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Doctor's Dissertation

A Study of the Power Factor and Specific Inductive Capacity of a Paper Dielectric as Influenced by Certain Constituents of the Paper

by Paul D. Harben

May, 1941
A STUDY OF THE POWER FACTOR AND SPECIFIC INDUCTIVE CAPACITY

OF A PAPER DIELECTRIC AS INFLUENCED BY

CERTAIN CONSTITUENTS OF THE PAPER

A thesis submitted by

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By reason of its possession of certain desirable properties, paper occupies an extremely important place as an electrical insulating material. Responsible for this prominent position of cellulosic material are its relatively high dielectric constant (about 7 for pure cellulose), high resistivity \(10^{15}\) ohm-cm., fairly low power factor when dry, flexibility, strength, and the ability to be applied in a number of ways.

Like other dielectrics, however, paper is not perfect, and there is always a loss of power when an alternating electric stress is applied to it. In this respect it is somewhat inferior to materials such as hydrocarbon oils, glass, quartz, certain synthetic resins, and other materials.

Usually paper insulation is impregnated with oils or other liquid or low melting point materials. This serves two purposes; first, impregnation greatly retards the reabsorption of water by dry paper and, second, by proper selection of impregnants the dielectric constant of the combination can be increased over that of paper. This is desirable in capacitors where the greatest energy-storing ability must be associated with as small a volume as possible. In the latter instance, the gains resulting from the use of impregnants having high dielectric constants are limited by the paper.

These limitations have made paper insulation the subject of much research. Strides have been made, to be sure, in improving its
properties, but there are many questions yet unanswered regarding the
exact causes of the observed phenomena and the influence exerted by
the components present in the very complex structure of paper.

Delevante (1), in 1941, initiated an investigation at The Institute of
Paper Chemistry in which the electrical properties of cellulosic
materials were to be considered, not so much from the standpoint of the
electrical engineer as from that of the paper and cellulose chemist.
The present study may be considered to have grown out of his work.

DEFINITIONS OF TERMS

Dielectric Constant

The dielectric constant, or specific inductive capacity, as
it is more properly called, is the property of a dielectric which
determines its ability to store electrical energy. The capacity of a
condenser is the electrical charge it can store per unit potential
difference. The specific inductive capacity of a dielectric is usually
expressed as the ratio of the capacity of a condenser which it may fill
to the capacity of the same condenser with empty space between the
plates. \( K \), the specific inductive capacity, is given by the expression

\[
K = \frac{C}{C_0}
\]  

(1)

\( C \) being the capacity with the material filling the space and \( C_0 \) that
without it. \( K \) is a measure of the electrostatic energy stored per unit
volume per unit potential gradient.

Dielectric Phase Angle

When a sinusoidal alternating voltage is impressed on a perfect
condenser, the resulting current is exactly 90 electrical degrees out of phase with the impressed voltage. When an imperfect dielectric fills the capacitor, a current of the same frequency as the voltage will flow but it will lead the voltage by less than 90 degrees; this angular difference in phase is the phase angle.

Dielectric Loss Angle

The dielectric loss angle is the difference between 90 degrees and the phase angle. Reference to Figure 1 will make this clearer. The vector \( V \) represents the magnitude of the impressed voltage, and \( V_{wC_p} \) is the quadrature component of the current. \( C_p \) and \( R_p \) are the equivalent parallel capacitance and resistance, respectively. \( \omega \) is the angular velocity, or \( 2\pi \) times the frequency in cycles per second. \( \Theta \) and \( \delta \) are the phase and loss angles, respectively. Figure 1b shows the equivalent circuit.

![Diagram a](image-a)

![Diagram b](image-b)

**Figure 1**
It is seen that a component of the current is in phase with the voltage and that, when this condition exists, there is always dissipation of power. This power is given by the equation

$$P = VI \cos \theta.$$  \hspace{1cm} (2)

in which I is the current and \(\cos \theta\) is the power factor. When \(\theta\) is nearly 90 degrees, \(\delta\) is very small, and it is seen that

$$\cos \theta = \sin \delta_2 \delta_2^* 1/(\overline{\kappa_{L}} \overline{\mu}) = \tan \delta.$$  \hspace{1cm} (3)

When \(\tan \delta\) is less than 0.1 and the power factor is considered equal to \(1/(\overline{\kappa_{L}} \overline{\mu})\), the error is less than 0.0005. Also, the approximation \(\tan \delta = \delta\), when \(\delta\) is small, is so close that throughout this study power factor will be represented simply as \(\delta\).

**Dielectric Loss Factor**

The dielectric loss factor of a material is the product of its specific inductive capacity and power factor. The power loss per unit volume of an insulator at a stated frequency, voltage gradient, and temperature is proportional to its loss factor.

**CELLULOSE AS A DIELECTRIC**

Delevahti (1) has given a good review of the general dielectric properties of paper, covering both direct current and alternating current phenomena. Direct current charge and discharge effects were considered, and the equation relating these currents to a negative exponential function of time after application of stress or short circuiting is given.
The losses observed under alternating stresses were pointed out. It was indicated that these are caused almost entirely by absorption effects, true conduction contributing less than 1 per cent to the loss in dry paper.

The importance of minimizing these losses cannot be over-emphasized. In the case of large condensers, the heat developed may reach dangerous levels; in the case of high voltage transmission cables, the actual energy losses as well as damage to the insulation may be serious. Lastly, in the field of communication, these undesirable effects result in attenuation and distortion of the signals. Any research, therefore, which would result in a lowered power factor for paper would be most useful.
REVIEW OF PREVIOUS WORK

Delevan (1) has given a good general review of the existing knowledge of the behavior of cellulosic materials under electrical stresses. Reference should be made also the excellent paper by Kohman (2), who has given evidence for the existence of a low temperature region of power factor dispersion for dry paper.

The work of Argue and Basses (3), Whitehead and Greenfield (4-5), Bace, Nesphill, and Endicott (7), and Carton (9) has demonstrated that the presence of water in cellulosic material has a marked influence on its specific inductive capacity and power factor. The commonly observed effect is that increases in moisture content bring about corresponding increases in dielectric losses. Delevan observed that paper samples, freely exposed to an evacuated space and heated at 70° C. under a pressure of approximately 1 micron of mercury, reached an equilibrium value for power factor in about 6 hours.

With regard to the drying of paper, uncertainty still exists concerning the possibility of actually removing all the water from the structure. Carton (9) claimed that paper can be brought to complete dryness at a temperature as low as 60° C. by the circulation of dry air; according to his results, reduction of pressure merely accelerated the process and did not influence the final electrical properties of the cellulosic. Greenfield (5), on the other hand, gave curves showing different equilibrium values of electrical properties for different drying pressures. These differences may well be caused by differences in techniques employed by the two investigators; Carton used continuous
flushing, whereas Greenfield employed only periodic flushing with dry air. However, Delevani showed that the equilibrium conditions were the same, regardless of whether the system was flushed periodically with dry gas or pumped with no flushing at all. Murphy and McLean (9) analyzed the gases evolved from paper during drying, and concluded that part of the water came from decomposition of the organic material. They suggested that the dry state might arbitrarily be assumed to be that at which the gases given off are of constant composition. It is not improbable that the removal of the last traces of water from cellulose is a practical impossibility.

That electrolytic impurities influence the properties and life of paper dielectrics is also without doubt. Vogel (10), in studies of power factor as a function of temperature, found a sharp increase in power factor for most papers above 75° C., which he attributed to the presence of electrolytic contaminants. The papers tested presumably had an ash content of 0.5 to 0.6 per cent. The adsorption of low molecular weight organic acids has been shown by Piper, Kerstein, and Mauger (11) to have a deleterious effect on power factor. Finch (12) demonstrated that the presence of chlorides materially decreased the life of paper insulation.

McLean (13) discovered that only by treatment of pulp with dilute acid could most of the cationic material be removed; extraction with distilled water was not effective below a very appreciable ash content. The acid-neutralizing ability of cation-containing paper was demonstrated, and the theory advanced that most of the cationic material
is held in chemical combination with organic acidic groups present in the pulp. Exchange reactions were shown to be involved in the introduction or removal of cations from paper. Evidence that this adsorption takes place on ionic acid groups was presented. McLean, Egerton, Kohman, and Brotherton (14) suggested that the superior ability of kraft pulps (as compared with more highly purified cellulose) to adsorb cations is partially responsible for its longer life in units impregnated with chlorinated organic materials. McLean (15), following this line of thought, suggested the incorporation of metallic salts of carbohydrate gums in condenser papers to absorb the hydrochloric acid formed by the decomposition of these chlorinated impregnants and thereby reduce the rate of deterioration of the cellulose.

Stoops (16), in reporting the results of studies on regenerated cellulose and very pure cellulose triacetate, stated that the substitution of the ester for the alcoholic groups is responsible for a 50 per cent decrease in specific inductive capacity. In this work the samples were dried previous to testing in a cell utilizing mercury electrodes, the whole being placed in a toluene bath for temperature control. For pure cellulose he reported regions of dispersion of specific inductive capacity and power factor; the maxima in the power factor curves shift toward lower frequencies with increasing temperature. This behavior suggests that the polar hydroxyl groups exert some influence on the properties. Hill (17) stated that cellulose nitrate has a higher power factor at low frequencies than either regenerated cellulose or cellulose acetate. Campbell (18) reported a value of 0.7 for the specific inductive capacity of regenerated cellulose; Stoops' value for 60 cycles
per second at 30°C is 7.3, rising to about 8.0 at 90°C.

Stoops found a negative temperature coefficient of power factor in the intermediate frequency range. Relevantly, in attempting to establish the relationship between power factor and temperature of dry paper, found a similar trend but observed a hysteresis in taking the sample through a temperature cycle. He attributed this to partial regain of water from the surrounding atmosphere at the lower temperatures; it is not possible to say from his work whether a true temperature effect exists or not.

THEORIES ON THE DIELECTRIC BEHAVIOR OF HETEROGENEOUS MATERIALS

It is an established fact that the behavior of cellulose in alternating fields can be attributed to reversible absorption, and that losses resulting from true conductivity account for less than 1 percent of the total loss in reasonably well-dried paper. However, the causes of reversible absorption in structurally heterogeneous materials such as paper are by no means clear.

