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A Study of the Relationship Between the Dielectric Constant and Crystallinity of Cellulose

by Herman Ward Verseput

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A STUDY OF THE RELATIONSHIP BETWEEN THE DIELECTRIC CONSTANT AND CRYSTALLINITY OF CELLULOSE

A thesis submitted by

Herman Ward Verseput

B.E. 1943, Yale University
M.S. 1946, Lawrence College

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INTRODUCTION

Many of the properties of the cellulose fiber have been explained on the basis of evidence obtained from microscopic observations, and a long history of chemical research has yielded a fairly clear understanding of the makeup of the cellulose molecule. In recent years, however, there has grown the realization that many properties of cellulose are due to the nature of its supermolecular structure--i.e., the manner in which the cellulose chain molecules are assembled.

The nature of this structure has complicated its characterization, but by the use of indirect methods, the searchers have pieced together theories to explain phenomena, discarded them when new evidence has been brought to light, and developed new theories, until a concept has been developed which helps to explain x-ray diffraction, the rates of certain reactions, the sorptive power of cellulose for water and other liquids, variations in density and optical properties, and now the electrical properties of cellulose.

Mark (1), in a concise survey of the submicroscopic structure of cellulose, describes this concept as follows:

> "The individual macromolecules of cellulose can be very differently arranged in respect to each other, and it is this difference in arrangement which represents the submicroscopic structure of a cellulose sample. The following cases seem to be particularly characteristic:
>
> "(a) The individual macromolecules are arranged completely at random. According to Hermans and Kratky, there is always a tendency for a certain order of the chain segments in very small domains (say 20 to 30 A) but, within an individual chain, it changes its direction in a random fashion, and there is no

regularity in the arrangement of the neighboring chains. Such domains are usually referred to as 'amorphous' or 'disordered' areas; they have low specific gravity, high water absorption, and high chemical reactivity with many reagents; they are responsible for softness and flexibility of the sample, and they produce a diffuse halo in the x ray diagram.

"(b) The individual macromolecules are arranged in such a manner that their axes are parallel and that there exists also a complete lateral order in the sense that corresponding groups in the individual chains point in the same direction. As a consequence, one has a perfect three-dimensional order which resembles closely the arrangement of atoms, ions, or molecules in a crystal lattice. Therefore, the areas in which such a high degree of order prevails are usually designated as the 'crystallized' or 'completely ordered' domains. They have a high specific gravity, low water absorption, poor reactivity, impart to the material a high Young's modulus, stiffness, and tenacity, and produce an x ray diagram having a number of sharp and intense spots.

"(c) If the individual chains are parallel with their long axes but are not completely ordered as far as their lateral arrangement is concerned, an intermediate state of axial order, but lateral disorder exists. Areas in which this type of organization prevails are referred to by Baker and Fuller as 'mesomorphous domains'. Their specific gravity, water absorption, and reactivity are intermediate between those of the amorphous and crystalline areas. If, in a given sample, the mesomorphous areas have a tendency to crystallize, the sample will show a tendency to stiffen; if the mesomorphous domains are on the verge of becoming amorphous, the material will show a tendency to soften.

"In defining the physical structure of a cellulose sample, it is of great importance to know how much of it is in the different states of organization as enumerated above. The presently available methods do not provide for an exact answer to this question but permit only an approximate estimate of the degree of order in a given material. Usually, the results of the various methods are presented as the percentage of crystalline or difficultly accessible areas in a given sample, which probably always comprises the fully ordered domains and in addition a certain, unknown proportion of the mesomorphous areas."

Reviews of the development of modern concepts of the submicroscopic structure of cellulose, which is summarized briefly here, have been given by Meyer (2), Sisson (3), and Heuser (4).

CRYSTALLINE STRUCTURE

Although earlier workers realized that cellulose was anisotropic, Nägeli (5), in 1858, was the first to propose a theory as to its structure. His theory was that cellulose was composed of submicroscopic, anisotropic crystalline particles, which he named micelles. Even though Gilson (6), in 1893, and Ambronn (7), in 1911, determined that cellulose was crystalline, Nägeli's theory did not receive much support until the technique of analysis by x-ray diffraction was developed.

The crystallinity of cellulose was first confirmed by means of x-ray analysis in 1913 by Nishikawa and Ono (8), who concluded from their diagrams of hemp fiber that small crystallites are present, oriented parallel to the fiber axis. Their work remained hidden for a number of years, however.

