increase. Unfortunately, no analytical data are given for the residue.

The comparison of reported data and the evaluation of the results are not always entirely reliable. Nevertheless, it is believed that the following statement can be made. Improvements in the dielectric characteristics of present-day electrical papers may be achieved by the elimination of those fractions of the noncellulosic constituents which contribute excessively to the dielectric loss and, particularly, in the elimination of the carboxyl groups.

INVESTIGATION OF THE DIELECTRIC PROPERTIES OF REGENERATED CELLULOSE

Previous sections have been concerned with native celluloses which possess the normal crystal lattice (Cellulose I) and are largely crystalline. Regenerated celluloses differ in two respects. The cellulose exists in a different crystal lattice and is largely amorphous as a consequence of the regeneration, according to Hermans (13). Most regenerated celluloses possess the hydrate cellulose lattice (Cellulose II). The terms crystalline and amorphous are used in the qualitative sense (discussed earlier) to indicate regular ordered arrangement and disordered random arrangement of cellulose chains, respectively.

Changes in the dielectric properties, in comparison with native cellulose, are possible as a consequence of these differences. In particular, if the amorphous content were related to the dielectric behavior, a valuable analytical tool might be developed.

Celluloses K, F, and J were prepared as previously described. Sheets were made and dried both conventionally and by solvent replacement. The moisture regain of these celluloses was approximately twice that of native cellulose. Hermans has reported that amorphous cellulose has a much higher moisture regain than crystalline cellulose and, on the basis of his results, these celluloses must be considered amorphous. Celluloses K, F, and J all exhibited plastic flow at low pressures, a property of amorphous materials.

A preliminary test upon a specimen of Cellulose F indicated that the dielectric constant at room temperature at standard density

was approximately 3.3, in comparison with a value of 2.4 for native cellulose. This was not conclusive since equilibrium, as evidenced by loss angle measurements, was not reached.

Because of the difficulty of obtaining satisfactory test specimens by air drying, the previously described solvent replacement technique was utilized to prepare a series of specimens of Cellulose J. Two experiments were made with these sheets. The results are given in Tables XXXIV and XXXV. The calculated loss angle values at standard density are presented as a function of temperature in Figures 34-37. Similar curves for native cellulose are included on each figure for comparison. The dielectric constant data, calculated to standard density at 1000 cycles, are presented in Figure 38, together with a similar curve for native cellulose. Similar results were found at all frequencies tested. Both loss angle and dielectric constant values are substantially higher than are the corresponding values for native cellulose. Before the cause and significance of these results are discussed, it is necessary to be certain that these differences are characteristic of the celluloses.

The possible effects of the solvent-replacement treatment must be investigated. It has been shown previously that a very small amount (0.3%) of methyl alcohol was absorbed by the cellulose, and that a final wash with petroleum ether reduced this to 0.04%, a negligible quantity.

It was assumed that no ether could be present, since Martell and Garbaczewska (12) have reported that ethyl ether is not retained by

Figure 34

Loss Angle of Cellulose J
at 500 Cycles

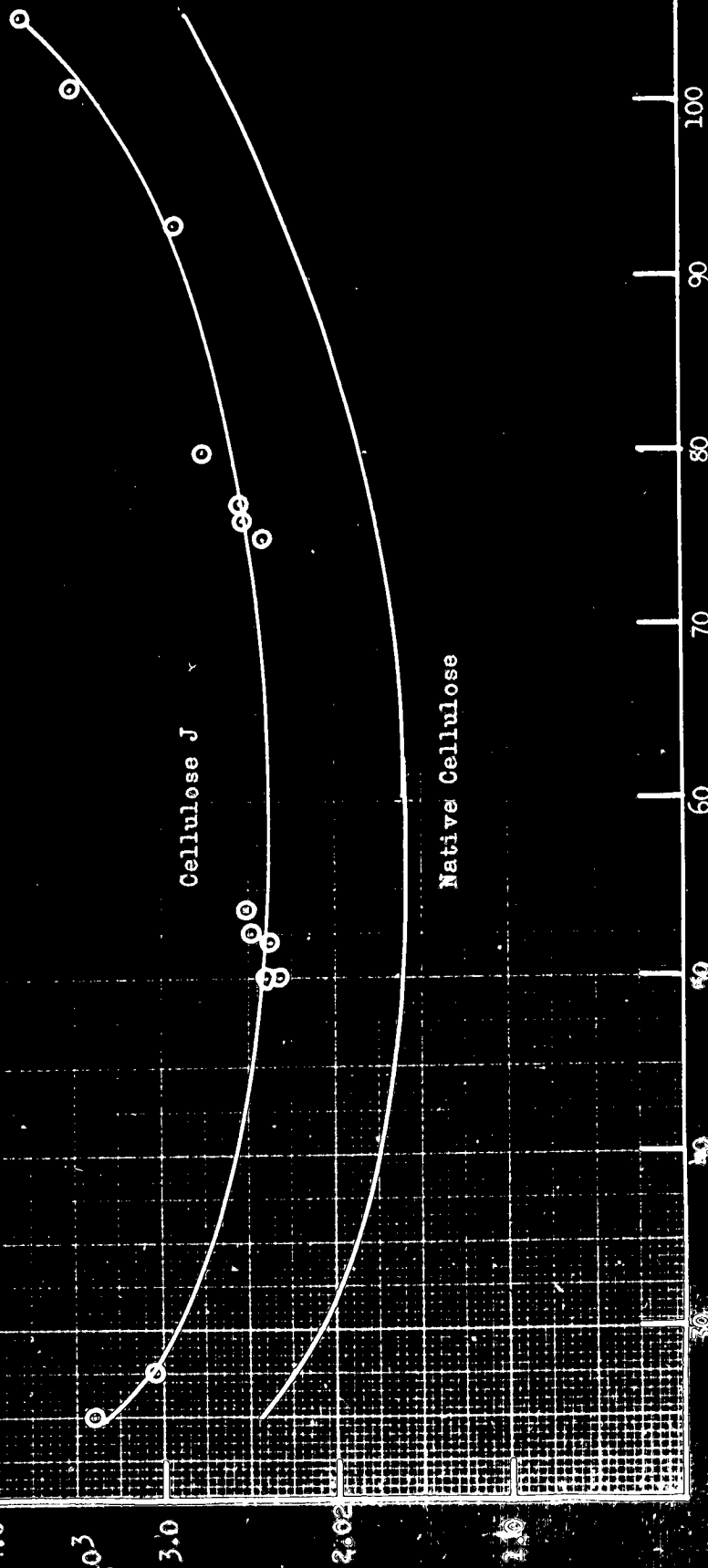


Figure 35
Loss Angle of Cellulose J
at 1000 Cycles

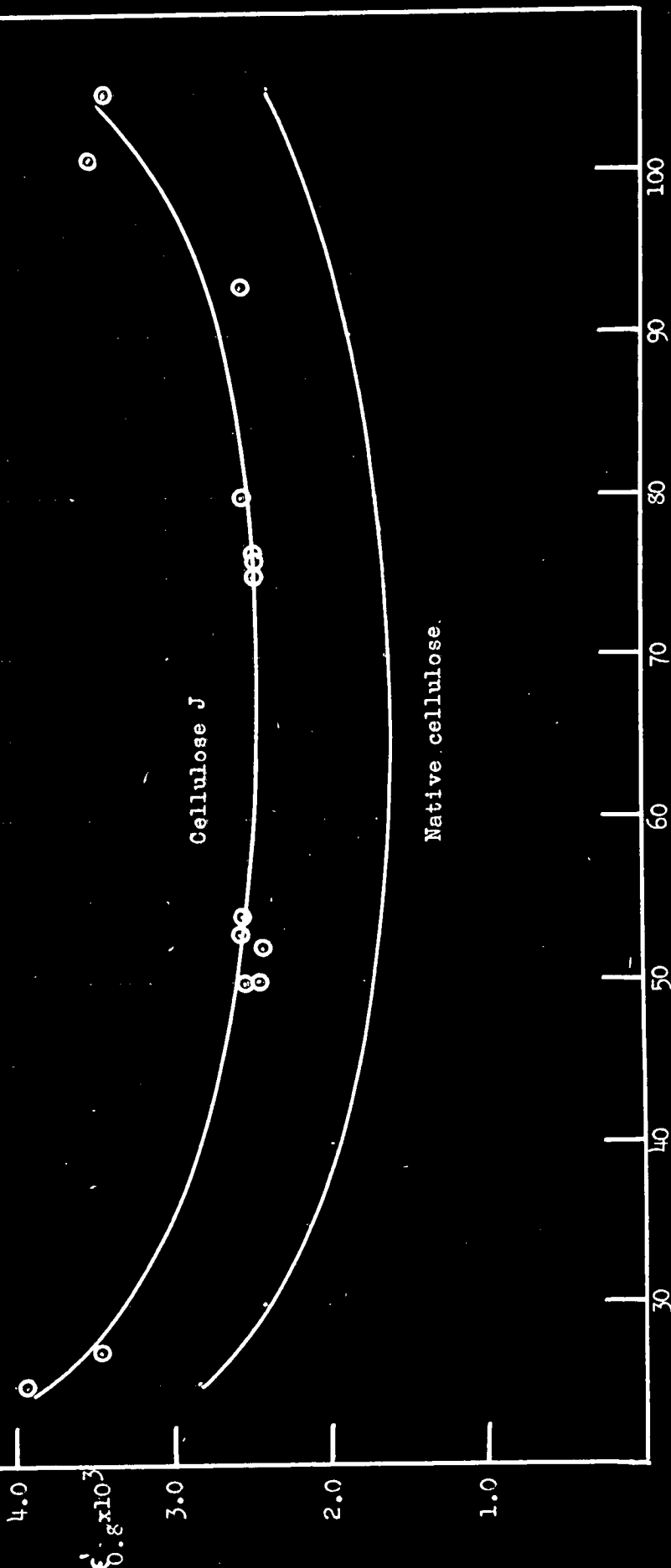


Figure 36

Loss-Angle of Cellulose J
at 2000 Cycles

Cellulose J

Native cellulose

Temp., °C.