Manning and Bell (12) have given an excellent review of the mathematical analysis of dielectric behavior and showed that, when an alternating field is applied to a dielectric exhibiting reversible absorption, loss of energy is a natural consequence. The absorption current in a dielectric at any instant is shown to consist of a quadrature component which contributes to the specific inductive capacity, and an in-phase component which contributes to the loss. Relating the absorption current-time relationship to an expression called the
relaxation time, which is the time required for a dielectric to acquire 1/e of its total charge, expressions are obtained which relate frequency to specific inductive capacity and loss factor. These basic theoretical equations involve but one relaxation time, however, and give curves which do not agree with the experimentally determined curves for most materials, notably substances like paper. Von Schweidler (20) and Wagner (21) have proposed empirical methods by which observed data can be fitted to the theoretical equations. These methods have been reviewed by Yager (22).

Polarization in a dielectric is considered the cause of all absorption phenomena. Murphy and Morgan (23) have given a thorough survey of the various types of polarization, which are listed under four general headings:

1. **Electronic polarization.** This form of polarization is regarded as being instantaneous, and results from the displacement of electronic charge within the atoms. In the electrical frequency range, it contributes a fixed amount to the specific inductive capacity. It is only at optical frequencies that absorption effects are observed. In materials having nonpolar molecules (such as benzene), electronic polarization is the only one of importance; the specific inductive capacity experiencing no change throughout the spectrum and being equal to the square of the index of refraction.

2. **Atomic polarizations.** This is also regarded as instantaneous, and is attributed to the relative motion of atoms in ionic or molecular structures. It is usually negligible for organic compounds. Atomic polarizations begin to contribute to the specific
inductive capacity in the near infrared.

3. The Debye orientational polarization. This is of the absorptive type, characterized by relaxation times corresponding to relaxation frequencies in the electrical range (frequencies of 10 to 10^10 cycles per second), and includes polarizations resulting from the orientation of polar molecules (dipoles—molecules having permanent electric moments) in an applied field. Dipole polarization is superimposed on electronic and atomic polarizations, and is a partial explanation of the increase of specific inductive capacity at lower frequencies. Debye has shown that the magnitude of dipole polarization is proportional to the square of the electric moment, and his theory has been very useful in the elucidation of the structure of many organic compounds.

Since dipole polarizations depend on orientation rather than displacement, the relaxation time for any given material will be some function of the internal friction of the material.

4. Interfacial polarizations. Orientational polarizations are characteristic chiefly of homogeneous media, which are the exception rather than the rule. When a dielectric consists of layers of different materials or dispersions of one in the other, interfacial polarizations must exist. The simplest case is that of two layers whose respective specific inductive capacity and conductivities are different. Maxwell showed that, in such a system, the capacity was dependent upon the charging time. This is the result of the accumulation of charge on the interface, for this charge must flow through a layer of dielectric whose
resistance may be high enough so that the interface does not become completely charged during the time allowed for charging. For alternating currents this implies decreasing capacity with increase of frequency, and results in an effect similar to that observed with polar molecules in a homogeneous medium.

Several special types of interfacial polarization have been proposed to explain the dielectric properties of various nonhomogeneous dielectrics where something regarding the nature of the inhomogeneity is known. The specific inductive capacity of cellulose, for example, may receive a contribution from an interfacial polarization caused by the water and the dissolved salt it contains.

The loss factor maxima are always in the vicinity of the relaxation frequency for the type of polarization under consideration, and are greatest for those materials showing the greatest change of specific inductive capacity in passing through the dispersion region.

Morgan and Yager (24) have discussed comprehensively the effects of polarity, dipole moment, viscosity, structure, temperature, and other factors on the specific inductive capacity and loss factor of various organic liquids and some of the synthetic polymers of high molecular weight. The probable existence of dipole orientation under electrical stress even in the solid state is discussed. It is suggested that for substances having very large molecules, elastic movement of polar substituent groups in alternating fields may be responsible for some of the phenomena observed.
Murphy and Lowry (25) have considered in detail, with particular reference to cellulose, the interfacial polarizations mentioned above. An "interstitial conduction system" which follows some feature of the submicroscopic structural pattern is suggested. The conduction paths are considered to be thin layers of moisture on the internal surfaces, with small amounts of salts present in solution. Some of the ions are presumed to be adsorbed to different degrees on the solid surfaces, whereas others may be free to migrate along the paths which may be discontinuous. The absorption currents observed are considered to be produced by (1) the migration of the free ions to form space charges at the electrodes or at boundaries within the structure or to form minute electrolytic cells, (2) the elastic displacement of adsorbed ions—changes in distribution which effectively would result in the formation of large dipoles, and (3) the polarization of structural molecules themselves. To the latter might be added effects caused by the elastic displacement of substituent groups, as suggested by Norgen and Yager.

The dielectric loss would be made up of components corresponding to the various components of the absorption currents. Joule heating would result from the free-ion migration, and the formation of space charges would contribute in the manner pointed out earlier. The adsorbed ions could be considered in terms of a distribution of elemental equivalent resistance-capacitance circuits, of varying relaxation times and power factors. (This would give a distribution of relaxation times as suggested by Wagner.) These considerations enabled Murphy and Lowry to explain the form of the absorption current-time relation, the
Hopkinson-Gurie superposition principle (which states that the current in a dielectric at any instant is related to previous changes in impressed field strength and polarity), and the power losses observed.

It is noteworthy that, by the use of the equivalent circuits proposed, they were enabled to obtain expressions for specific inductive capacity and loss factor similar in form to those derived by other investigators for homogeneous materials.
GENERAL AIMS OF THE STUDY

Part of Dalevanti's work was aimed at the establishment of the functional relationship between the electrical properties of paper and its density, but lack of apparatus to take suitable measurements of electrode separation with the sample in situ resulted in uncertainty regarding the validity of the result. This investigation, therefore, included the following aims:

1. Design and construction of an apparatus with which to measure accurately the electrode separation under the conditions outlined above.

2. Establishment of the density-electrical property relationships mentioned above. It is necessary to know this relation so that all data can be put on the same basis.

3. Investigation of the possible effects of metallic cations introduced into paper by exchange reactions.

4. Investigation of the possible influence of varying amounts of lignin in the paper.

5. Investigation of the properties of isolated lignin.

All these studies were to be carried out with the specimens in an extreme state of desiccation, in order to eliminate the effects of adsorbed moisture.
PULPS, APPARATUS, AND METHODS

PULPS

In order that the entire history of the pulps used would be known, kraft cooks were made on well-seasoned black spruce. Three different pulps were prepared, ranging in properties from very raw to well cooked. All cooks were carried out at a sulfidity of 33 per cent, changes in temperature, time, and total chemical giving the variations desired. These pulps are listed with their respective permanganate numbers and lignin contents in Table I.

Table I

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<th>Pulp</th>
<th>Permanganate No.</th>
<th>Lignin %</th>
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<tr>
<td>I</td>
<td>28.75</td>
<td>6.80</td>
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<tr>
<td>II</td>
<td>26.37</td>
<td>6.00 (estimated)</td>
</tr>
<tr>
<td>III</td>
<td>17.51</td>
<td>2.28</td>
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A sample of another pulp, which had been cooked to about the same degree as Pulp III and given a one-stage hypochlorite bleach, was obtained from the Pulping Group of the Institute of Paper Chemistry. This was designated Pulp IV and was used in the lignin study.

BRIDGE AND TEST CHAMBER

All electrical testing of the paper samples was done by means of a modified conjugate Schering capacitance bridge, the design of which was adapted from the A.S.T.M. standards on electrical testing of
insulating materials. The bridge was constructed by Delevanti and described in detail by him; therefore, only a schematic diagram of the bridge network (Figure 2) and the working equations will be given here. \( C_2 \) was a General Radio precision capacitor having a negligible power factor. The detector (D) was a high-sensitivity vacuum-tube amplifier, and the indicating device was a Weston Model 440 galvanometer, which measured the rectified alternating current output of the amplifier.

Although Delevanti has described the operation of the bridge in detail, it is desirable to mention this briefly. With the sample in the test capacitor (\( C_x \)), the bridge was brought to two successive balances with and without \( C_x \). \( C_p \), the equivalent parallel capacitance of the test capacitor, is given by the equation

\[
C_p = C_2 - C_2'
\]

(4)

to a very close approximation, where \( C_2 \) is the capacitance of the precision capacitor without \( C_p \), and \( C_2' \) is its value with the unknown. The power factor is given by the approximate formula

\[
\sin \delta \approx \tan \delta \approx C_2 / (C_2 - C_2') \cdot (C_4 - C_4') / (2 \pi \times 3000) / 10^{12}.
\]

(5)

When \( \sin \delta \) is less than 0.01, this equation holds with a high degree of accuracy.

The test capacitor and chamber have also been considered in detail by Delevanti, but a short review of this part of the apparatus is also given. The two electrodes were circular brass discs, \( 1/4 \) inch thick to give rigidity; the working surfaces were polished and platinum plated. The lower electrode was provided with a guard ring, this assembly being supported by three glass pillars \( 3/4 \) inch high which,
in turn, rested on the brass base plate of the chamber. The upper electrode was suspended from a brass sylphon (bellows) which was connected to the evacuation system. Suitable stopcocks and connections in this system made it possible to raise or lower the plate without the necessity of breaking the vacuum or disturbing the chamber in any way. A bell jar placed over the electrode and sylphon assembly constituted the top and sides of the chamber; a greased rubber gasket between the ground surface of the bell jar and the brass base plate served as a seal. The system was evacuated by a Genco Hyvac pump, when all connections and stopcocks were properly sealed, a pressure of about 1 micron of mercury could be maintained easily.

Sources of Alternating Voltages

Delevani carried out his work at only one frequency (1000 cycles per second), for which he used a General Radio tuning-fork hummer. In this study it was considered desirable to make measurements over a range of frequencies, varying from 60 to 10,000 or 20,000 cycles per second. Because no variable-frequency oscillator was available, one had to be built.

Construction of a Hartley oscillator was considered, but the idea was abandoned because of the prohibitive amount of copper wire required for the lower frequencies. A new type of oscillator, the so-called Transitron oscillator, which has been described by DeLaup (27) and Jordan (28), appeared to give promise. This type of signal generator, instead of requiring inductance-capacitance combinations, utilizes resistance-capacitance circuits, eliminating inductances entirely.
Figure 3 is a schematic diagram of the fundamental circuit.