Such an x-ray examination is based upon the fact, discovered by von Laue (9) in 1912, that the regular pattern of atoms in a crystal lattice behaves as a three-dimensional diffraction grating to x-radiation. This was made applicable to the study of cellulose by the discovery, by Debye and Scherrer (10) and by Hull (11) that fine powders, as well as large single crystals, may be analyzed for ultimate crystalline structure. Clark (12) describes the principle as follows:

> "The diffraction depends upon the fact that in a fine powder the grains are arranged in an entirely chaotic manner. There should be enough particles in this array, turned at just the right angle to the incident primary beam of monochromatic x-rays, to allow strong reflection from one set of parallel planes; other particles turned at another angle will produce

reflection from another set of planes (the same set in many particles cooperating). Thus a beam passing through a powder specimen will fall upon a perpendicular flat photographic film as a series of concentric rings, each uniformly intense throughout and corresponding to one set of planes."

Scherrer began x-ray examination of cellulose in 1918, but did not obtain a crystalline fiber-diagram until 1920 (13).

Other workers have carried on this program, notably Herzog and Jancke (14), Polanyi (15,16), Sponsler and Dore (17), and Meyer and Mark (18-21), and have produced the well-accepted dimensions of the unit cell of the two most common forms of cellulose shown in Table I.

TABLE I

DIMENSIONS OF CELLULOSE UNIT CELLS

Axis	Cellulose I (21) (Native)	Cellulose II (22) (Mercerized)
a	8.35 A.	8.1 A.
b	10.30 A.	10.3 A.
c	7.90 A.	9.1 A.
α	84°	62°

These x-ray data were combined with the chemical data available, and a structure for the cellulose unit cell proposed by Meyer and Misch (21), as shown in Figure 1. This unit cell is generally accepted at this time.

MICELLAR STRUCTURE

In a cellulose fiber, this unit cell is repeated in all directions to form a crystalline region. This crystalline region cannot