100

90

80

70

60

50

40

30

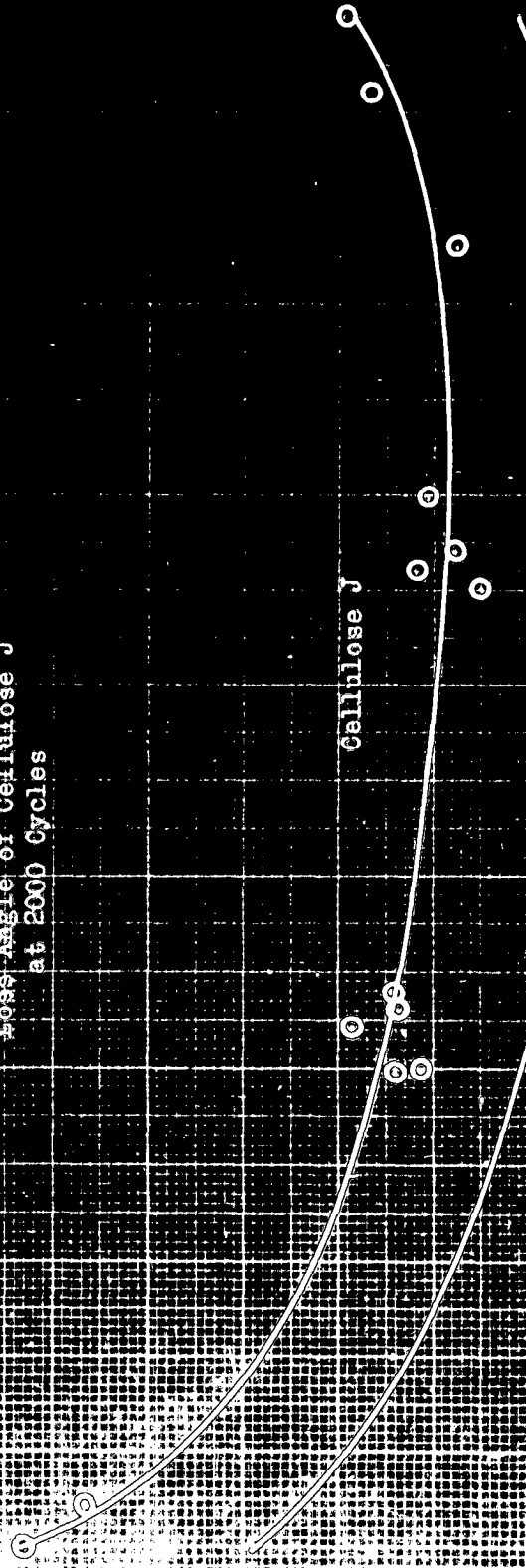


Figure 37
Loss Angle of Cellulose J
at 1000 Cycles

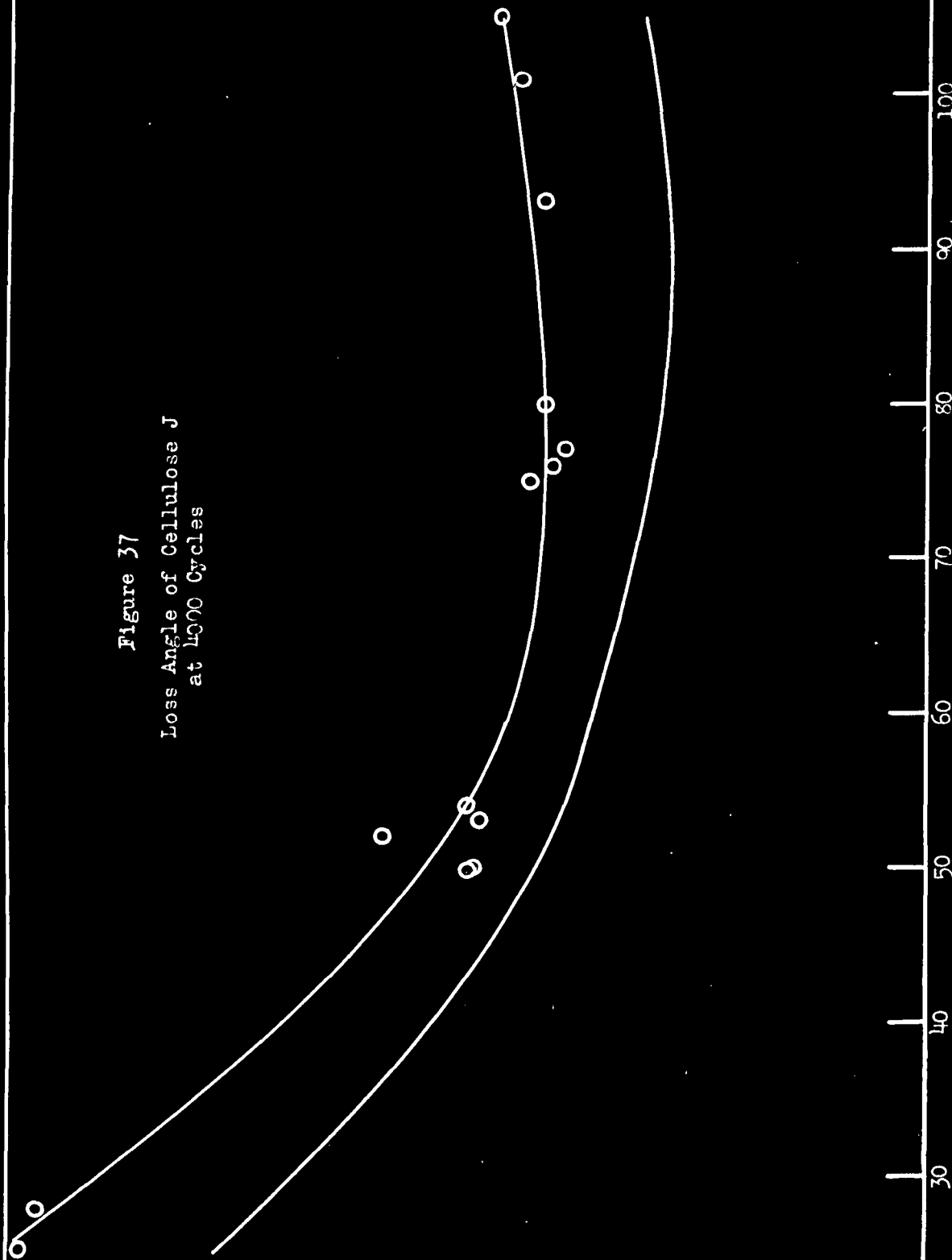
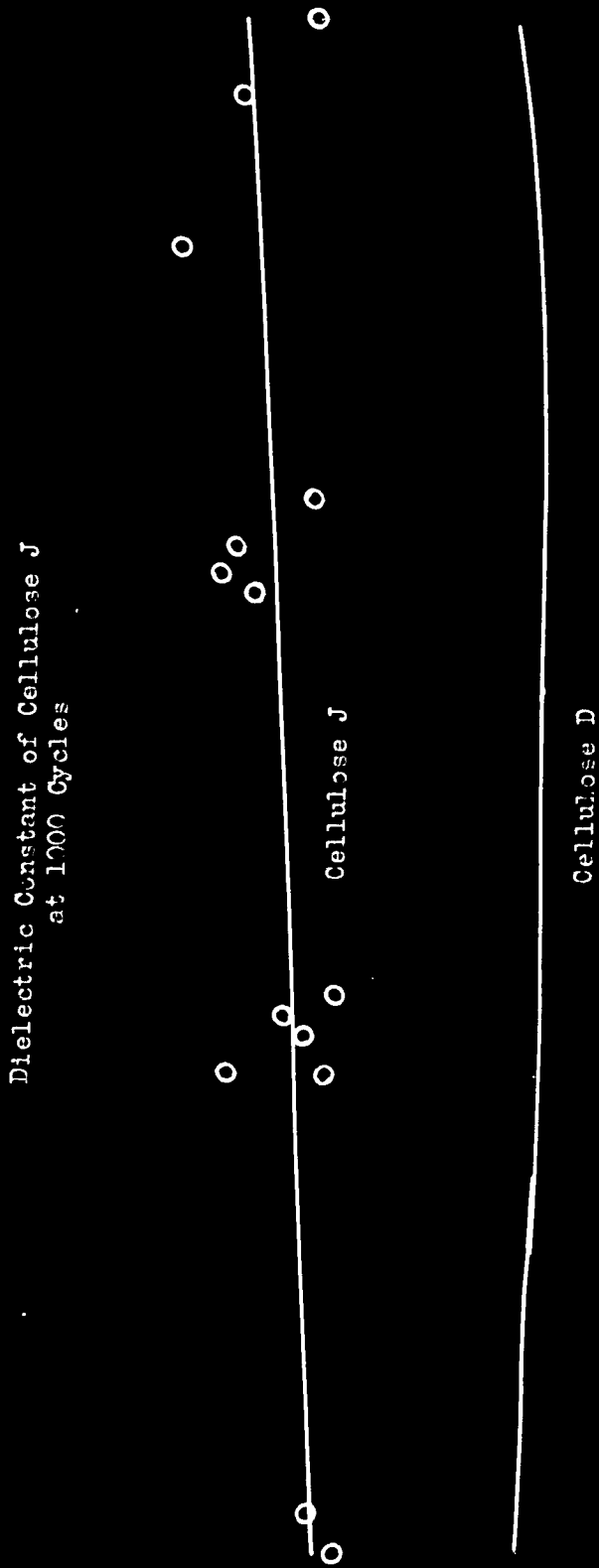


Figure 38
Dielectric Constant of Cellulose J
at 1000 Cycles



cellulose upon heating. Any ethyl alcohol which might be absorbed by the cellulose from the ether would be included in the methoxyl determination, but would be removed by the petroleum ether wash.

A nonpolar hydrocarbon, such as cyclohexane, would not be expected to be retained by cellulose to any degree. However, Staudinger and Föhle (41) found that native cellulose retains 5 to 8% of cyclohexane after drying by this technique. Tests carried out as previously described show that native cellulose absorbs 2 to 4.5% of cyclohexane. Tests upon Cellulose J indicated that no cyclohexane was retained. Evidently, the open structure of the amorphous cellulose permits the cyclohexane to escape.