Practically any type pentode or tetrode can be used. The frequency of oscillation is given by the equation

\[ f = \frac{1}{2\pi \sqrt{\frac{R_2}{R_1 R_2 C_1 C_2}}} \]  

(6)

in which \( R_1, C_1 \), and \( C_2 \) are the elements as shown in the sketch, and \( R_2 \) is the parallel resistance of \( R \) and the screen-to-cathode resistance. It is apparent that frequency variation is possible by changing the values of one or several of these circuit elements. It is preferable to keep \( R_1 \) and \( R_2 \) constant, in order to avoid changing the grid excitation, and to control the frequency by means of the two capacitances. However, this allows only stepwise changes. Jordan presented a modified circuit, which is shown in Figure 4. With the indicated parallel arrangement of \( R_3 \) and \( R_4 \) (which together constitute \( R_1 \)), a nearly continuous adjustment of frequency is possible.
Design and Construction of Transistor Oscillator

No definite design data were given in the published literature; therefore, a breadboard layout was built, using the circuit of Figure 4 and a 6J7 type pentode, and suitable values of circuit elements and operating conditions were determined experimentally. After suitable values for $E_3$, $R_4$, $R_6$, and the operating voltages had been established, the screen current was measured while the system was oscillating; this permitted calculation of the screen-to-cathode resistance. $R_2$ could then be estimated. For the purpose of calculating the values of the capacitances required for the range of frequencies desired, it was assumed that $C_4$ would always equal $C_2$. Then, from Equation (6), the capacitances required for a given frequency could be calculated by the expression

$$C = \frac{1}{2\pi f \sqrt{R_2}}.$$  \hspace{1cm} (7)
$C_1$ and $C_2$, as selected, were exactly similar banks of fixed mica condensers, which were connected in series as shown in Figure 5. The units were mounted on strips of bakelite, and the assemblies provided with bus bars and single-pole, double-throw knife switches, which permitted using any one of the individual condensers or any combination of them. Selection of these capacitors was a compromise between the units desired and their availability.

![Diagram showing terminals of bank and values of condensers]

Values of Condensers:

1. 0.06 μF.
2. 0.01 μF.
3. 0.005 μF.
4. 0.002 μF.
5. 0.0001 μF.

Figure 5

By the proper selection of these combinations and suitable adjustment of $R_3$ and $R_4$, it was possible to obtain a wide range of frequencies.

In order to isolate the oscillating circuit from the lead and provide amplification of the generated signal, the latter was fed to the grid of an amplifier tube. The amplified output was delivered to the primary of a small transformer, which latter presented approximate impedance matches to the tube and to the primary of the isolation transformer.

A diagram of the complete circuit is shown in Figure 6, together with a description of the components. The apparatus was mounted in a steel cabinet, the adjustable capacitors being arranged so as to be
FIGURE 6

CIRCUIT DIAGRAM OF TRANSITRON OSCILLATOR

Legend:

- $C_1, C_2$: Variable mica condenser banks
- $C_3$: 0.005-µF, mica coupling capacitor
- $C_4, C_5$: 40-µF, 150-volt electrolytic condensers
- $R_1, R_2$: 500,000-ohm potentiometers
- $R_3$: 10,000-ohm potentiometer
- $R_4$: 75,000-ohm resistor
- $R_5$: 60,000-ohm wire-wound 2-watt resistor
- $R_6$: 12,000-ohm wire-wound 2-watt resistor
- $R_7$: 1-megohm resistor
- $T_1$: Matching transformer, 10,000-ohm primary, 200-ohm secondary
- $T_2$: Shielded isolation transformer
- $V_1$: Voltmeter for control of grid biasing voltage
- $V_2$: Voltmeter for control of high-voltage supply
- $S_1, S_2$: Switches
- $E_1$: Four flashlight cells in series
- $E_2$: Two flashlight cells in series
easily accessible for making changes. R3 and R4 were connected to vernier dials; a shaft and knob on R5 permitted adjustment of the grid voltage, for the measurement of which external connections were provided. This voltage was supplied by four 1.5-volt flashlight cells in series. The filaments were supplied from a storage battery, a rheostat being provided in the circuit to adjust the voltage to 5.0 volts. The plates of the tubes were supplied by the arrangement shown, the voltage delivered to the terminals of the voltage divider being controlled by a rheostat built into the rectifier.

The calibration of this unit will be discussed in the next section; let it suffice to say here that the unit would deliver nearly perfect sinusoidal alternating voltages of frequencies ranging from 200 to 10,000 cycles per second.

To make tests at 60 cycles per second, the secondary winding of an adjustable autotransformer (General Radio Variac) was connected to the primary of the isolation transformer, the Variac then being plugged into the 60-cycle lighting circuit.

Calibration of Transitron Oscillator

It was noted that the frequency generated by this unit was extremely sensitive to fluctuations of grid voltage and was affected to a lesser degree by variations of plate voltage. It was further observed that oscillations could be obtained if the grid voltage were anywhere in the range from 2 to 7 volts. However, near the extremes of this range oscillations were unstable, and it was very difficult to
duplicate any desired frequency by adjustment of $R_3$ and $R_4$. In the middle of the range the stability was excellent, and duplication of any frequency by adjustment of the two resistances was a relatively simple matter. A value of 5.00 volts, therefore, was arbitrarily selected as the grid voltage to be maintained at all times. Maximum plate and filament voltages were maintained at 135 and 6 volts, respectively.

A cathode-ray oscilloscope was used in calibration. For this purpose, a General Radio 1000-cycle tuning fork hummer, which constituted the frequency standard, was connected to the horizontal sweep circuit of the oscilloscope; the output of the Transitron, which was connected to the balanced bridge, was fed to the vertical sweep. The Lissajou figures thereby attainable permitted identification of the frequencies generated. The procedure was as follows: with the frequency standard operating and with $C_1$ and $C_2$ at the desired settings, $R_3$ and $R_4$ were adjusted simultaneously until the desired pattern was obtained on the fluorescent screen. The dial settings of these resistances and the condenser connections were recorded for a number of frequencies, including 200, 500, 1000, and 10,000 cycles per second. It was found that the frequency was critically dependent on the dial setting of $R_3$ and relatively independent of $R_4$ over a considerable range; $R_4$ functioned chiefly as a control over the conditions of oscillation. Further, the best sine waves were obtained when $R_4$ was set just past the point at which oscillations started. To reproduce any desired frequency, therefore, $R_3$ was set at the point determined by calibration and $R_4$ adjusted to the point at which oscillations began. Subsequent check calibrations showed that this method of use resulted
in excellent duplication of frequencies, and that the oscillator possessed
very good stability.

It was estimated that the oscillator could be set to give
frequencies accurate to 5 parts or less in 1000, or a variation from
the standard of not more than 0.5 per cent.

Measurements of the voltages available at the bridge input
terminals, using an a.c. voltmeter in series with a high resistance,
gave the values shown in Table II. In making these measurements, it
was necessary to be very careful that \( E_L \) was set at just the proper
point, because the voltage delivered increased rapidly when the signals
became distorted.

**TABLE II**

**VOLTAGES DELIVERED TO BRIDGE AT VARIOUS FREQUENCIES**

<table>
<thead>
<tr>
<th>Frequency cycles/sec.</th>
<th>Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>15</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>10,000</td>
<td>6.75</td>
</tr>
</tbody>
</table>

For 60-cycle measurements, the Variac was set at 10 volts;
because the ratio of secondary to primary windings of the isolation
transformer was 1.5, the total voltage across the bridge was about 4.5
volts. At balance, the applied voltage should be equally divided be-
tween the two sides of the bridge, so that the actual voltage existing
across the samples would be approximately half the values given above.
Because these were all low voltages, it could be assumed that measure-
ments would not be affected by saturation phenomena, such as might occur when the applied voltages approached the dielectric breakdown values.

MEASUREMENT OF ELECTRODE SEPARATION

When the specific inductive capacity and power factor of a solid sheet material are to be determined, the separation between the electrodes will, in general, be greater than the measured thickness of the specimen. This is particularly true of paper, the surface of which is naturally irregular and the magnitude of the discrepancy must be known so that proper corrections can be made. Delevaniti showed that, when there is a difference between these values, the specific inductive capacity is given by the expression

$$\kappa' = 1/\omega \pm \frac{\delta}{\text{t}} + 1.11\sqrt{\frac{\text{L}}{4\pi\text{Cp}}}$$  \(8\)

and the corrected value of the power factor is

$$\delta' = \delta - \frac{\kappa'(d-t)}{\text{t}}$$  \(9\)

in which

- \(d\) = electrode separation,
- \(t\) = sample thickness,
- \(A\) = area of electrodes, and
- \(Cp\) and \(\delta\) are the values given in Equations 4 and 5.

A technique often used involves insulating spacers which maintain a constant electrode spacing, the specimens being aligned into the opening when the measurements are to be made. In some cases, however, it is more desirable to allow the electrodes to assume the minimum separation permitted by the specimen, so that the capacitance will be as great as possible. Delevaniti designed the test chamber with this
in mind but, because he had no means for measuring \( \Delta \) with the sample in situ and in vacuo, he was obliged to depend on measurements made in an external device which necessitated exposure of the dried specimen to the atmosphere. The values thus obtained were subject to uncertainty as a result of possible changes in the characteristics of the specimen (such as cockling or change of thickness) resulting from readesorption of moisture, and, as can be seen from Equations 3 and 9, these uncertainties could be the cause of appreciable errors in the calculated values of \( k' \) and \( \delta' \).

Design and Construction of Plate-Separation Gage

To minimize these uncertainties, a gage was devised and incorporated with the testing chamber. The contrivance is shown in Figure 7 and consisted essentially of a lever of known length, a screw of accurately known pitch, and a spirit level which served as an indicating device.

A small spirit level (\( L \)) was fitted with a single spring steel point at one end, and two steel wire points at the other. A rigid brass post (\( P \)) was soldered to the chamber base plate and fitted with an adjusting screw in its top. The head of the screw was filed flat and a small depression formed in its center with a punch; the post and screw formed the support for one end of the level, the spring steel foot resting in the depression. A small plate of glass, which was held in place on the center of the upper electrode by short pins set into holes, formed the support for the other end of the level, one of the wire points resting in a small depression in the surface.
The whole chamber, with its shielding, was mounted on a steel plate bolted to a beam (B), a 1 x 3-inch steel channel. This beam was supported by three points, two being at the ends of a steel bar welded transversely to the beam at the end under the chamber, and the other being the hardened steel screw S which was threaded into a brass nut bolted to the end of the beam. The chamber was placed so that the post R was directly above a line drawn between the two supporting pins, and the level was directly above and parallel to the center line of the beam. The whole assembly rested on an adjustable base (B') made from 1/4-inch pipe and welded in the form of an isosceles triangle. The point of the screw S rested on a hardened steel face (H) at its apex; a bar bolted parallel to its base carried punched depressions into which the other two points rested. Similar points at the base of B' and its adjusting screw S' rested on steel blocks sunk into the wooden table top. S' was threaded into a steel nut welded between the legs of the triangular base, and passed up through a hole drilled in the base B. A supplementary level L' was rigidly bolted to B', so that it could be brought to a standard position when measurements were to be made.