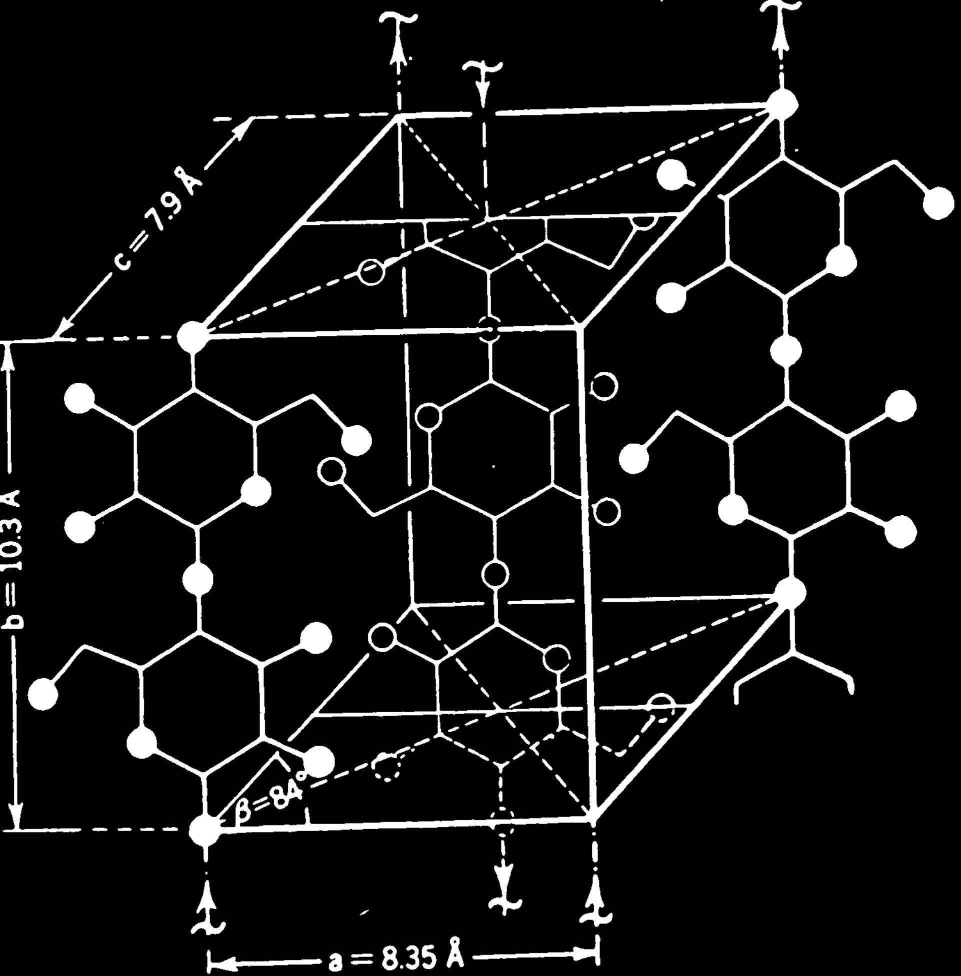


Figure 1
The Cellulose Unit Cell (Mark)

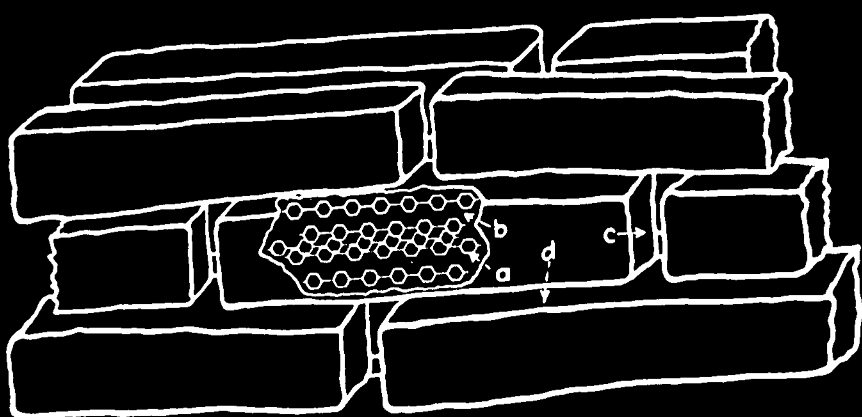


Figure 2
The Micellar Theory (Seifriz, 28)

extend indefinitely, however, since it is known that the cellulose fiber is not a single crystal, but the crystallinity is confined to limited domains known as micelles, or preferably crystallites. The extent of these crystallites has been estimated by Meyer and Mark (23), Hess (24), and more recently confirmed by Hosemann (25) and Morehead (26) as being at least 60 to 70 A. wide (at right angles to the fiber axis) and at least 600 A. long (along the fiber axis).

The exact nature of these crystalline portions and their relationship to the less organized, or amorphous portions, has been the subject of considerable discussion, theorizing, and experiment.

MICELLAR THEORY

When the crystalline nature of cellulose was definitely established by x-ray data, Nägeli's micellar theory was revived. Herzog (27), for example, considered the fiber as a two-phase system, containing a crystalline and an intercrystalline material. Meyer and Mark (18,23) used the micellar theory to explain the physical and chemical data then available. The micellar concept embraces a brickwork sort of structure, in which the bricks represent the crystalline portions, or micelles, and the mortar is the amorphous material (Figure 2).

In the 1930's the realization grew that the cellulose molecule is probably more than 10 times as long as the 600 A. estimated for the micelle, so that the micellar theory was discarded. It was replaced by the continuous structure theory.

CONTINUOUS STRUCTURE THEORY

Since there was nothing about the x-ray data that proved the existence of discrete crystalline micelles, it seemed to some, particularly Astbury (29), Neale (30), Peirce (31), and Sponsler (32), that the discontinuity implied by the x-ray data could be better rationalized with the chain length of the macromolecule by postulating a continuous, approximately crystalline structure, interspersed occasionally by localized disorganization, as shown in Figure 3.

Although the physical properties of native fibers are explained more satisfactorily by this continuous structure theory, the properties of regenerated materials seem to be better explained by the micellar theory. Therefore, several attempts have been made to develop a compromise theory which would fit both sets of circumstances.

CELLULOSE PARTICLE THEORY

Farr (33,34) has proposed that fibers are made up of microscopic particles. This theory fulfills many of the x-ray requirements and is useful in explaining the formation and morphological structure of native fibers, but it is not in agreement with many of the chemical properties of cellulose, nor is it of much value in connection with regenerated fibers.