The presence of a small amount of cyclohexane should have little effect upon the electrical measurements. It is not probable that such a simple nonpolar molecule as cyclohexane would show high dielectric loss. Canwood and Turner (48) reported the dielectric constant of cyclohexane to be 2.0 at 20° C. with a low temperature coefficient. Therefore, the effect of its presence would be to lower the observed dielectric constant of the cellulose.

The validity of these observations was confirmed in the following manner. Several sheets of Cellulose D were dried by the solvent-replacement technique and tested in the usual manner. The experimental data are presented in Table XXXVI. A comparison of the final results with the values for untreated Cellulose D is presented in Table XVIII.

The differences noted are not significant and it may be concluded that the solvent treatment has no effect upon the observed dielectric properties of cellulose.

TABLE XVIII

EFFECT OF SOLVENT TREATMENT UPON THE DIELECTRIC PROPERTIES OF CELLULOSE D

Frequency, Cycles/sec.	Temp., ° C.	$\epsilon'_{0.8 \times 10^3}^a$ Treated	$\epsilon'_{0.8 \times 10^3}^a$ Untreated	$\epsilon_{0.8}$ Treated	$\epsilon_{0.8}$ Untreated
500	97	2.63	2.40	2.53	2.39
1000		2.10	2.04	2.51	2.39
2000		1.95	1.82	2.53	2.39
4000		1.83	1.71	2.52	2.39
500	60	1.63	1.60	2.27	2.35
1000		1.81	1.66	2.27	2.35
2000		1.88	1.80	2.27	2.35
4000		2.30	2.19	2.27	2.35

^a Radians

The auxiliary dielectric constant apparatus was utilized to make a series of determinations upon Celluloses E and J, which had been dried in several ways. The condensed results are presented in Table XIX.

TABLE XIX

DIELECTRIC CONSTANT OF SEVERAL REGENERATED CELLULOSES

Cellulose	Method of Drying	Density, g./cc.	ϵ	$\epsilon_{0.8}$	$\epsilon_{0.8}/2.4$	ϵ/ϵ_N^a
J	solvent	0.368	1.75	3.31	1.38	1.15
J	solvent	0.538	2.30	3.45	1.44	1.26
J	solvent	0.553	2.55	3.90	1.63	1.38
E	air dried	0.518	2.08	3.09	1.29	1.17
J	ether ^b	0.329	1.94	5.20	2.16	1.34
J	ether ^b	0.335	1.85	4.37	1.82	1.27

^a ϵ_N is ϵ of native cellulose sheet at the density of the regenerated cellulose sheet.

^b Dried by solvent replacement through ether.

In all cases a definite increase in the dielectric constant is found. The regenerated cellulose specimens are of substantially lower density than the native celluloses. The results are calculated to standard density by means of the Clausius-Mosotti relation. If this is not applicable to regenerated cellulose, the apparent increase could be a result of the calculation. In Table XIX the dielectric constant of native cellulose has been calculated to the apparent density of each regenerated cellulose sample. Significant differences still exist. Therefore, the observed increases are not caused by an error in calculation.

It is possible, particularly in the auxiliary dielectric constant apparatus with air-dried celluloses, that the specimen does not completely fill the space between the electrodes. However, the effect of this error, as previously shown, would be to lower the apparent dielectric constant.

It has been shown also that the possible presence of a small amount of water in the specimens in the auxiliary apparatus will have no significant effect upon the observed dielectric constant.

Therefore, it may be concluded that the observed phenomena are not a result of the drying techniques, the condition of the test specimen, or the inherent error in the method of calculation.

The regenerated celluloses possess the cellulose hydrate lattice (Cellulose II). It is conceivable that the observed effects are characteristic of this lattice structure. Kubo (49) has reported

that heating Cellulose II in glycerin at an elevated temperature shifts the lattice to Cellulose I (native cellulose). Hermans (13), however, believes that the treatment shifts the lattice to Cellulose IV (very similar to native cellulose) and may cause some crystallization of the amorphous areas. The latter is unlikely in this case, as will be shown below. The dielectric constant of a specimen of solvent-treated Cellulose J was measured in the auxiliary apparatus. The specimen was heated in a glycerin bath at 240° C. for 40 minutes, a procedure adopted from Kubo. The specimen was thoroughly washed with distilled water and retested. The results are presented in Table XX. A specimen of Cellulose II was carried through the same procedure and tested. No change

TABLE XX
EFFECT OF HEATING AT 240° C. IN GLYCERIN
UPON CELLULOSES

Cellulose	$\epsilon_{0.8}$		Moisture regain	
	Before	After	Before, %	After, %
J	3.95	4.3	11.6 ₅	9.6 ₅
D	2.3	2.5	6.1 ₅	--

has been introduced by this treatment. The moisture regain has dropped only 2.0%. A crystallization, which would make the cellulose comparable with native cellulose, would reduce the moisture regain to 6.15% if the lattice was shifted entirely to Cellulose I. Since the treatment had no significant effect upon Cellulose II, the possible retention of glycerin or other extraneous effects are not factors which should be considered. It may be concluded that the lattice form has no significant effect upon the dielectric constant of cellulose.

During the measurements with Cellulose J in the main apparatus, it was noted that the specimens adsorbed diffusion pump oil from the atmosphere even at 0.1 micron pressure, a phenomenon not observed with any other cellulose. The oil could be removed easily with ether. It is possible that the presence of this oil would affect the loss angle determination in two ways. First, it could contribute directly to the dielectric loss and, secondly, it could prevent thorough drying of the specimen. The first is unlikely, since oils generally possess low power factor and the amount present was negligible on a weight basis. The second possibility was discarded for the following reason. In one case the amount adsorbed was definitely higher (because of a loss of vacuum through power failure). No differences were noted in the results of the two experiments, which would be expected if the presence of the oil significantly affected the data.

Whether the surface activity demonstrated by these celluloses is the result of their high amorphous cellulose character or to their high specific surface is not known. They are definitely better absorbants than native cellulose.

It would appear that the cause of the increased loss angle and dielectric constant of these celluloses is due to the increased percentage of amorphous cellulose present. Examination of the loss angle curves shows that the shapes are similar to comparable native cellulose curves. The observed minimum is explained by the previously discussed concept of cellulose as a heterogeneous linear polymer. The increased values, as compared with native cellulose, might be explained

by the fact that more hydroxyl groups are free to oscillate, since they are no longer bound in a crystalline area where the groups are close enough to permit hydrogen bonding. Possibly, portions of chains in the amorphous areas are free to oscillate. The observed increase in dielectric constant may be explained in the same way. A similar increase in dielectric loss and dielectric constant with increasing amorphous content has been observed in the case of another linear polymer (polydecamethylene sebacamide) by Baker and Yager (11).

If these deductions are correct, the dielectric constant of Cellulose L, a cellophane having the same moisture regain as Cellulose J and, presumably, a similar amorphous content, should show a similar increase. The results of two tests are presented in Table XXI.

TABLE XXI
DIELECTRIC CONSTANT OF CELLULOSE L

Specimen	Density, g./cc.	ϵ	$\epsilon_{0.8}$
L-1	1.50	4.27	2.16
L-2	1.43	3.37	1.99

Cellulose L does not show the expected increase in dielectric constant values. It had been stored in formaldehyde solution previous to drying. Formaldehyde is known to cause cross linkages in cellulose and it is possible that these linkages could cause a lowered dielectric constant. Stoops (12) found a dielectric constant of 7.9 for cellophane at 1000 cycles at 65° C. If a density of 1.5 g./cc. is assumed, a value of 3.0 at standard density may be calculated, definitely higher than that of native cellulose.

The regenerated celluloses, whether air dried or treated with solvents, showed thermoplastic properties. Under moderate pressures, they flowed and suffered substantial increases in apparent density. Native cellulose, even when pressed at much higher pressures, did not show a similar behavior.

Investigation disclosed that this pressing caused definite changes in the observed electrical properties. A specimen of Cellulose F was pressed at 2000 p.s.i. and 110° C. for ten minutes and tested in the usual manner. The experimental data and results are presented in Table XXXVII. The loss angle values at standard density at 1000 cycles are presented in Figure 39, together with similar curves for native cellulose and unpressed regenerated cellulose. Similar results were found at other frequencies. The loss angle values at lower temperatures are similar to those of native cellulose, but they rise considerably at higher temperatures. This rise may be accounted for, at least partially, by the presence of carboxyl groups and the very high ash content of this cellulose (see Table X). The dielectric constant values are similar to those of native cellulose. The hot pressing caused a change in the observed dielectric properties.

This effect, in the case of dielectric constant, was confirmed by studying several of the celluloses in the auxiliary apparatus, pressing the specimens as described, and measuring the dielectric constant of the pressed specimen. The results of several experiments are reported in Table XXII. The pressing in each case reduced the calculated dielectric constant to values similar to those for native cellulose.

Loss Angle of Cellulose F (Hot
Pressed) at 1000 Cycles

○ Cellulose F

Cellulose J

Native Cellulose

18

30 40 50 60 70 80 90 100

TABLE XXII

DIELECTRIC CONSTANT OF PRESSED
REGENERATED CELLULOSES

Cellulose	Description	ϵ	Density, g./cc.	$\epsilon_{0.8}$	Moisture regain at 54% R.H., %
J	Solvent dried, unpressed	1.75	0.368	3.31	11.6
J	Solvent dried, pressed	2.51	0.83	2.44	10.3
F	Water dried, unpressed	2.08	0.518	3.09	10.7 ₅
F	Water dried, pressed	1.86	0.68	2.07	10.1
J	Solvent dried, glycerin heated, unpressed	2.57	0.552	4.00	9.6
J	Solvent dried, glycerin heated, pressed	4.03	1.19	2.52	--
F	Air dried, pressed	2.54	0.978	2.15	10.0

It is possible that this treatment caused a reversion of amorphous to crystalline areas. This would account for the changes if the amorphous areas are responsible for the increase in the loss angle and dielectric constant. Cold pressing of Cellulose J induced changes in the observed dielectric constant in the same direction, shown by the data in Table XXIII.