It will be seen that rotation of B would cause rotation of B about the points x and, if the angular displacement of the beam were small, a point on the outer end would experience an essentially vertical movement. The point y would be displaced vertically a proportionately smaller distance, and the point x, although it would be displaced horizontally, could be considered fixed as far as vertical motion is concerned. If the distances a and b and the pitch (p) of the screw S
are known, this arrangement can be used to measure changes in the position of the upper electrode, and this use could be extended to the measurement of the separation of the plates at their centers.

Suppose that, with the upper electrode at some arbitrary point—for example, with distance \( d_0 \) between the two electrodes—the base \( b \) were brought to a standard position as indicated by \( L' \), and the bubble in \( L \) were brought to some arbitrary point by adjustment of \( S \). If the distance between the plates be changed by an amount \( \Delta d \), rotation of \( \bar{S} \) in the proper direction will restore the bubble in \( L \) to its original position by giving a point on the end of the beam a vertical displacement \( \Delta S \). By similar triangles

\[
\frac{\Delta d}{\Delta S} = \frac{b}{a},
\]

or

\[
\Delta d = (\frac{b}{a}) \Delta S.
\]

Expressing \( \Delta S \) in terms of screw pitch and rotation, Equation 11 becomes

\[
\Delta d = (p \times \varphi) / a,
\]

in which \( p \) is the pitch of the screw and \( \varphi \) the number of revolutions.

The distance \( b \) was measured and found to be 2.40 inches. A 10-degree rotation of \( \bar{S} \) was arbitrarily selected as being equivalent to a \( \Delta d \) of 0.0002 inch, and rough calculations indicated that a screw having 30 threads per inch would be satisfactory. Using these values in Equation 12 and solving for \( \varphi \) gives

\[
(1/30)(1/36)(2.40/0.0002) = 13.32 \text{ inches}.
\]

The rotation of the screw \( S \) was measured by means of a pointer \( A \) set into the beam, and a 4-inch dial on the screw. The dial was divided into 10-degree divisions which were each further divided into
five parts, so that rotations of 2 degrees could be read quite accurately. It was found that the position of the bubble was sensitive to rotations of about 2 degrees; this would mean that the system was sensitive to a $d$ of 0.00004 inch and, for a separation of 0.010 inch, would be accurate to about one part in 250 or 0.4 per cent.

Method of Use of Plate-Separation Gage

In measuring $d$, the following general procedure was followed:

1. After the specimen had been allowed to condition sufficiently, the upper plate was lowered and allowed to rest in contact with the specimen until its equilibrium position had been attained, which usually required 2 to 3 hours. The electrical measurements were then made, the caliper system was balanced, and the dial reading $D$ (10-degree divisions) noted.

2. Without disturbing the caliper system, the vacuum in the chamber was broken, the specimen was removed from the test capacitor, and three small spacers of mica were placed on the lower electrode near its edge and 120 degrees apart. The bell jar was replaced and the system warmed with the upper plate resting on the spacers for about an hour, so that the pressure and temperature would be approximately the same as when the specimen was in place. The caliper system was again balanced, the dial reading $D_0$ and the number of revolutions necessary being noted. Then, employing the bridge, the capacitance $C_0$ of the test cell was determined.

3. Knowing $C_0$ and the area of the plates in square cm., it
was possible to compute accurately the spacing $d_0$ (in cm.) maintained between the plates by the mica spacers, using the expression

$$d_0 = 1.11 \frac{A}{4 \pi \rho_0}.$$  \hspace{1cm} (13)

Further, knowing $D$ and $D_0$ and the number of complete revolutions of the screw required to re-establish balance, the number of 10-degree divisions ($N$) through which the screw had turned could easily be determined. Using the proper factor to convert centimeters to inches, the plate separation when the sample was in place was

$$a = 1.11 \frac{A}{2 \pi \rho_0^{1/2}(4 \pi \rho_0)} + 0.0002 \frac{N}{\text{inches}}. \hspace{1cm} (14)$$

**ELECTRODE HEATER AND MEASUREMENT OF PLATE TEMPERATURE**

In the original apparatus, the testing chamber and the accompanying shield box were heated by radiant heat from spotlights directed at the blackened surfaces of the box, and temperature was measured by a thermocouple. This arrangement, although it produced uniform temperatures inside the enclosure, was cumbersome and awkward to handle; furthermore, when such general heating was employed with the spirit level, the thermal expansion of the liquid in the vial caused the bubble to disappear. This necessitated the design of a heater which would give local heating of the electrodes but would have only slight effect upon the rest of the assembly.

A small electrical heater was therefore constructed, using Nichrome wire wound on a horseshoe-shaped piece of mica, which was cut so that it fit inside the three glass electrode supports. A heat dissipation of 30 watts was considered adequate; on the assumption that the maximum voltage obtainable was 12 volts (in case the use of direct
current was found necessary), a resistance of about 4.3 ohms was required. Power for the heater was brought into the chamber by means of a metal vacuum-tube base, which was soldered to the bottom of the base plate concentric with a hole drilled in the latter. The general arrangement is shown in Figure 5 (a) and (b).

At first it was thought that alternating current would be used during the exhausting periods, the direct current from batteries supplied to the heater while measurements were being made. However, by use of the circuit shown in Figure 5 (c), it was possible to dispense with a d.c. source and employ a.c. altogether. The heater (H) was connected, in parallel with a potentiometer (P), to the secondary of a small step-down transformer (T) of the type used in vacuum tube filament supplies. Its primary was connected to the 110-volt a.c. supply in series with a rheostat (R) which, with the a.c. voltmeter (V) connected permanently to the heater terminals, permitted fairly close control of the applied voltage and, hence, of the plate temperature. The center tap of the potentiometer was grounded and, when it was adjusted so that the voltage swings in each direction were equal with respect to ground potential, the fields effectively neutralized each other and caused no signals to be introduced into the bridge network.

Measurement of Electrode Temperature

The thermocouple originally built into the chamber was arranged so that it would not measure directly the temperature of the electrodes if they were heated locally and, therefore, some other method of measurement was necessary. The use of a small mercury-in-glass thermometer was found satisfactory.
FIGURE 6. ELECTRODE HEATER
A small domestic-oven type thermometer having a range of 20° to 500° C. was employed. A small brass block was drilled to accommodate the bulb of the thermometer, and soldered to the bottom of the lower plate near its center. Because the temperature was not expected to exceed 110° C., the thermometer was cut in two in an oxygen flame; it was then of such a length that it fitted very comfortably under the electrode when the bulb was inserted into the cavity.

The thermometer in its original form was mounted in a metal holder, on which were printed the graduations; because no marks appeared on the tube itself, some means of establishing and marking the desired points was necessary. First, the positions of the mercury at 20° and 100° C. were determined. The distance thus established was measured on the edge of a small sheet of copper foil and divided into eight equal parts. At each division a small point was filed; then the foil was trimmed to the proper size, bent into an open sleeve and slipped onto the thermometer, the 20° and 100° C. marks being brought into register with the corresponding points previously established on the glass tube. The open sleeve left the mercury column exposed, and with the points marking each 10-degree interval the temperature could be read with sufficient accuracy. The arrangement is shown in Figure 8 (b).

Calibration of Heater

The thermometer could be seen and read through the glass of the bell jar, but only with some difficulty; another inconvenience was that, in order to see the thermometer, one side of the shield box had to be removed. Therefore, a calibration which would give the relation
between the plate temperature and applied voltage was desirable. Since changes in pressure would mean variations in heat dissipation from the electrodes because of varying convection currents, these temperature-voltage relationships had to be determined as a function of pressure.

Two curves were obtained, one at a pressure of approximately 120 microns of mercury and the other at 10 microns and below. The temperature read at each voltage was the equilibrium value. The data obtained are presented in Table III and graphically in Figure 9.

**TABLE III**

**CALIBRATION OF PLATE HEATER**

<table>
<thead>
<tr>
<th>Pressure (microns)</th>
<th>Voltage</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.0</td>
<td>23</td>
</tr>
<tr>
<td>130</td>
<td>2.3</td>
<td>33</td>
</tr>
<tr>
<td>125</td>
<td>2.8</td>
<td>41</td>
</tr>
<tr>
<td>125</td>
<td>3.2</td>
<td>47</td>
</tr>
<tr>
<td>125</td>
<td>4.0</td>
<td>57</td>
</tr>
<tr>
<td>124</td>
<td>5.0</td>
<td>75</td>
</tr>
<tr>
<td>123</td>
<td>6.0</td>
<td>92</td>
</tr>
<tr>
<td>110</td>
<td>6.95</td>
<td>113</td>
</tr>
<tr>
<td>1.5</td>
<td>4.00</td>
<td>80</td>
</tr>
<tr>
<td>2.5</td>
<td>4.40</td>
<td>80</td>
</tr>
<tr>
<td>3.0</td>
<td>5.00</td>
<td>97</td>
</tr>
<tr>
<td>0.5</td>
<td>5.00</td>
<td>100</td>
</tr>
<tr>
<td>2.5</td>
<td>5.50</td>
<td>112</td>
</tr>
<tr>
<td>1.5</td>
<td>6.00</td>
<td>130</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>125</td>
</tr>
</tbody>
</table>

Below 10 microns, variation in pressure is seen to cause slight temperature variations for any voltage; however, since these deviations are small, a single curve was considered representative of these points. For most of the work, evacuation and testing was done at a heater voltage of 5.3 volts; this will be seen to correspond to about 105° C.
RELATION BETWEEN HEATER VOLTAGE AND PLATE TEMPERATURE AT DIFFERENT PRESSURES

- **120 microns**
- **12 microns and below**
Relation between Plate and Paper Temperatures

It will be recalled that, during the evacuation period, the upper plate is held some distance above the lower electrode to permit faster diffusion of water vapor from the specimen. It is apparent that with the local heating the paper would be at a somewhat lower temperature than the plate, and it was thought desirable to know the approximate magnitude of the difference.