FRINGE MICELLAR THEORY

At the present time, the theory most generally accepted is the micellar network, or fringe micellar theory, which Sisson (35)

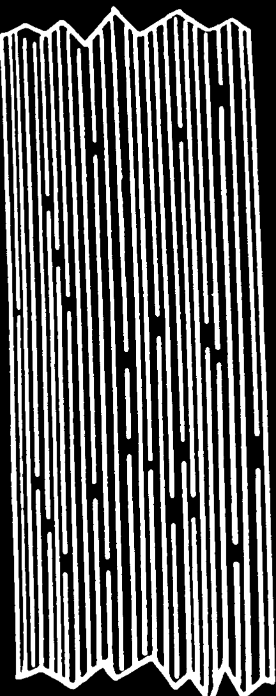


Figure 3

inuous Structure Theory

(Mark)

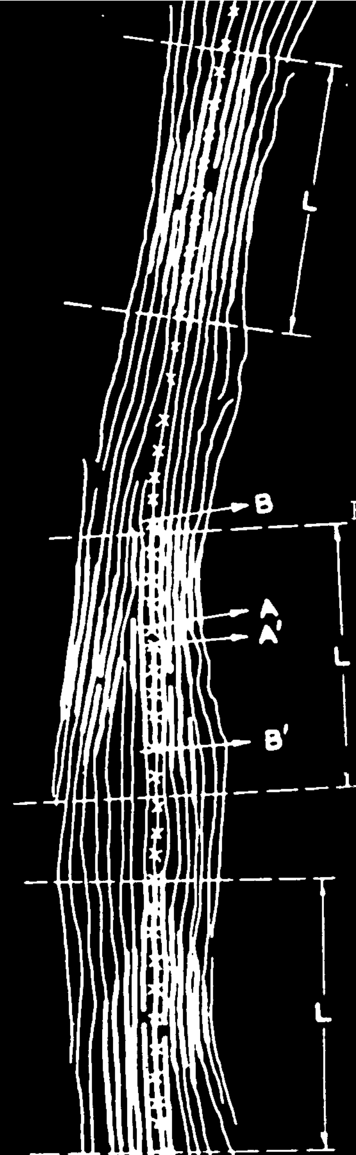


Figure 4

Fringe Micellar

Theory

(Mark)

describes as follows:

> "According to this theory the crystalline areas are not clearly separated from each other by a distinct micellar surface, but rather by an area of partially parallel but disorganized chains. Long crystalline particles are postulated whose outer form is irregular, and defined, especially at the ends, by the projecting, irregularly arranged, primary valence chains which may pass through several micelles and thus tie them together. This gives a netlike structure in which chains occur that are partially crystalline and partly amorphous. Furthermore, it has been proposed that the crystallites are formed as a result of the free rotation of glucose units around the oxygen bridges; crystalline areas result when a group of chains coalesce in a three-dimensional arrangement, while amorphous regions are produced when there is a divergence from the crystalline arrangement. As a consequence, cellulose gives a discontinuous pattern (36)."

This theory is illustrated in Figure 4.

As can be seen, one macromolecule may extend through the length of several micelles. Since the intermolecular forces are stronger in the well-organized or crystalline areas than in the amorpheus regions, the physical properties of the fiber will be greatly affected by the relative proportions of crystalline and amorpheus material. As a result, many investigators have interested themselves in methods for the determination of this ratio.

THE RATIO OF CRYSTALLINE TO AMORPHOUS MATERIAL

As has already been shown, the concept of the crystallinity of cellulose is a rather nebulous one, since it is apparent that the crystalline regions are not sharply defined, but rather consist of groups of molecules which happen to have fallen together, at least along a portion of their lengths, with the aid of intermolecular forces, into a definite pattern. The amorphous areas are those where no particular organization exists. However, a sharp distinction cannot be made, since there must be a certain amount of transitional material, where the organization of the structure is not as complete as that of the crystallites, nor as disorganized as the amorphous areas. This "mesomorpheus" portion may thus include every sort of arrangement from nearly perfect order to random disorder.

Obviously, any quantitative measure of "crystallinity" will depend upon the method employed and, indeed, upon the definition of the terms used. There have been two fundamentally different approaches to the problem, one based upon chemical behavior, and the other upon physical properties.