TABLE XXIII

DIELECTRIC CONSTANT OF COLD-PRESSED
SOLVENT-DRIED CELLULOSE J

Treatment	ϵ	Density, g./cc.	$\epsilon_{0.8}$	Moisture regain at 54% R.H., %
Unpressed	3.39	0.537	3.57	11.6
Pressed 15 sec. at 2000 p.s.i.	2.67	0.712	3.01	11.1
Pressed 10 min. at 2000 p.s.i.	2.74	0.785	2.79	10.8 ₅

Even the short duration of the first pressing significantly reduced both the dielectric constant and the moisture regain. Further pressing, although it substantially increased the density, lowered these values only slightly.

The calculated dielectric constant values obtained in both apparatus are presented as a function of moisture regain in Figure 40. The mean value from Figure 38 at 65° C. has been taken as the value for the main apparatus determinations. A direct relation between the two quantities is clearly indicated. If Hermans (13) is correct in correlating moisture regain and amorphous content, the dielectric constant may be regarded as a measure of this property.

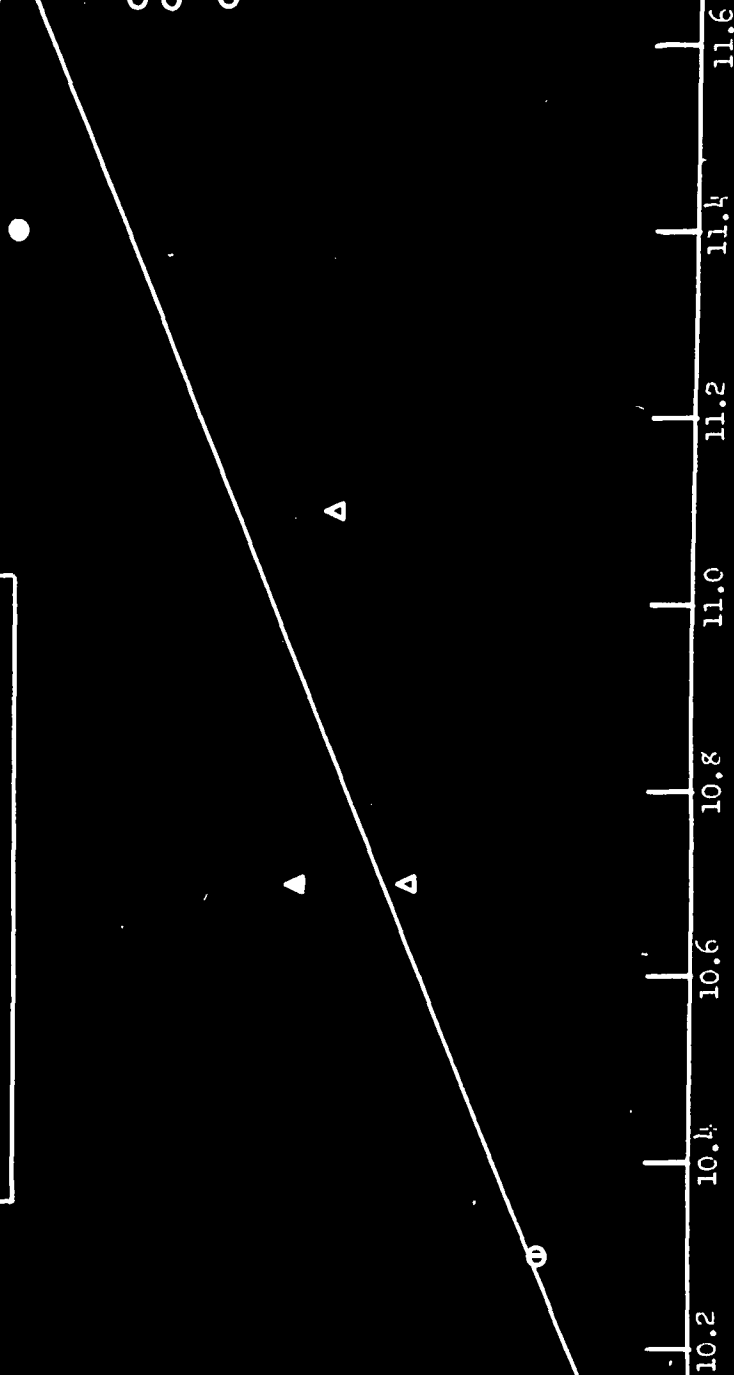
However, the data obtained with Cellulose L (cellophane) are contradictory since, on the basis of its moisture regain value, it is amorphous and yet it has a low dielectric constant.

The regenerated celluloses had, in general, a low density, whereas the cellophane approached the density of pure cellulose. It is possible that both the dielectric properties and the moisture regain values are related in some way to the apparent density differences, entirely apart from the differences in density between crystalline and amorphous cellulose reported by Hermans. The regenerated celluloses are probably comparable to a sponge, filled with small voids. This concept readily explains the low density, the ease of compressibility, and the escape of cyclohexane. If the surfaces of these voids contribute to the dielectric constant and dielectric loss by the presence of free hydroxyl groups, as discussed before, the observed differences can be

Figure 40

Dielectric Constant of Regenerated
Cellulose as a Function
of Moisture Regain

- J (Unpressed).
- J (Main Apparatus).
- ⊙ E, F, J (Hot Pressed).
- △ J (Cold Pressed).
- ▲ E (Unpressed).



Moisture Regain at 50% P. H.

accounted for. Portions of chains in the amorphous areas would be free to move in the field and contribute to the dielectric loss. In a high-density cellulose, such as cellophane, the relatively close packing would prevent the oscillations of chains and, perhaps, the freedom of hydroxyl groups. The swelling action of water would explain the high moisture regain values of this cellulose. However, this explanation would not account for the lowered moisture regains observed upon pressing, since presumably water would still be able to penetrate these areas as in the case of cellophane. The moisture regain test has not been applied over wide humidity ranges and its exact meaning is not clear. The possibilities of interference in the case of cellophane has been pointed out. In view of these facts, no definite conclusions can be drawn.

However, this investigation has revealed a possible relation between the regularity of the polymeric structure of cellulose and its dielectric properties. Further investigation seems warranted.

SUMMARY AND CONCLUSIONS

A test capacitor system has been constructed for use with the Schering bridge of The Institute of Paper Chemistry, incorporating several desirable features. With this apparatus, measurements of loss angle and dielectric constant can be made at temperatures from 25 to 105° C. in a vacuum as low as 0.1 micron. Considerable pressure can be exerted upon the specimen during testing for the purpose of eliminating the error resulting from incomplete filling of the test capacitor.

An apparatus for rapid and reasonably accurate measurement of dielectric constant has been constructed.

The applicability of the Clausius-Mosotti relation to native cellulose has been confirmed.

The loss angle and dielectric constant of several native celluloses have been measured at 500, 1000, 2000, and 4000 cycles per second at temperatures from 25 to 105° C. No significant differences were noted between various native celluloses. Loss angle-temperature curves exhibited a minimum, the temperature of the minimum increasing with increasing frequency. Dielectric constant-temperature curves showed a slight minimum and rose slightly at higher temperatures. No frequency effect was noted. These observations may be adequately explained by the present theory if cellulose is regarded as a heterogeneous linear polymer with many polar groups.

Similar measurements upon degraded native celluloses confirmed these relationships. The presence of carboxyl groups caused an increase

in the dielectric loss at higher temperatures, whereas carbonyl groups had little effect. The dielectric constant was not affected.

The loss angle and dielectric constants of specially prepared regenerated celluloses were higher than the corresponding values for native cellulose at all frequencies. The dielectric constant of cellophane, however, was comparable with that of native cellulose. Pressing of regenerated cellulose specimens at moderate pressures caused a lowering of these values. A possible correlation between the amorphous cellulose content and the dielectric properties was found, but the evidence is conflicting and no definite conclusions can be drawn.

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APPENDIX

TABLE XXIV

EFFECT OF ELECTRODE PRESSURE UPON DIELECTRIC
PROPERTIES OF CELLULOSE D

All values at 1000 cycles

Time, hr.	Temp., ° C.	Vacuum ^a	Pressure ^b	$\epsilon_{cor.}^c$	$\frac{C_0}{\mu\mu f}$	$\frac{C}{T^2 f}$ $\mu\mu f$	ΔC_d	ϵ	$\epsilon' \times 10^3$, radians	d., r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
14	104	0.5	265	48.3	899	457	12.9	2.45	1.82	0.885	2.26	1.78
			520	49.0	899	487	14.9	2.57	1.97	0.898	2.32	1.94
			800	50.7		510	17.6	2.60	2.22	0.948	2.25	2.16
			930	52.6		521	18.4	2.56	2.28	0.984	2.16	2.12
20	105	0.5	265	49.8	899	474	15.8	2.46	2.15	0.932	2.18	2.08
			520	50.4		499	17.2	2.57	2.22	0.941	2.24	2.15
			800	52.0		516	18.6	2.57	2.32	0.972	2.18	2.25
			930	51.9		522	19.7	2.61	2.22	0.970	2.21	2.16
37	77	0.5	265	50.6	899	470	9.8	2.40	1.34	0.945	2.11	1.24
			520	50.0		488	11.5	2.53	1.52	0.935	2.23	1.47
			800	50.3		503	12.5	2.59	1.60	0.940	2.26	1.56
			930	50.2		519	12.8	2.68	1.59	0.938	2.32	1.56
44	79	0.5	265	53.0	899	470	11.0	2.30	1.51	0.991	1.97	1.42
			520	53.0		488	11.8	2.39	1.56	0.991	2.03	1.49
			800	50.0		504	13.3	2.61	1.70	0.935	2.28	1.66
			930	49.5		510	13.1	2.66	1.65	0.925	2.34	1.63
60	50	9.0	265	48.2	725	463	15.4	2.49	1.73	0.901	2.25	1.70
			520	47.1	725	481	15.9	2.64	1.71	0.880	2.43	1.69
			800	47.5		495	17.5	2.70	1.83	0.889	2.45	1.82
			930	48.9		502	18.2	2.66	1.88	0.933	2.37	1.81
66	50	9.0	265	47.5	725	471	14.9	2.57	1.64	0.889	2.45	1.50
			520	48.4		483	16.4	2.58	1.76	0.905	2.32	1.73
			800	47.8		495	16.8	2.68	1.76	0.894	2.42	1.75
			930	48.6		503	17.4	2.68	1.80	0.910	2.39	1.77
87	25	200+	265	46.5	725	458	24.3	2.55	2.54	0.869	2.36	2.53
			520	47.0		477	26.8	2.63	2.96	0.879	2.41	2.93
			800	47.0		489	30.3	2.69	3.26	0.879	2.47	3.23
			930	46.9		494	30.3	2.73	3.23	0.876	2.49	3.21

For footnotes, see Table XXV.