Experiments based on the change of brightness of paper with thermal aging were carried out. A mimeograph bond was selected because it exhibited a greater change of brightness for a given exposure than other papers immediately available. Samples were cut larger than the electrodes and the brightness determined (using the General Electric reflection meter) at 5 points, great care being taken to avoid contamination of the surfaces; all readings were made with the samples backed by an opaque pad of the same kind of paper. Each sample was placed in the test cell, held close to the electrode surface by a wire ring which served as a weight to prevent curling; and heated for 4 hours. Samples were tested at three different temperatures at a pressure of about 1 micron, and parallel experiments were carried out on samples placed for the same length of time in a drying oven, in which their aging temperatures would be accurately known. After heating, the brightness of each specimen was again measured; the average change in brightness ($\Delta B$) computed, and these values plotted as a function of temperature. Table IV contains this data, which is graphically shown in Figure 10.
TABLE IV
RESULTS OF AGING EXPERIMENTS

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>78</th>
<th>98</th>
<th>112</th>
</tr>
</thead>
<tbody>
<tr>
<td>2℃</td>
<td>0.48</td>
<td>1.75</td>
<td>3.62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>78</th>
<th>100</th>
<th>116</th>
</tr>
</thead>
<tbody>
<tr>
<td>2℃</td>
<td>0.28</td>
<td>0.56</td>
<td>1.16</td>
</tr>
</tbody>
</table>

From these data it is seen that, when the plate temperature is 105°C, the paper temperature is in the neighborhood of 32°C. When the top electrode is lowered, the temperature of the paper at equilibrium will approach that of the lower plate, although it will probably be a few degrees lower because of the lower temperature of the upper electrode as a result of radiation.

MEASUREMENT OF SHEET THICKNESS

In this work it was necessary that the thickness be known as accurately as possible; it will be seen from Equations 8 and 9 that errors in its measurement may be responsible for large errors in $K'$ and $S'$. A Schopper caliper was used, the areas of the anvil and foot of which were 2 sq. cm.; the moving element was weighted so that the pressure on the sample was 1 kg. per sq. cm. This pressure was sufficient to cause considerable compression of soft samples, which would have been intolerable for the projected experiments because the pressure exerted by the upper electrode was very small and could be assumed to cause no changes in sheet thickness. However, when the weight on the caliper was removed, the pressure was about 300 grams per sq. cm.
FIGURE 10

Curves should approximate those conditions of aging corresponding to values indicated on ordinate.

- Even aged
- Coll. aged
Experiments carried out to determine the effects of different loading showed that, between 300 grams and 1 kg. per sq. cm., an increase of load caused an appreciable decrease of \( t \), whereas loads less than 300 grams per sq. cm. (obtained by hanging weights on the end of a cord which passed over a pulley and was attached at its other end to the moving caliper element) resulted in no change of indicated \( t \) until the load became so small as to result in instability and poor reproducibility of the measurements. The readings given with the 300-gram loading were therefore regarded as accurate, after the gage had been calibrated against a set of feeler gages tested by the Bureau of Standards and a correction chart had been prepared.

The average of 10 readings on each sheet was taken as the thickness \( t \).

PREPARATION OF TEST SHEETS

The use of distilled water in making handsheets was necessary; since many sheets were required, the use of the standard British sheet mold would not have been feasible because of the prohibitively large amounts of water required. Further, the metal of the mold might have caused undesirable contamination of the pulp.

A small mold was therefore constructed, using a Mohrner funnel and a glass cylinder; this is shown in Figure 11. The cylinder was a bottle, with the top and bottom removed, of a diameter which allowed it to fit easily inside the funnel. A length of small rubber tubing cemented to the inside of the funnel served as a gasket. A disk of 20-
FIGURE 11

SHEET MOLD AND DRYING ARRANGEMENT
mesh copper screen rested on the bottom of the funnel and supported the forming wire, which was a disk of 120-mesh bronze wire cloth soldered at its edges to a similar disk of somewhat stiffer and coarser screen. A three-way stopcock connected to the stem of the funnel provided means for filling and draining the completed mold. The whole was supported on a wooden frame, and hooks on rubber bands held the glass cylinder tight against the gasket.

The sheets made in this mold were only about 4 inches in diameter; therefore, the standard British drying rings were of no use. In order to hold the sheets flat against the polished disks during drying, special drying rings were turned from 4-inch steel pipe; these were held firmly against the sheet and plate by placing the assembly between a flat board and a batten, which was tightened down by means of a bolt and wing nut. The drying arrangement is shown in Figure 11.

The sheetmaking procedure was, in general, as follows: The sample of pulp, after having received the necessary treatment, was filtered in a Büchner funnel and the consistency of the resulting cake determined. Portions which would give the desired sheet weight were then weighed and disintegrated for 1 minute in about 500 cc. of distilled water. After the wire and glass cylinder were put in place, the mold was partially filled with water, the pulp poured in, and the suspension stirred with a glass stirrer. The latter was made from a long glass rod, a portion of which was bent into a spiral whose plane was at right angles to the rest, which served as a handle. The mold was then drained by gravity through a rubber tube into the sink. When the mold and tube were completely drained, the glass cylinder was removed, the
wire and wet sheet pulled out with a small wire hook, and the sheet couched onto a clean blotter, using three blotters below and two on top. The stack was rolled about eight times with a brass roller. The blotter carrying the sheet was then placed on a fresh blotter, a metal disk centered over it, and the sheet transferred to the disk by rolling the stack several times.

Some of the sheets were pressed in the British press for 5 minutes at an indicated pressure of 25 pounds per square inch. (Because the area of the sheet was approximately half that of a standard sheet, the actual pressure would be in the vicinity of 50 pounds per square inch. This would not necessarily be true, however, because of the compressibility of the blotters and the probability that they would assume part of the load. For this reason, the selection of a standard pressure was somewhat arbitrary.) In some experiments it was desired to change the densities of the sheets within fairly wide limits. In these cases the sheets were given a first pressing as outlined above, and were then pressed with fresh blotters for 5 minutes at indicated pressures ranging from 10 to several hundred pounds per square inch.

After pressing, the sheets and disks were placed on the boards already mentioned, the rings centered upon the sheets, and the battens screwed down tightly.

When the sheets were dry, they were trimmed just inside the marks left by the rings; this left them slightly larger in diameter than the electrodes. As a rule, small tabs were left on the circular sheets to facilitate handling. Because the surfaces of the sheets away
from the disks were usually somewhat irregular, the rough side of each specimen was sealed lightly with very fine sandpaper wrapped around a flat block. The paper trimmed from each sheet was saved for ashing.

It was standard practice to make at least five sheets of each sample and to select the best four, by visual inspection, for the electrical tests. In only a few cases, which will be noted, were less than four sheets of any sample prepared. The prepared specimens were numbered and stored in a desiccator prior to conditioning and testing.

ANALYTICAL PROCEDURES

Ash

The inorganic matter present in the samples was estimated by ignition of duplicate samples. Because the samples for these tests were usually small, the microbalance was employed in weighing the residues.

Lignin

Lignin in the different pulps was determined by Institute Method 428.

Density

After the electrical tests had been carried out, the specimens were heated in a drying oven for 1/2 hours at 105° C. and weighed immediately after removal therefrom in a covered and tared Petri dish. Areas were determined by the use of a planimeter. Knowing the weight, area, and thickness (as measured by the modified Schopper caliper), it was
possible to calculate the density of each specimen. Density is reported in grams per cc.

GENERAL METHOD OF MAKING ELECTRICAL TESTS

The prepared specimens were placed in the test capacitor, and the system was sealed and pumped for about 8 hours with the heater operating at 5.3 volts. Pressures of about 1 micron of mercury were usually attained in 4 hours. Delevanti had shown that samples dried to constant electrical properties in 5 to 6 hours; conditioning for 8 hours, therefore, should leave no doubt that equilibrium was reached. At the end of this period, the upper electrode was lowered and allowed to rest on the sample for about 2 1/2 hours before any measurements were made. This final period was required to permit the system to reach thermal and mechanical equilibrium.

When steady-state conditions had been established, the electrical balances were made at the desired frequencies and the necessary data taken for the calculation of the plate separation $(d)$. Sheet thickness $(t)$ was usually measured after the specimen had been removed from the cell.

Early in the work the testing was done at only 1000 and 10,000 cycles per second but, because of the great interest in the properties of paper at commercial frequencies, the desirability of testing at 60 cycles was obvious. However, it will be seen from Equation 5 that, for given values of power factor $(\epsilon_2$ and $\epsilon_0$) at low frequencies, $\Delta \phi$, will be very large. In fact, for plate separations less than about 0.015
inch, measurements at 60 cycles were beyond the range of the instrument, even when \( C_2 \) was at its maximum permissible value. Therefore, when 60-cycle tests were to be made, double sheets were tested, the values obtained for the combinations being very close to the averaged values for the separate sheets. To be sure, the advantage of using two sheets at 60 cycles was lost at 10,000, because at this frequency only was very small. By making \( C_2 \) as large as possible at 60 cycles and as small as permitted by the standard capacitor at 10,000, this difficulty was partially overcome.

Except where noted, the values reported are the averages of tests on four different specimens. When double sheets were tested, the combinations used were I and II, II and III, III and IV, and I and IV, the numerals designating the number of the sheet in whatever set was being tested.

The data obtained for Set II, which may be considered typical, are presented in Table V. It was desired to know the standard deviation and standard errors associated with the results; these are shown for \( k'\), \( \delta'\), and the loss factor at different frequencies in Table VI.