CHEMICAL BEHAVIOR

The chemical methods all depend upon the topochemical nature of certain reactions. Hess and Trogus (37) suggested in 1931 that cellulose reacted in two stages: a rapid reaction of the crystal surfaces, which slows down to a lower rate as the surface material becomes converted and the reaction progresses into the interior of the micelles. Centola (38), who used x-ray techniques, concluded similarly that acetylation of cellulose is a heterogeneous micellar reaction, in which the reagent penetrates into the interior of the fibers, surrounds the micelles, and transforms into triacetylcellulose the chains of glucoside residues situated on the micellar surfaces. He estimated that these surface, or accessible, molecules represented 70% of the total. It is thus that the concept of "accessibility" arose.

Acid Hydrolysis

Nickerson was the earliest to make use of the accessibility determination as an approach to the amount of amorphous material present in a cellulose. His method (39-46) involves hydrolysis with hydrochloric acid, following the course of the hydrolysis by catalytic oxidation with ferric chloride of the glucose produced, and measuring the carbon dioxide evolved. The method was improved by Conrad and Scroggie (47), who increased the reproducibility, and modified by Lovell and Goldschmidt (48), Philipp, Nelson, and Ziifle (49), and Nelson and Conrad (50), all of whom discarded the carbon dioxide measurement in favor of weighing the residual cellulose. Battista and Coppick (51) used milder hydrolysis conditions and followed the course of the reaction through cuprammonium viscosity measurements. All of these variations gave uniformly low values for the "amorphous" content of cellulose. Nickerson, in 1942 (43), for example, found a 6% amorphous content in cotton linters and 21% in viscose rayon, although by 1946 (45) he concluded that noncrystalline cellulose seems to be divisible into two roughly equal parts, which he termed the "amorphous" and the "mesomorphous" portions. The amorphous portion is much more hygroscopic and more susceptible to hydrolysis than the crystalline portion. The so-called mesomorphous portion is intermediate in its properties, but more nearly crystalline than amorphous. He estimated that cotton linters contain 3% each of amorphous and mesomorphous material, and 94% crystalline, whereas viscose rayon contains 8% amorphous material, 14% mesomorphous, and 73% crystalline.

A serious objection to the use of hydrolysis as a method of measuring amorphous content was raised by Mark and co-workers (52), who, using density measurements, found that additional crystallization occurred during the initial stages of hydrolysis. This was confirmed, using x-ray methods, by Hermans and Weidinger (53), who found that hydrolysis for four hours in 2.5 N sulfuric acid increased the crystalline content of viscose fibers from 39 to 49%. Howsmon (54) reached the same conclusion from the fact that the loss in sorptive power on hydrolysis is disproportionate to the weight loss. Battista (55), using viscosity measurements, found that the calculated crystallinity was influenced by the conditions of hydrolysis, and concluded that the weight loss on hydrolysis depended upon a combination of the rate at which hydrolysis proceeds and upon crystallization and crystal growth, which appear to occur simultaneously with hydrolysis.

This crystallization has been explained, tentatively (56) by the cutting of part of the chains in the amorphous regions, which may remove part of the entanglements, or restore some of the inhibited segmental freedom of movement and rotation which had prevented further growth of the crystalline regions.

Periodate Oxidation

A similar approach, but with a different reaction, was that of Mark and co-workers (57,58), who oxidized the cellulose with an aqueous solution of potassium metaperiodate at very low pH; the reaction was followed by the chemical analysis of the oxidizing solution. The results obtained are in rough agreement with those secured from hydrolytic methods.

Thallation

Purves and co-workers (59) objected to the foregoing methods, which depend upon reaction rate, as likely to give high results, due to partial penetration of the crystallites by the reagent during the early stages. In their method, the sample, highly swollen in caustic soda and dried with methanol and benzene, was immersed in a large excess of 0.1 *N* thallous ethylate solution. The thallium cellulosate thus formed was methylated with excess methyl iodide in a benzene solution. The methoxyl content of the product was accepted as proportional to the percentage of the cellulose wetted by the liquid in which the thallous ethylate was dissolved--in this case any of several nonhydroxylic, nonswelling liquids. "Amorphous" cellulose was defined as the percentage wetted by an ether of zero molecular volume and was estimated by extrapolating the linear methylation-molecular volume plots of three or more straight-chain ethers, in this way attempting to eliminate the effect of molecular volume upon the results. By this method, swollen linter samples showed amorphous fractions as high as 27 ± 2%, but that of unswollen fibers was only 0.25 to 0.5%; this very low result was due to the lack of penetration into the unswollen interior of the fibers.