TABLE XXV

DIELECTRIC PROPERTIES OF HIGH DENSITY CELLULOSE I

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\rho_{\text{cor.}}$ ^c	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_1 ^d	ϵ	$\epsilon' \times 10^3$, radians	$\frac{d...}{\epsilon \cdot \text{cc.}}$	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
22	105	0.1	500	61.8	1105	883	--	3.70	--	1.125	2.50	--
44	106			62.3		886	--	3.69	--	1.132	2.50	--
68	50			63.5		849	46.0	3.46	2.15	1.155	2.37	2.18
22	105		1000	61.8	1105	885	33.9	3.71	3.04	1.125	2.50	3.20
44	106			62.3		886	30.9	3.69	2.76	1.132	2.50	2.88
68	50			63.5		849	22.5	3.46	2.10	1.155	2.37	2.13
22	105		2000	62.5	1105	885	13.6	3.67	2.44	1.140	2.47	2.55
44	106			62.3		881	12.9	3.66	2.30	1.132	2.48	2.40
68	50			63.5		849	14.2	3.46	2.65	1.155	2.37	2.68
22	105		4000	62.5	1105	885	6.0	3.67	2.16	1.138	2.47	2.25
44	106			62.3		882	6.0	3.67	2.15	1.132	2.49	2.23
68	50			63.5		846	8.2	3.45	3.06	1.155	2.36	3.09

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVI

CELLULOSE D DIELECTRIC PROPERTIES AT ROOM TEMPERATURE

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}^c$	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_d	ϵ	$\epsilon' \times 10^3$, radians	d., F./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
16	27	180	500	48.9	1078	491	52.1	2.60	4.12	0.916	2.34	4.05
24				48.9	1077	489	48.5	2.59	3.83	0.915	2.30	3.77
36		250		48.9	980	494	49.0	2.62	3.48	0.916	2.33	3.42
52		250		48.8	980	488	49.4	2.59	3.57	0.915	2.30	3.51
120		250		48.0	694	491	61.1	2.65	3.35	0.903	2.37	3.32
136		0.1		48.0	693	491	52.5	2.65	2.66	0.903	2.37	2.63
154		0.1		47.7	693	491	45.0	2.67	2.28	0.896	2.41	2.25
166		0.1		47.7	693	489	44.6	2.65	2.26	0.896	2.39	2.23
180		0.1		48.0	693	490	44.7	2.64	2.26	0.898	2.39	2.23
16	27	180	1000	48.9	703	492	44.8	2.61	4.65	0.916	2.33	4.53
24				48.9	1078	489	25.7	2.59	4.05	0.915	2.30	3.99
36		250		48.9	710	490	39.4	2.60	4.10	0.916	2.30	4.04
52				49.1	981	491	26.4	2.59	3.79	0.922	2.29	3.71
120				48.0	694	490	34.3	2.64	3.48	0.903	2.37	3.43
136		0.1		48.0	693	489	29.5	2.64	2.99	0.903	2.37	2.95
154		0.1		47.7	693	490	26.9	2.66	2.73	0.896	2.40	2.70
166		0.1		48.0	693	490	26.1	2.65	2.65	0.903	2.37	2.63
180		0.1		47.7	693	491	25.1	2.66	2.54	0.894	2.40	2.53

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_d in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVI (Cont.)

CELLULOSE D. DIELECTRIC PROPERTIES AT ROOM TEMPERATURE

Time, hr.	Temp., °C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$ ^c	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_d	ϵ	$\epsilon' \times 10^3$, radians	d., r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
16	27	180	2000	48.8	704	489	24.1	2.60	4.97	0.914	2.32	4.86
24				48.9	710	490	21.8	2.60	4.52	0.915	2.30	4.49
36		250		48.9	710	489	21.3	2.60	4.43	0.916	2.30	4.37
52				48.9	981	490	14.5	2.60	4.14	0.916	2.30	4.08
120				48.2	694	490	19.5	2.63	3.96	0.905	2.36	3.90
136		0.1		48.1	693	489	17.3	2.63	3.51	0.904	2.36	3.46
154				47.7	693	489	16.5	2.65	3.34	0.896	2.40	3.29
166				47.7	693	491	15.2	2.67	3.07	0.896	2.40	3.05
180				47.7	693	489	15.8	2.65	3.20	0.894	2.40	3.16
16	27	180	4000	48.8	704	489	14.0	2.60	5.76	0.914	2.32	5.64
24				48.9	710	491	12.8	2.60	5.30	0.915	2.30	5.22
36		250		48.9	710	487	13.0	2.58	5.40	0.916	2.34	5.20
52				48.9	693	491	12.5	2.60	5.05	0.916	2.30	4.98
120				48.2	694	489	11.6	2.63	4.71	0.905	2.36	4.65
136		0.1		48.1	693	488	10.3	2.63	4.16	0.904	2.36	4.10
154				47.7	693	488	10.2	2.64	4.14	0.897	2.39	4.07
166				48.2	693	490	9.9	2.63	4.00	0.905	2.36	3.95
180				47.0	693	488	10.0	2.69	4.07	0.880	2.46	4.04

a Microns

b Cycles per second

c Specimen thickness in reciprocal cm.

d ΔC_d in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVII
DIELECTRIC PROPERTIES OF CHYLLOSE A

Time. hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_1	d	ϵ	$\epsilon' \times 10^3$, radians	d., K./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
22	106	0.1	500	79.2	970	756	63.5	2.47	2.47	2.91	0.735	2.67	2.93
48	56	3.0		82.5		726	33.1	2.28	2.28	1.58	0.765	2.36	1.60
64	26	200		78.7		714	52.6	2.35	2.35	2.57	0.730	2.55	2.59
80	53	200		78.7		729	33.5	2.40	2.40	1.64	0.730	2.61	1.66
94	79	3.0		78.0		740	35.1	2.45	2.45	1.65	0.724	2.68	1.67
110	92	6.0		77.8		759	49.5	2.52	2.52	2.27	0.721	2.75	2.31
130	102	25.0		78.0		759	55.8	2.52	2.52	2.56	0.723	2.74	2.60
22	106	0.1	1000	79.5	970	757	25.4	2.47	2.47	2.33	0.737	2.67	2.34
48	56	3.0		82.5		725	17.8	2.28	2.28	1.70	0.765	2.36	1.72
64	26	200		79.1		714	30.5	2.33	2.33	2.98	0.734	2.52	3.00
80	53	200		78.4		727	18.0	2.40	2.40	1.72	0.726	2.62	1.73
94	79	3.0		78.5		740	16.3	2.41	2.41	1.54	0.728	2.63	1.55
110	92	6.0		76.1		758	21.4	2.58	2.58	1.96	0.705	2.93	1.96
130	102	25.0		78.2		761	23.4	2.52	2.52	2.13	0.725	2.77	2.14
22	106	0.1	2000	79.8	970	762	11.2	2.47	2.47	2.04	0.740	2.66	2.05
48	56	3.0		82.7		725	10.2	2.27	2.27	1.95	0.767	2.36	1.96
64	26	200		79.4		712	18.6	2.33	2.33	3.63	0.736	2.50	3.68
80	53	200		78.5		724	10.2	2.38	2.38	1.97	0.729	2.59	1.98
94	79	3.0		78.6		742	8.0	2.44	2.44	1.49	0.729	2.66	1.57
110	92	6.0		75.8		755	9.8	2.56	2.56	1.81	0.703	2.92	1.81
130	102	25.0		78.2		762	10.0	2.53	2.53	1.83	0.725	2.77	1.85
22	106	0.1	4000	80.0	970	767	5.3	2.48	2.48	1.92	0.742	2.65	1.93
48	56	3.0		82.6		723	6.2	2.27	2.27	2.36	0.766	2.35	2.38
64	26	200		79.1		711	11.9	2.33	2.33	4.65	0.735	2.51	4.70
80	53	200		78.4		724	6.4	2.39	2.39	2.44	0.726	2.61	2.46
94	79	3.0		78.5		742	4.5	2.45	2.45	1.71	0.728	2.67	1.73
110	92	6.0		77.0		755	4.5	2.54	2.54	1.64	0.714	2.85	1.64
130	102	25.0		78.2		764	5.1	2.53	2.53	1.85	0.725	2.77	1.87

^a Microns

^b Cycles per second

^c Specimen thickness in reciprocal cm.