It was of interest to calculate the expression \((k-1)/(k+2)\), and the magnitudes of the errors involved. By differentiation, an expression is obtained by which the standard deviation and error may be calculated. If

\[
\delta k_0 \text{ is found to be } \delta k_0 = 3 \delta k'/(k'+2)^2; \tag{16}
\]

\[
(k-1)/(k+2) = k_0, \tag{15}
\]
### Table V

**DATA FOR SET II**

<table>
<thead>
<tr>
<th>Sheet Combination</th>
<th>Frequency cycles/sec</th>
<th>$C_2\ \mu F$</th>
<th>$C_p\ \mu F$</th>
<th>$AC_i$ (div.)</th>
<th>Plate Separation inches</th>
<th>Sheet Thickness inches</th>
<th>$\xi x 10^3$ radians</th>
<th>$\xi' x 10^3$ radians</th>
<th>$g x 10^3$ radians</th>
</tr>
</thead>
<tbody>
<tr>
<td>I and II</td>
<td>60</td>
<td>1002.4</td>
<td>118.3</td>
<td>11.55</td>
<td>0.0254</td>
<td>0.0204</td>
<td>2.41</td>
<td>1.511</td>
<td>2.401</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1002.4</td>
<td>118.1</td>
<td>10.05</td>
<td></td>
<td></td>
<td>1.220</td>
<td>1.940</td>
<td>4.68</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>114.2</td>
<td>118.5</td>
<td>6.85</td>
<td></td>
<td></td>
<td>1.300</td>
<td>2.068</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>114.2</td>
<td>118.4</td>
<td>0.82</td>
<td></td>
<td></td>
<td>1.554</td>
<td>2.463</td>
<td>5.94</td>
</tr>
<tr>
<td>II and III</td>
<td>60</td>
<td>998.1</td>
<td>129.5</td>
<td>50.70</td>
<td>0.02422</td>
<td>0.01997</td>
<td>2.46</td>
<td>1.681</td>
<td>2.572</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>998.1</td>
<td>129.2</td>
<td>12.40</td>
<td></td>
<td></td>
<td>1.373</td>
<td>2.100</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>322.1</td>
<td>129.5</td>
<td>8.20</td>
<td></td>
<td></td>
<td>1.960</td>
<td>2.234</td>
<td>5.34</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>322.1</td>
<td>129.4</td>
<td>1.05</td>
<td></td>
<td></td>
<td>1.870</td>
<td>2.860</td>
<td>7.10</td>
</tr>
<tr>
<td>III and IV</td>
<td>60</td>
<td>1005.3</td>
<td>128.5</td>
<td>18.40</td>
<td>0.02468</td>
<td>0.01981</td>
<td>2.665</td>
<td>1.629</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1005.3</td>
<td>128.2</td>
<td>12.90</td>
<td></td>
<td></td>
<td>1.449</td>
<td>2.400</td>
<td>6.40</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>335.3</td>
<td>128.6</td>
<td>7.25</td>
<td></td>
<td></td>
<td>1.356</td>
<td>2.250</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>335.3</td>
<td>128.2</td>
<td>0.83</td>
<td></td>
<td></td>
<td>1.651</td>
<td>2.735</td>
<td>7.29</td>
</tr>
<tr>
<td>I and IV</td>
<td>60</td>
<td>997.6</td>
<td>118.4</td>
<td>39.25</td>
<td>0.02617</td>
<td>0.02025</td>
<td>2.463</td>
<td>1.421</td>
<td>2.328</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>997.6</td>
<td>118.1</td>
<td>10.10</td>
<td></td>
<td></td>
<td>1.220</td>
<td>2.000</td>
<td>4.94</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>313.9</td>
<td>118.7</td>
<td>7.10</td>
<td></td>
<td></td>
<td>1.344</td>
<td>2.200</td>
<td>5.41</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>313.9</td>
<td>118.6</td>
<td>0.80</td>
<td></td>
<td></td>
<td>1.513</td>
<td>2.190</td>
<td>6.15</td>
</tr>
</tbody>
</table>

*Heater voltage 5.3 - equivalent to 105° C.*

* $AC_i$ given in terms of divisions on dial. Multiply by 1.14 to obtain value in $\mu F$.

**Thickness of single sheets:**
- I - 0.01026 inch
- II - 0.01015 inch
- III - 0.00982 inch
- IV - 0.00999 inch
TABLE VI

STANDARD DEVIATIONS AND STANDARD ERRORS OF TYPICAL DATA

<table>
<thead>
<tr>
<th>Property</th>
<th>Frequency cycles/sec.</th>
<th>Standard Deviation, ( \sigma )</th>
<th>Standard Error, ( \sigma_x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K' )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 60 )</td>
<td></td>
<td>0.0956</td>
<td>0.055</td>
</tr>
<tr>
<td>( 700 )</td>
<td></td>
<td>0.1415x10^{-3}</td>
<td>0.0840x10^{-3}</td>
</tr>
<tr>
<td>( 1000 )</td>
<td></td>
<td>0.0958</td>
<td>0.0535</td>
</tr>
<tr>
<td>( 10,000 )</td>
<td></td>
<td>0.1768</td>
<td>0.1020</td>
</tr>
<tr>
<td>( K'8' )</td>
<td></td>
<td>0.1668</td>
<td>0.0965</td>
</tr>
</tbody>
</table>

or, if \( \delta K' \) is the standard error \( \sigma_x \) for \( K' \), the following expression is obtained:

\[
\sigma_x \text{ for } K_0 = 3 \frac{\sigma_x}{K'+2)^2}. \quad (17)
\]

Usually deviations less than \( 3\sigma_x \) from the true mean are considered within experimental error; from the data in Table VI it is seen that when \( K' \) is 2.5,

\[
3 \sigma_x = (3 \times 0.17)(0.5)^2 = 0.025. \quad (18)
\]

This result would hold for a paper density of about 0.3. When the density becomes very low, \( K' \) likewise decreases and \( 3\sigma_x \) increases.
EXPERIMENTAL RESULTS

RELATION BETWEEN ELECTRICAL PROPERTIES AND DENSITY

Delevanit (1) attempted to establish the functional relations between sheet density and $k^\prime$ and loss factor but met with little success, probably because of the uncertainties in his measurement of $a$. He attempted to fit his data to the Clausius-Clapeyron relation, which states that $(k^\prime-1)/(k^\prime+1)$ is directly proportional to density; although he obtained straight lines, they intersected the density axis at a density of about 0.3. With regard to the loss factor, it can be shown theoretically that this should also be directly proportional to density but, again, although straight line relations were obtained, they intersected the density axis some distance to the right of the origin.

To check this work a series of sheets were prepared from Rup III (acid-washed, for reasons which will explained in a subsequent section), and a fairly wide range of densities were obtained by wet-pressing. Data on these sheets are presented in Table VII.

<table>
<thead>
<tr>
<th>Set</th>
<th>Density</th>
<th>$k^\prime$</th>
<th>$\delta^\prime \times 10^3$ radians</th>
<th>$k^{18^\prime} \times 10^3$ radians</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.771</td>
<td>2.45</td>
<td>2.03</td>
<td>4.99</td>
</tr>
<tr>
<td>11</td>
<td>0.343</td>
<td>2.51</td>
<td>2.50</td>
<td>5.25</td>
</tr>
<tr>
<td>13</td>
<td>0.547</td>
<td>1.75</td>
<td>1.69</td>
<td>2.96</td>
</tr>
<tr>
<td>14</td>
<td>0.936</td>
<td>3.03</td>
<td>2.28</td>
<td>6.91</td>
</tr>
<tr>
<td>15**</td>
<td>0.292</td>
<td>1.28</td>
<td>1.10</td>
<td>1.44</td>
</tr>
</tbody>
</table>

* Data on only 2 sheets  
** Data on 1 sheet
Inspection of Figure 12 will show that the agreement with the Clausius-Mosotti relation is rather good, and well within experimental error. Loss factor is plotted against density in Figure 13; here there is more scattering of the points but, if the dotted line is regarded as the true curve, most of the points are within experimental error. The relationship between $\overline{K^1}$ and density is shown in Figure 14.

It appears, therefore, that the Clausius-Mosotti relation can be used as a means for correcting values of $K^1$ to a standard density, and that the assumption of direct proportionality between loss factor and density is justified (see Figure 13). In the two sections immediately following, all values were corrected to a density of 0.8 gram per cc. by the following procedure:

1. Using the Clausius-Mosotti relation, a corrected value of $K^1$, which will be referred to as $K''$, was obtained.

2. Assuming direct proportionality between loss factor and density and assuming also that the averaged values of loss factor calculated from the data were correct, corrected values of $K''S''$ were obtained graphically.

3. Corrected values of power factor, $S''$, were calculated by dividing the corrected loss factors by the corresponding $K''$.

EFFECTS OF METALLIC CATIONS

The work of McLean (13) has given strong indication that the inorganic constituents of paper may be chiefly metallic ions held by
Figure 10

Relation between sheet density and \((\frac{L-1}{L+1})\)

Vertical error bars indicate the uncertainty.
FIGURE 14

RELATION BETWEEN DENSITY AND H2

Dotted curve computed from Clusius-Vennel relation, Figure 12
carboxyl groups. Further, he showed that acid washing would remove most of this material and that, by treating the washed pulps in salt solutions, the ash content was restored to very nearly its original value. It appeared that, by modifying this technique, it should be possible to exercise some control over the amount of cationic material adsorbed by the pulps, which could then be tested to discover whatever influence the metal ions had on electrical properties.

A sample of Pulp III was beaten for 30 minutes in the lampen mill. This pulp was extracted for two periods of 4 and 17 hours, respectively, in cold 0.05 N hydrochloric acid at 1 per cent consistency with slow agitation. The pulp was then extracted for 10 hours in boiling distilled water, using three changes of water. The acid extraction was intended to remove as much ash as possible, and the residual acid was removed by the water. This pulp was divided into portions and several sets of sheets were prepared, as follows:

Set 1. Sheets made from the extracted pulp.

Set 2. Sheets prepared from the extracted pulp treated for 3.5 hours at 2 per cent consistency in cold 1⁄4 calcium chloride solution, then filtered and washed with distilled water until the extract gave no precipitate on addition of silver nitrate.

Set 3. Sheets prepared exactly as in Set 2 except for the time in contact with the 1⁄4 calcium chloride solution, which was 20 hours.

As controls, additional sheets were made from samples of Pulp III, as follows:
Set 4. Beaten but unextracted pulp, sheets prepared with tap water.

Set 5. Acid-washed pulp (remainder from Set 1) given a 70-hour extraction in cold distilled water.

Set 6. Beaten but untreated pulp (no acid wash), extracted for 20 hours in cold distilled water, for 10 hours in boiling water, and finally for 30 hours more in cold water.

The resulting sheets were tested at 1000 and 10,000 cycles per second. The data obtained are presented in Table VIII and are shown graphically in Figure 15. It appears that acid washing and, to a lesser extent, water extraction are effective in reducing the power factor of kraft paper. The indication is that the inorganic constituents contribute to losses.