Reaction with Formic Acid

Recently, Tarkow (60) has pointed out that under certain conditions, formic acid will react with only the primary hydroxyl group of polyanhydroglucoses in the amorphous regions. He used this to obtain accessibility values which agree quite well with those obtained by deuterium exchange (see below).

Other Methods

Values comparable to those obtained by deuterium oxide exchange (see below) were found by Timell (61), who used the reaction of metallic sodium with ammonia cellulose.

Another method developed by Timell (62) involves allylation of the sample and following the addition of iodine bromide to the allylcellulose. The reaction takes place in two steps (in a fashion similar to the earlier chemical methods), from which the amounts of accessible material are calculated to be very nearly the same as those from hydrolytic methods.

PHYSICAL PROPERTIES

Physical studies of the submicroscopic structure have fallen into two general categories: those based upon the dimensional relationships within the various domains, and those based upon the sorptive power within and outside the crystallites.

X-ray Diffraction

Into the first class falls the method most thoroughly investigated to date, that of x-ray diffraction, in which x-ray diagrams similar to those used in determining the basic unit cell structure are evaluated quantitatively. Sisson and Clark (63) used a visual photometer as early as 1933, but their instrument was comparatively crude and the technique uncertain. Kratky (64) was another early investigator, and an important contribution was made by Berkley and Woodyard (65), who developed a photoelectric microphotometer for determining the visual densities of the x-ray films.

Probably the most significant work in this field has been that of Hermans (66- 68). His technique involves the diffraction of monochromatic x-rays by a small pellet of randomly oriented fibers, recorded on a rotating film. The absolute intensity is measured, and suitable corrections are made for air scattering, Compton radiation, and thermal effects. Then by a rational process, the area under the photometer curve is divided into that which is due to crystalline areas and that due to the amorphous portion. The amorphous background shows a flat maximum, the height of which is taken as a measure of the amorphous content of the sample. The area under the typical crystalline peaks is used as a measure of the crystalline content. Hermans (67,68) found that all native fibers (except wood) possess equal crystallinity (70%), as do all rayons (40%), with the exception of Fortisan (48.5% [69]) and Fiber G (53%), both of which are unusual in several other respects, as well.

Kast and Flaschner (70) and Ingersoll (71) used a somewhat similar technique, except that the film is not rotated, which results in sickles on the film rather than rings, so that both radial and azimuthal photometer traces must be used in evaluation.

Density

Since the molecules of the crystallites are more compactly arranged than they are in the amorphous portions, there is a difference in density between the two types of structure, and there should be a correspondence between the density of a cellulose and its amorphous content. Hermans (72,73) has found this to be true. Certain complicating factors prevent an exact relationship, but the correlation is very good, nonetheless.

Sorption Studies

An entirely different method is based upon the sorptive properties of fibers, which have been known for years, but have been associated with the amount of amorphous material only very recently, particularly by Hermans (74), Hailwood and Horrobin (75), and Howsmon (54).

Hermans' early work (74) brought out the view that: "....(1) differences in density of cellulose fiber can be attributed to differences in relative amounts of crystalline material, (2) there is a close parallelism between density and moisture sorptive capacity, and (3) that as a first approximation there is a direct relationship between the sorptive capacity and the quantity of amorphous material in the fiber." (54)

Taking the theory that all absorbed water is dissolved in the amorphous zones, he developed the concept of the sorption ratio, which is the ratio of the moisture content of a given cellulose under any conditions to that of a native cellulose under the same conditions. If the theory holds true, then the amount of amorphous material is in the same ratio.

This idea has been modified somewhat, so that at present the first strong sorption of water by cellulose is considered to be caused by the hydrogen bonding of water molecules to the accessible hydroxyl groups (76). Thus the values obtained are somewhat akin to those from chemical accessibility measurements, and crystal size must be considered, in addition to the crystalline-amorphous ratio. As Howsmon puts it, "On the basis of present [1949] data and theory of cellulose structure, a high proportion of the high reactivity, moisture sorption, and other properties of regenerated cellulose is directly traceable to the smaller crystal size and/or higher accessibility of the crystalline domains present, rather than entirely due to differences in amount of crystalline material present, as has been frequently assumed." (54) He illustrates the probable effect of crystallite size upon the crystallinity as calculated from sorption data, by the use of the very interesting data on crystallite size obtained by Morehead (26) from electron micrographs of hydrolyzed celluloses.