^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVIII
DIELECTRIC PROPERTIES OF CELLULOSE A

Time, hr.	Temp., °C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}^c$	$\frac{C_2}{\mu f.}$	$\frac{C_1}{\mu f.}$	$\Delta \epsilon_d$	ϵ	$\epsilon' \times 10^3$, radians	d., p./cc.	$\epsilon_{0.8}$	$\epsilon' \times 10^3$, radians
19	103	0.1	500	68.6	970	658	56.3	2.48	2.97	0.776	2.55	2.98
31	77			68.4		639	31.5	2.42	1.72	0.773	2.49	1.73
43	74			68.7		640	31.3	2.41	1.70	0.777	2.47	1.71
53	78			68.5		640	32.2	2.41	1.75	0.774	2.49	1.76
63	79			69.0		643	32.5	2.41	1.76	0.780	2.46	1.76
84	26			68.7		619	42.2	2.33	2.37	0.776	2.40	2.37
96	26			68.8		620	42.1	2.33	2.36	0.777	2.40	2.37
110	25			68.8		620	43.2	2.33	2.43	0.777	2.40	2.43
127	48			68.7		630	29.9	2.37	1.65	0.791	2.39	1.65
138	50			69.0		629	30.3	2.36	1.68	0.794	2.38	1.67
153	49			68.9		627	29.8	2.36	1.65	0.792	2.38	1.65
177	79			66.5		641	32.5	2.50	1.75	0.766	2.50	1.76
19	103	0.1	1000	68.1	970	656	22.9	2.49	2.42	0.770	2.58	2.43
31	77			67.8		639	15.0	2.43	1.64	0.766	2.52	1.65
43	74			68.7		637	14.9	2.40	1.63	0.777	2.46	1.63
53	78			68.9		640	17.4	2.41	1.89	0.779	2.47	1.90
63	79			68.9		642	15.0	2.41	1.62	0.779	2.47	1.63
84	26			68.7		619	25.3	2.33	2.84	0.776	2.40	2.84
96	26			68.7		619	25.7	2.33	2.97	0.776	2.40	2.98
110	25			68.7		618	25.5	2.33	2.86	0.776	2.40	2.87
127	48			68.7		629	16.2	2.37	1.79	0.791	2.39	1.79
138	50			69.1		629	16.1	2.35	1.78	0.795	2.36	1.78
153	49			69.1		627	16.2	2.35	1.79	0.796	2.36	1.80
177	79			66.5		641	15.0	2.49	1.63	0.766	2.59	1.64

a Microns

b Cycles per second

c Specimen thickness in reciprocal cm.

d $\Delta \epsilon_d$ in dial divisions. Multiply by 1.14 to obtain value in $\mu f.$

TABLE XVIII (Cont.)

DIELECTRIC PROPERTIES OF OXALIDE-A

Time, hr.	Temp., °C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$ ^c	$\frac{C}{\mu\mu f}$	ΔQ_d ^d	ϵ	$\epsilon' \times 10^3$, radians	$\frac{d..}{\epsilon./cc.}$	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
19	103	0.1	2000	68.1	970	9.8	2.47	2.09	0.770	2.55	2.10
31	77			67.9		7.3	2.44	1.59	0.767	2.53	1.59
43	74			68.7		7.6	2.41	1.65	0.777	2.47	1.66
53	78			69.2		7.9	2.40	1.72	0.782	2.48	1.73
63	79			68.6		7.5	2.41	1.63	0.775	2.48	1.64
84	26			68.7		15.9	2.33	3.56	0.776	2.40	3.57
96	26			68.7		16.0	2.33	3.61	0.776	2.40	3.62
110	25			69.0		16.0	2.32	3.61	0.780	2.39	3.62
127	48			68.6		9.1	2.37	2.01	0.790	2.39	2.02
138	50			69.8		9.3	2.33	2.06	0.803	2.33	2.06
153	49			68.9		9.5	2.36	2.10	0.792	2.38	2.10
177	79			66.5		7.2	2.49	1.56	0.766	2.59	1.57
19	103	0.1	4000	69.0	970	4.55	2.45	1.94	0.780	2.53	1.95
31	77			67.9		4.1	2.44	1.79	0.767	2.53	1.80
43	74			68.7		4.3	2.40	1.87	0.777	2.46	1.88
53	78			69.2		4.95	2.40	2.15	0.782	2.45	2.16
63	79			68.1		4.1	2.43	1.74	0.770	2.51	1.75
84	26			68.7		10.7	2.32	4.82	0.776	2.40	4.83
96	26			68.6		10.7	2.33	4.82	0.775	2.40	4.83
110	25			69.0		10.7	2.31	4.89	0.780	2.37	4.90
127	48			68.5		6.1	2.37	2.68	0.786	2.40	2.69
138	50			69.7		--	2.33	--	0.803	2.33	2.06
153	49			69.0		6.0	2.35	2.66	0.794	2.37	2.66
177	79			66.6		4.25	2.49	1.83	0.766	2.59	1.84

^a Microns
^b Cycles per second
^c Specimen thickness in reciprocal cm.
^d ΔQ_d in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXIX

DIELECTRIC PROPERTIES OF CELLULOSE D

Time, hr.	Temp., °C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$ ^c	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_1 ^d	ϵ	$\epsilon' \times 10^3$, radians	$d..$ p./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
34	60	0.5	500	50.3	704	520	35.2	2.68	1.71	0.945	2.30	1.66
46	26	1.6		48.6	704	509	45.1	2.71	2.23	0.911	2.39	2.21
56	26	1.6		49.5	704	509	47.2	2.66	2.34	0.93	2.32	2.30
68	66	0.5		47.7		520	36.2	2.81	1.75	0.896	2.51	1.74
82	105	0.5		54.3		537	61.5	2.57	2.88	1.021	2.10	2.86
100	63	100		51.6		522	35.4	2.62	1.71	0.97	2.22	1.66
120	27	225		48.1		510	53.4	2.74	2.64	0.904	2.43	2.62
146	27	200		49.5		511	53.1	2.67	2.62	0.93	2.33	2.58
166	63	118		51.9		522	34.6	2.61	1.67	0.975	2.20	1.62
186	105	68		53.1		542	60.8	2.64	2.82	0.996	2.19	2.72
189	105	65		53.2		541	58.4	2.63	2.72	0.998	2.19	2.63
18	105	0.5	1000	53.2	704	543	26.1	2.64	2.41	1.00	2.18	2.33
34	60	0.5		50.0	704	520	18.4	2.70	1.78	0.94	2.33	1.75
46	26	1.6		48.8	704	510	27.6	2.70	2.73	0.917	2.39	2.69
56	26	1.6		49.0		509	28.8	2.69	2.85	0.92	2.36	2.54
68	66	0.5		49.7		524	17.8	2.73	1.71	0.933	2.36	1.68
82	105	0.5		52.5		537	27.3	2.65	2.55	0.986	2.22	2.45
100	63	100		51.3		522	17.8	2.64	1.72	0.964	2.24	1.68
120	27	225		48.6		510	30.7	2.71	3.04	0.914	2.39	3.01
146	27	200		49.0		510	53.1	2.69	3.11	0.92	2.36	3.08
166	63	118		51.5		522	34.6	2.63	1.71	0.966	2.24	1.67
186	105	68		52.5		541	60.8	2.67	2.45	0.986	2.22	2.39
189	105	65		53.9		540	58.4	2.60	2.34	1.01	2.15	2.23

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXIX (Cont.)

PIEZOELECTRIC PROPERTIES OF CULLINUM D

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C_p}{\mu\mu f}$	$\frac{C_p}{\mu\mu f}$	ΔQ_d	ϵ	$\epsilon' \times 10^3$, radians	$d_{..}$ r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
18	105	0.5	2000	50.5	911	534	9.5	2.74	2.32	0.948	2.35	2.28
34	60	0.5		45.3	704	520	9.3	2.73	1.81	0.925	2.39	1.79
46	26	1.6		43.8	704	508	16.1	2.70	3.19	0.917	2.39	3.01
56	26	1.6		48.5		508	17.1	2.71	3.39	0.91	2.42	3.33
68	66	0.5		49.2		521	9.8	2.74	1.90	0.925	2.39	1.87
82	105	0.5		53.1		540	12.1	2.64	2.26	0.997	2.19	2.18
100	63	100		50.4		522	9.8	2.69	1.89	0.946	2.31	1.86
120	27	225		48.4		509	18.5	2.72	3.66	0.91	2.40	3.64
146	27	200		43.5		509	18.8	2.66	3.72	0.93	2.33	3.65
166	63	118		50.9		522	9.05	2.65	1.75	0.956	2.26	1.70
186	105	68		53.2		540	10.8	2.63	2.02	0.998	2.19	1.94
189	105	65		53.5		542	10.7	2.63	2.00	1.00	2.17	1.93
18	105	0.5	4000	51.0	704	535	5.4	2.72	2.04	0.968	2.19	2.08
34	60	0.5		48.6	704	516	5.7	2.75	2.22	0.914	2.42	2.21
46	26	1.6		48.6	704	509	10.4	2.71	4.11	0.911	2.39	4.07
56	26	1.6		48.5		526	11.1	2.70	4.41	0.91	2.40	4.36
68	66	0.5		49.4		521	5.3	2.72	2.04	0.928	2.37	2.01
82	105	0.5		54.5		537	5.2	2.56	1.95	1.024	2.10	1.85
100	63	100		48.7		521	5.8	2.77	2.24	0.915	2.43	2.22
120	27	225		48.4		508	11.5	2.72	4.57	0.91	2.40	4.56
146	27	200		49.0		507	11.7	2.68	4.64	0.92	2.35	4.61
166	63	118		50.9		522	5.3	2.65	2.03	0.956	2.26	1.99
186	105	68		53.2		539	4.9	2.63	1.84	0.998	2.19	1.76
189	105	65		53.5		541	4.7	2.62	1.75	1.00	2.16	1.70

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔQ_d in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXX
DIELECTRIC PROPERTIES OF CELLULOSE D

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C}{\mu\mu f}$	$\frac{C}{\mu\mu f}$	ΔQ_d	ϵ	$\epsilon' \times 10^3$, radians	d., r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
18 26 44	54 55 80	0.2	500	43.5 48.0 49.0	693	504 502 515	35.4 35.7 41.6	2.63 2.71 2.72	1.72 1.77 2.00	0.926 0.899 0.918	2.31 2.43 2.39	1.71 1.76 1.99
18 26 44	54 55 80	0.2	1000	49.5 48.5 48.3	693	504 502 514	18.3 18.0 19.1	2.63 2.68 2.75	1.77 1.78 1.85	0.926 0.908 0.904	2.31 2.39 2.46	1.74 1.76 1.83
18 26 44	54 55 80	0.2	2000	48.5 47.6 48.6	693	502 503 515	10.3 9.9 9.0	2.68 2.73 2.74	2.05 1.96 1.74	0.908 0.891 0.910	2.39 2.46 2.43	2.02 1.95 1.72
18 26 44	54 55 80	0.2 0.2	4000	49.5 48.0 48.8	693	501 503 515	5.9 5.3 5.0	2.61 2.71 2.73	2.34 2.09 1.93	0.934 0.899 0.913	2.29 2.43 2.41	2.29 2.08 1.92
17 37 63	112 79 33	0.2 0.5 200	500	52.7 50.3 49.0	1020 768	550 530 515	53.0 33.0 48.6	2.70 2.73 2.72	3.52 1.72 2.61	0.971 0.925 0.903	2.27 2.39 2.43	3.45 1.70 2.58
17 37 63	112 79 33	0.2 0.5 200	1000	52.7 50.4 49.1	693 768	550 530 515	30.6 15.6 21.3	2.70 2.73 2.71	2.76 1.61 2.93	0.971 0.927 0.905	2.27 2.39 2.42	2.70 1.60 2.90
17 37 63	112 79 33	0.2 0.5 200	2000	52.4 50.8 49.0	693 768	544 531 514	11.5 7.8 15.9	2.69 2.71 2.71	2.11 1.62 3.41	0.966 0.931 0.903	2.28 2.36 2.41	2.06 1.60 3.38
17 37 63	112 79 33	0.2 0.5 200	4000	51.9 51.3 48.7	693 768	542 531 513	5.1 4.55 9.9	2.71 2.68 2.70	1.37 1.96 4.28	0.956 0.945 0.905	2.30 2.33 2.41	1.84 1.90 4.24

^a Microns ^c Specimen thickness in reciprocal cm.