Examination of the ash data for Sets 1, 2, and 3 shows that the process of sheetmaking introduced an appreciable amount of contaminating material into the pulp. This was caused partially by copper, which was found to be present in the distilled water and which was apparently taken up by the pulp in the sheet formation. However, it was later found that even with water of great purity a certain amount of material was taken up by the pulp. Presumably the sheet mold was the source of this contamination and, regardless of the care taken in cleaning the apparatus, the trouble could not be completely eliminated.

It will also be noted that, even on long exposure of the washed pulp to a fairly strong salt solution, the ash content returned
## Table VIII

**Effects of Various Treatments on Kraft Pulp**

1000 and 10,000 Cycles per Second.

<table>
<thead>
<tr>
<th>Set</th>
<th>Ash Pulp</th>
<th>Ash Sheets</th>
<th>$E''$</th>
<th>$\frac{E''g'' \times 10^{3\circ}}{1000}$</th>
<th>$10,000$</th>
<th>$\frac{\delta'' \times 10^{3\circ}}{1000}$</th>
<th>$10,000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.19</td>
<td>2.30</td>
<td>3.55</td>
<td>3.74</td>
<td>1.543</td>
<td>1.627</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0.17</td>
<td>2.492</td>
<td>4.25</td>
<td>5.34</td>
<td>1.704</td>
<td>2.142</td>
</tr>
<tr>
<td>3</td>
<td>0.22</td>
<td>0.29</td>
<td>2.475</td>
<td>4.15</td>
<td>5.36</td>
<td>1.795</td>
<td>2.160</td>
</tr>
<tr>
<td>4</td>
<td>0.54</td>
<td>0.54</td>
<td>2.412</td>
<td>4.52</td>
<td>5.77</td>
<td>1.915</td>
<td>2.155</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>0.19</td>
<td>2.128</td>
<td>3.25</td>
<td>3.67</td>
<td>1.525</td>
<td>1.721</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>2.245</td>
<td>3.71</td>
<td>4.45</td>
<td>1.653</td>
<td>1.583</td>
</tr>
</tbody>
</table>

* The unit is the radian.
CURVES SHOWING EFFECTS OF DIFFERENT TREATMENTS OF PULP

FIGURE 15
to little more than half the ash of the original pulp. It is possible that a large part of the original ash was in the form of relatively free salt molecules and was washed out or, more likely, that the acid and water extractions removed part of the organic material responsible for ion adsorption.

In order to eliminate the possible existence of effects resulting from variations in the severity or method of treatment, two additional sets of sheets were prepared from another sample of Pulp III. The pulp was beaten for 15 minutes in the Jensen mill (shorter beating times resulted in better formation of the sheets), and given a 15-minute extraction in cold 0.1 M hydrochloric acid at 1 per cent consistency. (This short acid extraction was found to be as effective as longer times for the removal of cations.) The extracted pulp was filtered and washed until the extract gave no precipitate on the addition of silver nitrate, and the cake was shredded by hand; 1.5-gram (oven-dry basis) samples were weighed and disintegrated in several hundred cc. of distilled water in glass beakers with a motor-driven glass stirrer. Half of these samples were made into sheets without further treatment, and are designated Set 7. To each sample remaining, 4 cc. of a 1 per cent solution of calcium chloride were added during disintegration; these sheets form Set 8. Previous experiments had shown that this amount of salt was insufficient to utilize fully the cation-adsorbing capacity of the pulp; on the basis of McLean's work (13), it could be assumed, therefore, that all the calcium ions took part in exchange reactions and that most of the hydrochloric acid formed by the liberation of hydrogen ions would be washed out when the pulp was drained.
The data yielded by these sheets are presented in Table IX and are shown graphically in Figure 16.

**TABLE IX**

**DATA FOR SHEETS WITH CONTROLLED ADULTION OF SALT**

<table>
<thead>
<tr>
<th>Property</th>
<th>Set 7</th>
<th>Set 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash of pulp, %</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Ash of sheets, %</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>(k^p)</td>
<td>2.39</td>
<td>2.43</td>
</tr>
<tr>
<td>(k^p \times 10^3), radians</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>4.77</td>
<td>4.80</td>
</tr>
<tr>
<td>200</td>
<td>4.55</td>
<td>4.62</td>
</tr>
<tr>
<td>1000</td>
<td>4.38</td>
<td>4.62</td>
</tr>
<tr>
<td>10,000</td>
<td>5.45</td>
<td>6.85</td>
</tr>
<tr>
<td>(S^p \times 10^3), radians</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>2.00</td>
<td>1.93</td>
</tr>
<tr>
<td>200</td>
<td>1.91</td>
<td>1.86</td>
</tr>
<tr>
<td>1000</td>
<td>1.84</td>
<td>1.86</td>
</tr>
<tr>
<td>10,000</td>
<td>2.29</td>
<td>2.76</td>
</tr>
</tbody>
</table>

* Cycles per second

Because the sheets of these two sets were prepared under identical conditions, one is justified in assuming that any effects observed resulted from variations in the amount of inorganic material adsorbed. It will be noted that, in the preparation of Set 7, there appears to have been slight contamination; however, its ash was roughly half that of Set 8, so that any effects from adsorbed metallic ions should be apparent. It is seen in Figure 16 that, at the lower frequencies, power and loss factors for the two sets are practically identical, whereas at 10,000 cycles per second these properties increase much more rapidly for Set 8 than for Set 7.
FIGURE 16

LOSS FACTOR, LOSS ANGLE, AND $k''$ vs. FREQUENCY
FOR PULPS OF DIFFERENT CATION CONTENT
This result may give some insight into the known tendency for the losses in paper to become very large at high frequencies, which precludes the use of paper capacitors in high-frequency radio work. It is unfortunate that higher frequencies were not available; it would be interesting to extend this study over a greater part of the spectrum.

Effects of Variation of Lignin Content

Samples of Pulps I, II, III, and IV were beaten, acid washed, and formed into sheets in a manner identical to that followed with Set 7. The purpose of acid washing was to reduce the ash content of each pulp to approximately the same value. In order that all sheets should have about the same density, they were given wet pressings at different pressures, the proper values having been determined by previous experiment. Because the resulting sheets showed relatively slight density variations, the corrections would be small and any errors inherent in the correction procedure would be minimized.

The data from these experiments are shown in Table X and in graphical form in Figure 17.

Although some of the values of power factor obtained for different pulps differ by less than the experimental error, the consistency of the trends indicated in Figure 17 may be considered good evidence of the existence of true effects from the lignin present. There is certainly little question but that a real difference exists between Pulps I and III, for example.

It will be noted that, in spite of the acid wash given each
TABLE I

INFLUENCE OF LIGNIN CONTENT

<table>
<thead>
<tr>
<th>Property</th>
<th>Pulp I</th>
<th>Pulp II</th>
<th>Pulp III</th>
<th>Pulp IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set 9</td>
<td>Set 10</td>
<td>Set 11</td>
<td>Set 12</td>
</tr>
<tr>
<td>Ash, %</td>
<td>0.248</td>
<td>0.204</td>
<td>0.186</td>
<td>-</td>
</tr>
<tr>
<td>Lignin, %</td>
<td>6.80</td>
<td>6.00*</td>
<td>2.28</td>
<td>Bleached</td>
</tr>
<tr>
<td>$E^*$</td>
<td>2.41</td>
<td>2.41</td>
<td>2.41</td>
<td>2.20</td>
</tr>
</tbody>
</table>

$E^* 60^x \times 10^3$, radians

<table>
<thead>
<tr>
<th></th>
<th>60°</th>
<th>200</th>
<th>1000</th>
<th>10,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.70</td>
<td>6.25</td>
<td>5.92</td>
<td>4.98</td>
<td></td>
</tr>
<tr>
<td>5.62</td>
<td>5.52</td>
<td>5.02</td>
<td>4.33</td>
<td></td>
</tr>
<tr>
<td>6.53</td>
<td>5.30</td>
<td>5.17</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>8.50</td>
<td>7.74</td>
<td>6.20</td>
<td>5.68</td>
<td></td>
</tr>
</tbody>
</table>

$5^* 60^x \times 10^3$, radians

<table>
<thead>
<tr>
<th></th>
<th>60°</th>
<th>200</th>
<th>1000</th>
<th>10,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.78</td>
<td>2.69</td>
<td>2.45</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>2.33</td>
<td>2.29</td>
<td>2.08</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>2.71</td>
<td>2.20</td>
<td>2.14</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>3.56</td>
<td>3.21</td>
<td>2.57</td>
<td>2.58</td>
<td></td>
</tr>
</tbody>
</table>

* This value of lignin content was estimated from Permanganate No., which was very close to that for Pulp I.

** Cycles per second

In pulp, there were differences in content of inorganic material, and it might be thought that these would have some bearing on the results obtained. The relatively high ash of Set 9 may, to be sure, be partially responsible for the rapid rise of its power factor at 10,000 cycles per second. However, as was pointed out with reference to the data in Figure 16, approximately doubling the ash of paper appears to have little effect at lower frequencies. In the data of Table I, considerably smaller variations of ash appear than in Table IX; therefore, it is reasonable to assume that, at these low frequencies, the lignin, or factors associated with the lignin, are almost wholly responsible for the observed effects.
Loss Factor, Loss Angle, and $E''$ vs. Frequency for Pulps of Different Lignin Content
Because there is evidence that the presence of lignin is responsible for some of the dielectric losses in kraft paper, it seemed desirable to know something about the electrical properties of lignin itself. Therefore, a small sample of native lignin, prepared from black spruce by Dr. Brauns of The Institute of Paper Chemistry, was studied.

In attempts to transfer the substance to the test capacitor, sedimentation of the material from a water dispersion onto one of the electrodes was tried; this proved futile because, when the water was siphoned off and the layer dried, the material checked badly and did not adhere to the surface. A less accurate method was adopted; a 0.5-gram sample of the powdered lignin was spread as evenly as possible on the lower electrode with a spatula, and compressed into a more compact layer by pressing the upper electrode down firmly and giving it a slight random rotatory motion. Even this was not very satisfactory because, on lifting this plate, the material tended to adhere to its surface in spots, and there was no certainty that these patches would come into exact register with the corresponding holes in the main mass of the lignin. The experiment was carried out, however, to arrive at an approximate idea of its behavior.

The system was pumped at a pressure of about 1 micron of mercury for 24 hours with the electrodes at room temperature. The plate was then lowered, and sufficient time allowed for equilibrium to be established. Measurements were taken at 25°, 45°, 70°, and 82° C. for three different frequencies, at least 5 hours being allowed between the
change of the heater voltage and the measurements. \( d \) was estimated from a knowledge of the respective dial settings of the cellers obtained with the electrode surfaces in contact (before the introduction of the lignin) and with the upper electrode resting on the lignin layer. This distance was found to be 0.02736 inch. Knowing \( d \), the plate area, and the weight of the sample, the density of the material between the plates was found to be approximately 0.15 gram per cc.