^b Cycles per second ^d ΔQ_d in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXI

DIELECTRIC PROPERTIES OF CELLULOSE K (RAPID)

Time, hr.	Temp., ° C.	vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C}{\mu\mu f}$	$\frac{C}{\mu\mu f}$	δ	ϵ	$\epsilon' \times 10^3$, radians	d., g./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
20	102	0.1	500	78.6	1045	744	57.6	2.45	2.95	0.755	2.58	2.96
35	77	0.1		81.4		725	32.2	2.32	1.67	0.78	2.37	1.66
53	54	0.2		86.7		717	27.2	2.15	1.43	0.831	2.10	1.43
70	27	0.2		84.3		708	36.0	2.17	1.85	0.808	2.15	1.86
20	102	0.1	1000	78.4	1045	743	23.4	2.46	2.37	0.752	2.53	2.44
35	77	0.1		82.2		728	15.1	2.29	1.55	0.787	2.33	1.55
53	54	0.2		86.7		717	14.4	2.15	1.51	0.831	2.10	1.49
70	27	0.2		84.1		708	20.9	2.18	2.21	0.806	2.16	2.22
20	102	0.1	2000	78.3	1045	738	9.6	2.44	1.95	0.750	2.58	1.97
35	77	0.1		82.3		728	7.1	2.29	1.47	0.788	2.33	1.47
53	54	0.2		86.7		715	8.3	2.14	1.73	0.831	2.09	1.71
70	27	0.2		84.3		707	12.9	2.17	2.74	0.808	2.15	2.74
20	102	0.1	4000	77.8	1045	735	4.5	2.45	1.84	0.746	2.60	1.86
35	77	0.1		82.5		727	3.9	2.28	1.60	0.791	2.30	1.61
53	54	0.2		86.7		714	4.6	2.13	1.95	0.831	2.09	1.93
70	27	0.2		84.1		706	8.4	2.17	3.56	0.806	2.15	3.56

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d δC_0 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXII

DIELECTRIC PROPERTIES OF OXYCELLULOSE G

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$ ^c	$\frac{C_0}{\mu f}$	$\frac{C_0}{\mu f}$	ΔC_0	d	ϵ	$\epsilon' \times 10^3$, radians	d., r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
16	98	0.1	500	53.8	1045	507	48.9	2.44	3.60	0.855	2.29	2.29	3.60
36	48	0.1		54.7		488	23.7	2.31	1.82	0.87	2.17	2.17	1.78
56	28	0.1		53.6		482	30.6	2.33	2.38	0.852	2.22	2.22	2.31
16	98	0.1	1000	53.8	1045	509	18.2	2.45	2.66	0.855	2.30	2.30	2.65
36	48	0.1		54.7		488	13.5	2.31	2.08	0.87	2.17	2.17	2.03
56	28	0.1		53.6		481	18.7	2.32	2.91	0.852	2.21	2.21	2.77
16	98	0.1	2000	53.8	1045	511	7.9	2.46	2.32	0.855	2.52	2.52	2.30
36	48	0.1		54.7		488	7.55	2.30	2.32	0.87	2.15	2.15	2.27
56	28	0.1		53.6		481	14.1	2.32	4.40	0.852	2.21	2.21	4.38
16	98	0.1	4000	53.8	1045	512	3.6	2.47	2.11	0.855	2.32	2.32	2.10
36	48	0.1		54.7		485	4.65	2.30	2.87	0.87	2.15	2.15	2.73
56	28	0.1		53.6		480	7.25	2.31	4.54	0.852	2.20	2.20	4.48
47	87	200	500	43.4	1045	428	25.8	2.56	2.26	0.820	2.50	2.50	2.26
67	59	200		44.8		414	19.5	2.39	1.81	0.848	2.28	2.28	1.79
47	87	200	1000	43.4	1045	427	11.6	2.54	2.03	0.820	2.48	2.48	2.03
67	59	200		44.8		414	10.1	2.39	1.84	0.848	2.28	2.28	1.82
47	87	200	2000	43.4	1045	426	5.7	2.53	2.00	0.820	2.48	2.48	2.00
67	59	200		44.8		414	5.5	2.39	1.99	0.848	2.28	2.28	1.97
47	87	200	4000	43.4	1045	423	2.65	2.52	1.87	0.820	2.47	2.47	1.87
67	59	200		44.8		414	3.4	2.39	2.46	0.848	2.28	2.28	2.39

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d $\epsilon_{0.8}$ in die divisions. Multiply by 1.14 to obtain value in μf

TABLE XXXIII
DIELECTRIC PROPERTIES OF CELLULOSE B

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C}{\mu\text{f}}$	$\frac{C}{\mu\text{f}}$	ΔC_d	ϵ	$\epsilon' \times 10^3$, radians	d., g./cc.	$\epsilon_{0.8}$	$\epsilon' 0.8 \times 10^3$, radians
18	48	0.1	500	54.6	1045	498	29.9	2.36	2.24	0.867	2.22	2.20
35	50	0.1		55.2		523	45.0	2.45	3.50	0.876	2.27	3.45
50	49	0.1		56.2		504	26.1	2.32	1.94	0.892	2.13	1.90
72	26	0.1		54.8		497	33.0	2.35	2.48	0.870	2.20	2.43
18	48	0.1	1000	54.6	1045	498	15.3	2.36	2.30	0.867	2.22	2.26
35	50			56.3		523	18.9	2.40	2.70	0.892	2.17	2.68
50	49			55.6		504	14.0	2.35	2.09	0.882	2.18	2.04
72	26			54.1		497	20.0	2.38	3.02	0.860	2.24	2.98
18	48	0.1	2000	54.6	1045	499	7.7	2.36	2.32	0.867	2.22	2.28
35	50			55.2		518	8.45	2.44	2.44	0.875	2.25	2.40
50	49			55.0		504	8.0	2.37	2.38	0.875	2.20	2.33
72	26			54.5		496	12.4	2.35	3.76	0.866	2.21	3.71
18	48	0.1	4000	54.6	1045	498	4.7	2.36	2.82	0.867	2.22	2.77
35	50			55.0		518	3.9	2.44	2.26	0.870	2.28	2.22
50	49			55.0		502	4.8	2.36	2.86	0.875	2.20	2.80
72	26			53.7		495	7.85	2.38	4.76	0.855	2.25	4.72
20	94	1.0	500	46.5	1070	465	46.2	2.59	3.80	0.80	2.59	3.80
35	63			45.2		454	25.1	2.60	2.13	0.778	2.67	2.13
53	26			45.0		444	31.8	2.55	2.74	0.766	2.66	2.76
20	94	1.0	1000	46.5	1070	466	19.0	2.60	3.13	0.80	2.60	3.13
35	63			45.2		454	12.5	2.60	2.15	0.778	2.67	2.15
53	26			45.0		443	17.5	2.55	3.10	0.766	2.66	3.13
20	94	1.0	2000	46.5	1070	467	8.1	2.60	2.67	0.80	2.60	2.67
35	63			45.2		453	6.3	2.59	2.14	0.778	2.66	2.14
53	26			45.0		442	10.4	2.54	3.62	0.766	2.65	3.65
20	94	1.0	4000	46.5	1070	468	3.65	2.61	2.40	0.80	2.61	2.40
35	63			45.2		452	3.55	2.59	2.41	0.778	2.66	2.41
53	26			45.0		442	5.5	2.54	4.52	0.766	2.65	4.54

^a Microns

^b Cycles per second

^c Specimen thickness in reciprocal cm.

^d ΔC_d in dial divisions. Multiply by 1.14 to obtain value in μf

TABLE XXIV

DIELECTRIC PROPERTIES OF REGENERATED SOLVENT-DRIED CELLULOSE J

Time, hr.	T _{exp.} , ° C.	Vacuum ^a	Frequency ^b	$\frac{C_2}{\mu\mu f}$	$\frac{C}{\mu\mu f}$	ΔC_1 ^d	ϵ	$\epsilon' \times 10^3$, radians	d., π/cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
18	80	0.4	500	970	272	22.0	2.65	2.81	0.61	3.62	2.75
40	54	0.1		548	267	35.1	2.58	2.58	0.614	3.45	2.51
48	53	0.2		548	265	35.0	2.64	2.59	0.596	3.70	2.48
80	25	0.1			261	45.8	2.53	3.44	0.611	3.38	3.38
92	50	0.1	500	548	266	34.9	2.74	2.58	0.574	4.15	2.39
113	76	0.1			272	37.8	2.77	2.72	0.585	4.09	2.52
131	105	0.1			285	55.6	2.73	3.84	0.618	3.57	3.80
148	77	0.1			281	38.3	2.74	2.68	0.607	3.81	2.54
18	80	0.4	1000	970	271	10.2	2.64	2.61	0.610	3.59	2.52
40	54	0.1		548	266	17.7	2.57	2.61	0.614	3.42	2.55
48	54	0.2			266	18.1	2.64	2.68	0.596	3.70	2.57
80	25	0.1			261	26.6	2.53	4.00	0.611	3.38	3.92
92	50	0.1	1000	548	265	18.3	2.70	2.71	0.582	3.97	2.53
113	76	0.1			272	18.3	2.77	2.64	0.585	4.09	2.44
131	105	0.1			286	24.7	2.74	3.39	0.618	3.57	3.37
148	77	0.1			280	18.7	2.73	2.62	0.586	3.98	2.45

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXIV (Continued)
DIELECTRIC PROPERTIES OF REGENERATED SOLVENT-DRIED CELLULOSE J

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{cor.}$	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	$\Delta\epsilon_d$	ϵ	$\epsilon' \times 10^3$, radians	$\frac{\epsilon''}{cc.}$	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
18	80	0.4	2000	26.6	970	270	5.1	2.63	2.61	0.610	3.58	2.53
40	54	0.1		26.8	548	265	9.45	2.56	2.80	0.614	3.42	2.73
48	53	0.2		26.0		266	9.5	2.64	2.81	0.596	3.70	2.70
80	25	0.1		26.7		260	15.8	2.53	4.75	0.611	3.38	4.65
92	50	0.1	2000	25.6	548	265	9.7	2.68	2.88	0.586	3.88	2.72
113	76	0.1		25.5		271	9.6	2.75	2.78	0.585	4.03	2.59
131	105	0.1		27.0		288	11.0	2.76	3.00	0.618	3.61	2.97
148	77	0.1		25.6		279	9.1	2.73	2.56	0.586	3.98	2.40
18	80	0.4	4000	26.6	548	273	4.5	2.66	2.59	0.610	3.63	2.49
40	54	0.1		26.8		265	5.2	2.56	3.08	0.614	3.42	3.00
48	53	0.2		26.0		265	5.15	2.64	3.05	0.596	3.70	2.92
80	25	0.1		26.7		260	9.9	2.52	6.01	0.611	3.36	5.90
92	50	0.1	4000	25.4	548	268	5.45	2.72	3.20	0.582	4.00	3.00
113	76	0.1		25.5		271	4.55	2.75	2.64	0.585	4.03	2.46
131	105	0.1		27.0		288	5.2	2.76	2.83	0.618	3.61	2.80
148	77	0.1		25.6		279	4.5	2.73	2.53	0.586	3.98	2.36

^a Microns

^b Cycles per second

^c Specimen thickness in reciprocal cm.

^d $\Delta\epsilon_d$ in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXXV

DIELECTRIC PROPERTIES OF RECRYSTALLIZED SOLVENT-DRIED CELLULOSE J

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{\text{cor.}}$	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	$\frac{C_2}{C_1}$	d cm.	ϵ	$\epsilon' \times 10^3$, radians	$\frac{d}{\tau}$, cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
38	102	0.1	500	42.1	1045	446	44.5	21.5	2.74	3.74	0.586	4.00	3.50
60	75	0.1		42.1		438	29.9	15.5	2.69	2.56	0.587	3.89	2.42
73	52	0.1		43.0		428	28.0	14.2	2.58	2.45	0.598	3.57	2.37
89	27	0.5		42.8		421	35.5	20.1	2.55	3.15	0.595	3.53	3.06
108	50	0.5		41.3		428	28.4	14.5	2.68	2.48	0.575	4.00	2.31
130	93	0.1		41.2		448	38.0	16.4	2.82	3.18	0.573	4.32	2.90
38	101	0.1	1000	42.1	1045	443	21.5	21.5	2.72	3.64	0.586	3.97	3.46
60	75	0.1		42.1		437	15.5	15.5	2.69	2.61	0.587	3.89	2.46
73	52	0.1		43.0		428	14.2	14.2	2.58	2.49	0.598	3.57	2.41
89	27	0.5		42.8		421	20.1	20.1	2.55	3.57	0.595	3.53	3.46
108	50	0.5		41.3		428	14.5	14.5	2.68	2.64	0.575	4.00	2.46
130	93	0.1		41.2		447	16.4	16.4	2.81	2.76	0.573	4.30	2.52
38	100	0.1	2000	42.1	1045	452	9.05	9.05	2.77	3.00	0.586	4.07	2.83
60	75	0.1		42.1		437	7.0	7.0	2.68	2.39	0.587	3.89	2.25
73	52	0.1		43.0		428	8.7	8.7	2.58	3.04	0.598	3.57	2.94
89	27	0.5		42.8		420	12.5	12.5	2.54	4.45	0.595	3.51	4.33
108	50	0.5		41.3		428	7.9	7.9	2.68	2.76	0.575	4.00	2.57
130	93	0.1		41.2		446	7.8	7.8	2.81	2.62	0.573	4.30	2.39
38	100	0.1	4000	42.1	1045	453	4.35	4.35	2.78	2.82	0.586	4.10	2.65
60	75	0.1		42.1		435	4.05	4.05	2.68	2.75	0.587	3.89	2.59
73	52	0.1		43.0		428	5.25	5.25	2.58	3.67	0.598	3.57	3.55
89	27	0.5		42.8		420	8.35	8.35	2.54	5.96	0.595	3.51	5.80
108	50	0.5		41.3		427	4.55	4.55	2.68	3.19	0.575	4.00	2.97
130	93	0.1		41.2		448	4.1	4.1	2.82	2.74	0.573	4.32	2.50

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVI

DIELECTRIC PROPERTIES OF SOLVENT-DRIED CELLULOSE D

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\mu_{cor.}$	$\frac{C_2}{\mu\mu f}$	$\frac{C_1}{\mu\mu f}$	ΔC_1	d	ϵ	$\epsilon' \times 10^3$, radians	d., g./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
20	97	180	500	47.0	1045	493	32.0	2.71	2.66	0.865	0.865	2.53	2.63
32	60	200		48.9		473	21.5	2.51	1.71	0.90	0.90	2.27	1.63
20	97	180	1000	47.2	1045	493	13.9	2.70	2.12	0.869	0.869	2.51	2.10
32	60	200		48.9		475	11.7	2.51	1.85	0.90	0.90	2.27	1.81
20	97	180	2000	46.8	1045	490	6.45	2.71	1.97	0.862	0.862	2.53	1.95
32	60	200		48.9		475	6.1	2.51	1.92	0.90	0.90	2.27	1.88
20	97	180	4000	46.8	1045	487	3.0	2.70	1.85	0.862	0.862	2.52	1.83
32	60	200		48.9		475	3.25	2.51	2.05	0.90	0.90	2.27	2.01

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu f$

TABLE XXVII

DIELECTRIC PROPERTIES OF AIR DRIED REGENERATED CELLULOSE F (NOT PRESSSED)

time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	$\epsilon_{\text{cor.}}$	$\frac{C_2}{\mu\text{f}}$	$\frac{C_1}{\mu\text{f}}$	ΔC_1	ϵ	$\epsilon' \times 10^3$, radians	d., g./cc.	ϵ_0, g	$\epsilon' 0.8 \times 10^3$, radians
64	100	0.2	500	57.3	865	671	75.0	3.04	3.45	1.03	2.38	3.43
86	72	0.1		57.2	861	638	44.3	2.89	2.14	1.03	2.29	2.10
108	49	0.1		58.9	860	628	32.3	2.76	1.59	1.06	2.15	1.54
130	23	100		57.0	860	614	45.6	2.79	2.29	1.025	2.24	2.24
150	53	0.1		58.8		629	32.1	2.77	1.58	1.058	2.18	1.52
163	72	0.1		57.0		640	43.1	2.91	2.11	1.025	2.32	2.08
183	100	0.1		59.1		675	--	2.96	--	1.075	2.25	--
64	100	0.1	1000	57.7	1038	656	33.5	2.95	3.79	1.039	2.30	3.74
86	72	0.1		57.6	861	638	20.6	2.86	2.00	1.035	2.26	1.96
108	49	0.1		58.9		626	16.5	2.75	1.63	1.06	2.15	1.57
130	23	100		57.0		614	28.25	2.79	2.84	1.025	2.24	2.77
150	53	0.1		58.8		628	16.7	2.77	1.64	1.057	2.18	1.58
163	72	0.1		57.1		643	19.1	2.92	1.83	1.027	2.31	1.81
183	100	0.1		59.1		674	42.6	2.95	3.89	1.075	2.21	3.81

^a Microns^b Cycles per second^c Specimen thickness in reciprocal cm.^d ΔC_1 in dial divisions. Multiply by 1.14 to obtain value in μf

TABLE XXXVII (Continued)
DIELECTRIC PROPERTIES OF AIR UNDER CONCENTRATED COLUMBIUM F (NOT PREPARED)

Time, hr.	Temp., ° C.	Vacuum ^a	Frequency ^b	ϵ_{20} $\mu\mu\text{f}$	$\frac{\epsilon_{20}}{\mu\mu\text{f}}$	$\Delta\epsilon_d$	ϵ	$\epsilon' \times 10^3$, radians	d., r./cc.	$\epsilon_{0.8}$	$\epsilon'_{0.8} \times 10^3$, radians
64	100	0.2	2000	1038	660	13.4	2.96	3.02	1.039	2.31	2.97
86	72	0.1		861	642	9.2	2.84	1.77	1.05	2.21	1.73
108	49	0.1		861	624	9.4	2.79	1.86	1.06	2.15	1.79
130	23	100			614	16.4	2.79	3.32	1.025	2.24	3.24
150	53	0.1			625	9.25	2.76	1.82	1.054	2.18	1.75
163	72	0.1			644	9.2	2.91	1.76	1.029	2.30	1.73
183	100	0.1			671	18.6	2.95	3.42	1.072	2.25	3.34
64	100	0.2	4000	1038	662	9.6	2.95	3.52	1.03	2.33	3.48
86	72	0.1		861	642	4.65	2.85	1.79	1.049	2.23	1.75
108	49	0.1			622	5.3	2.75	2.10	1.055	2.16	2.03
130	23	100			613	12.4	2.80	4.98	1.02	2.24	4.88
150	53	0.1			624	5.45	2.75	2.16	1.052	2.17	1.67
163	72	0.1			644	4.9	2.91	1.73	1.029	2.30	1.70
183	100	0.1			656	7.7	2.95	2.85	1.061	2.27	2.87

^a Microns

^b Cycles per second

^c Specimen thickness in reciprocal cm.

^d $\Delta\epsilon_d$ in dial divisions. Multiply by 1.14 to obtain value in $\mu\mu\text{f}$