The data are presented in Table XI and are shown in Figures 18 and 19. There is evidence in these curves of a dispersion of the power factor with a change of frequency, with suggestions of the existence of maxima at the high frequencies for low temperatures. These maxima appear to shift to lower frequencies at higher temperatures, which is a characteristic of compounds containing polar groups. It is conceivable, therefore, that the highly polar carbonyl and phenolic hydroxyl groups, which are known to exist in lignin, may have some influence (16, 24).

\( K \) for a density of 0.15 gram per cc. is about 1.38; assuming that the substance follows the Clausius-Mossotti relation, \( K \) at a density of 0.5 gram per cc. would be about 3.5. Compared with paper of the same density, this is a relatively high specific inductive capacity. Further, it will be seen that, even at this low density, the loss factor of lignin is about the same as that of the papers tested; at comparable densities, the loss factor of lignin would be much greater than that of paper.

It is seen from the data that \( K \) increases slightly with an
TABLE XI

PROPERTIES OF NATIVE LIGNIN AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Cycles/Sec.</th>
<th>25° C.</th>
<th>45° C.</th>
<th>70° C.</th>
<th>82° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.278</td>
<td>1.290</td>
<td>1.301</td>
<td>1.333</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 x 10³, radians</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.165</td>
<td>1.183</td>
<td>1.218</td>
<td>1.483</td>
</tr>
<tr>
<td>1000</td>
<td>1.203</td>
<td>1.098</td>
<td>1.273</td>
<td>1.243</td>
</tr>
<tr>
<td>10,000</td>
<td>1.379</td>
<td>1.100</td>
<td>1.057</td>
<td>0.825</td>
</tr>
<tr>
<td>6 x 10³, radians</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.496</td>
<td>1.527</td>
<td>1.710</td>
<td>1.978</td>
</tr>
<tr>
<td>1000</td>
<td>1.539</td>
<td>1.418</td>
<td>1.642</td>
<td>1.618</td>
</tr>
<tr>
<td>10,000</td>
<td>2.355</td>
<td>1.307</td>
<td>1.336</td>
<td>1.069</td>
</tr>
</tbody>
</table>

* Estimated temperature of lignin

increase in temperature. Further, whereas at low temperatures it is constant over the frequency range, at the higher temperatures there appears to be a slight decrease associated with frequency increase.

The power and loss factors and $\kappa$ variations suggest that there may be regions of anomalous dispersion for this type of lignin in the solid state. Here, again, it would have been desirable to make measurements over a much broader range of frequencies. In attempting to correlate these data with those obtained for the pulps, one encounters apparent contradictions; it will be observed that for Set 9 (6.80 per cent lignin) the power factor at 105° C. increases more rapidly between 1000 and 10,000 cycles per second than that of papers containing less lignin, whereas for the native lignin at the same temperature this
FIGURE 16
LOSS FACTOR AND LOSS ANGLE FOR NATIVE LIGNIN
AT DIFFERENT TEMPERATURES AND FREQUENCIES
Figure 13

Tension x, vs. 6 on wire links
against load conditions

<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10,000 cycles/sec.</td>
</tr>
<tr>
<td>2</td>
<td>1000 cycles/sec.</td>
</tr>
<tr>
<td>3</td>
<td>50 cycles/sec.</td>
</tr>
</tbody>
</table>

Indicated late temperature °C.
property shows a considerable decrease in the same frequency range. This could be interpreted to mean that factors other than the amount of lignin present in the paper exert the controlling influence in determining the shape of loss factor versus frequency curves. However, variations in the lignin content will determine the relative positions of the curves on the graph.
GENERAL DISCUSSION

An attempt has been made to obtain information which would further elucidate the behavior of cellulosic materials in alternating electric fields. The specimens were dried at elevated temperatures and under conditions which allowed fairly free exposure to an ambient atmosphere of very low pressure (usually less than 2-3 microns of mercury). It could be assumed, therefore, that the moisture content of the material was very low, although in the absence of adsorption data at these low pressures it is not possible to estimate the amounts present. At any rate, the samples, when tested, had reached a condition which resulted in constancy of electrical properties as pumping continued.

The possible influence of variations of water-vapor pressure inside the chamber was a source of concern in so far as these variations might conceivably affect water removal from the samples. If the system had been perfectly tight, one could assume that at equilibrium the atmosphere in the chamber would consist entirely of water vapor at whatever pressure was being maintained. However, it is more probable that minute leaks existed in the chamber, which would mean that at equilibrium the water-vapor and gas pressures would be in the same ratio as their respective pressures in the outside atmosphere; consequently, the water-vapor pressure would be very low, although not zero. By surrounding the chamber with thoroughly dried air, one could expect the water-vapor pressure inside would be reduced to a minimum, as the constant replacement of this atmosphere by dry air would gradually sweep out most of the
water molecules. To check this supposition, a stream of air which had been passed through concentrated sulfuric acid and anhydride was run into the well-sealed shield box surrounding the chamber. The results obtained, however, were not significantly different from those secured without such dried air. The uncertainties involved in this method of controlling conditions inside the evacuated space will be apparent when one considers the impossibility of controlling the leaks around the gasket—one time they may be large and another time negligible.

A much better system would have involved the use of a needle valve capable of very fine adjustment, so that any pressure could be maintained simply by controlling the rate at which gas was admitted.

Assuming that all samples tested had the same attraction for water, it may be further assumed that, for constant temperature and pressure conditions, the amounts of water in the various samples were the same. This would mean that the water remaining in the sheets would make a constant contribution to the specific inductive capacity and loss factor, and that all variations could be interpreted in terms of the other variables under consideration.

The Clausius-Mosotti expression was derived originally in terms of relatively simple systems, i.e., gases and simple liquids, in which only polarization resulting from molecular distortion in the applied field was considered. When the influence of permanent dipoles is also taken into account, the expression becomes more complicated; for solids it would be extremely so, if consideration were to be given to every factor contributing to $\kappa$. On the basis of the original simple
assumptions, it may seem surprising that the results for paper fit the expression. The simplified form of the equation is

\[
\frac{(k-1)}{(k+2)} = \beta \phi.
\]

In the original derivation of the expression, \( \beta \) is a constant term which includes the molecular weight, Avogadro's number, and the polarizability per molecule. However, it may be considered to include all forms of polarization per unit mass—that is, it would represent the sum of electronic, atomic, and molecular polarizations, as well as those resulting from interfacial effects such as the movement of ions along boundaries. If it is assumed that tighter packing of these unit masses caused no changes in polarizability, increasing the density would be expected to yield the result which has been obtained.

It must be pointed out that this explanation does not present a complete picture of the effects observed, inasmuch as it considers merely the total polarization and gives no key as to the types involved or the relative magnitudes of each. Therefore, although it appears to offer an excellent means of putting data for different sheets on a comparable basis, it offers no explanation of the fundamental causes of the observed behavior of paper.

The data presented indicate that the power factor of paper is a minimum at about 1000 cycles per second. Between this frequency and 10,000 cycles per second there is a marked increase in loss; in other words, a region of anomalous dispersion is indicated. The evidence shows that the increase is in some way associated with the metallic ion content, although the mechanism is not apparent. On the basis of the
Murphy and Lowry theory, it might be the result of the motion of the ions in water films. However, the results of Bolam's studies do not substantiate this; if his conclusion (that the cations are chemically attached to carboxyl groups) is correct, it seems more probably that they would function more in the manner of polar groups oscillating elastically about their points of attachment. This latter hypothesis is strengthened by the fact that the samples tested had been prepared with very small amounts of added salt, so small, in fact, that the point of saturation with salt was not reached and the amount of free ionic material present should have been extremely small. It is appreciated, of course, that the removal of all ionic material from paper is very difficult, and no doubt traces of such material remained. Therefore, the possibility exists that, although displacement of chemically bound cations about fixed positions may be responsible for most of the loss due to inorganic material, movements of free ions may make some contribution.

Morgan and Yager, in comparing the properties of different high polymers, showed that the losses in those having no polar groups (such as polystyrene) were substantially less than those containing such groups. Because cellulose materials contain alcoholic hydroxyl groups, as well as phenolic hydroxyl groups and carbonyl groups in the associated lignin, it could logically be thought that these might make appreciable contributions to \( K \) and the losses. Evidence for this is presented in the results which show some dependence of these properties on the lignin content of paper and in those obtained with native lignin. Here, again, it may be considered that the polar groups oscillate about
fixed positions, because the size of the molecules involved would make molecular orientation rather difficult, if not impossible.
CONCLUSIONS

As a result of the work carried out in this study, the following conclusions are presented:

A means for measuring the separation between two electrodes with the sample in situ and in vacuo has been devised and found to give satisfactory results.

Paper has been found to follow the Clausius-Mosotti expression, which relates $k$ to density.

Pulp washing experiments have shown that extraction with dilute acid followed by washing with water and, to a lesser extent, water extraction alone are effective in reducing the loss factor of kraft pulp.

The influence of metallic cations, presumably held in chemical combination with certain constituents of the pulp, has been investigated. It appears that the presence of such materials exerts little influence at power frequencies, but has a considerable effect at frequencies which approach the upper limit of the audible range.

The dielectric losses of papers of different lignin contents were studied; it is evident that papers having a high lignin content will have higher losses than those containing little or no lignin.

A study was made of the properties of native lignin over the frequency range of 60 to 10,000 cycles per second. Although the use of a broader range of frequencies would have been desirable, the existing data gives strong evidence of regions of anomalous dispersion for this
material. It is thought that this behavior is associated with the presence of strongly polar groups in the lignin molecules. Whereas the size of the molecules would probably prevent molecular orientation in an applied field, elastic displacement of these groups about their points of attachment could be regarded as responsible for the energy absorption.

At comparable densities, lignin has a greater specific inductive capacity and power factor than kraft paper. It might be expected, then, that even a small amount of lignin would be responsible for an appreciable contribution to the dielectric loss in paper. This would be in confirmation of results reported above on papers of different lignin contents. At 50 cycles per second, an increase of power factor of about 15 per cent was shown to be associated with an increase of lignin from 0.00 to 6.30 per cent.