Hailwood and Horrobin (75) interpret the sorption data differently. By assuming an ideal solid solution of unhydrated cellulose, hydrated cellulose (as the monohydrate of the accessible anhydroglucose), and dissolved water, they developed the equation for the sorption isotherm, from which accessibility can be calculated. In spite of theoretical defects in such assumptions, the calculated curve agrees remarkably well with experimental data.

If one allows for the limitations of the theory involved, moisture sorption data can be quite useful as a means of comparing crystallinities.

Calorimetry

The nature of the moisture in fibers was examined calorimetrically by Magne, Portas, and Wakeham (77). Using the method of mixtures, they calculated the amount of freezing and nonfreezing water for several fiber-moisture combinations. Plotting nonfreezing water against freezing water, they extrapolated to zero freezing water, and, allowing three molecules of water per glucose residue in amorphous regions and one-half molecule per glucose residue in crystalline zones, calculated the amount of noncrystalline material necessarily present. Their results are very close to those obtained by hydrolytic methods.

Deuterium Exchange

Some very promising work was done by Mark and co-workers (78), which involved the exchange of deuterium from heavy water with the hydrogen of accessible hydroxyl groups; the extent of the rapid reaction was taken as a measure of accessibility. From these accessibility values, the amounts of amorphous materials were estimated as 21% for cotton, 46% for wood pulp, and 66% for rayon. Some doubt has arisen, however, concerning the proposed mechanism of the reaction. Plyler (79) found from infrared absorption spectra that only a small fraction of the hydroxyl groups in regenerated cellulose participated in the deuterium exchange, so that further work on this method seems necessary. Possibly the fact that Plyler was working with regenerated films had some influence upon his results.

COMPARISON OF METHODS

Table II shows a comparison of the various methods from the viewpoint of results. As can be plainly seen, all methods show the same order of decreasing crystallinity; however, the absolute values are widely different. In particular, the chemical methods, which are fairly consistent among themselves, give results of a different order of magnitude from those obtained by physical methods (with the exception of the formic acid reaction and the calorimetric method). Thus arises the question of which method or methods afford the best measure of the amount of crystalline material.

TABLE II

PERCENTAGE "CRYSTALLINITY" OF CELLULOSE[a]

Method	Cotton	Wood Pulp	Mercerised Cotton	High-Tenacity Rayon
Hydrolysis				
Nickerson (40,41,43,45)	94	90	89	79
Conrad & Scroggie (47)	92-94	88-91	85-89	69-73
Philipp (49)	88	--	82	67
Thallation (59)	99.6	--	78-91	96.7
Periodate oxidation				
Mark (57)	94	--	--	--
Timell (58)	94	90-93	--	82
Formic acid (60)[b]	72	53-65	48	23
Deuterium exchange (78)	78	63	--	20
X-ray diffraction (67)	69	65	47[c]	49
Density (73)	58	53	40	24-32
Calorimetry (77)	87	--	77	52
Sorption (54)	67	57	--	16-27[d]

[a] After Howsmon (54).

[b] Values shown are 100 minus formic acid accessibility, and are recognized by Tarkow as not necessarily a true measure of crystallinity.

[c] Mercerized ramie.

[d] Depends upon crystal size assumed.

There is a certain amount of consistency among the various chemical methods of measuring accessibility; however, accessibility is not necessarily what one is seeking. As Howsmon puts it (80), "...the accessibility of a cellulose fiber is usually defined as that fraction of total cellulose which is available for reaction with a certain reagent under certain specified conditions, such as concentration, time, and temperature. The experimental values of accessibility are dependent upon the size and polarity of the molecule used and upon the degree of swelling of the cellulose in the medium used in the determination, but for any given set of conditions the accessibility of a cellulose can be determined as an exact empirical value."

Tarkow warns that accessibility values are not necessarily measures of crystallinity or of general reactivity:

> "It is of interest that those methods that meet certain requirements (swollen cellulose, nonchain-splitting reaction, small reactant molecule with high specific reactivity) give values that are in general accord with each other. It should be emphasized, however, that these values are not necessarily measures of the amount of x-ray measured noncrystalline material. The cellulose is assumed to have a dual structure: a readily accessible and a difficultly accessible region. The latter, it has been seen, is composed not only of regions having at least a certain degree of lateral order, but also of those regions containing extremely small but truly crystalline regions (therefore not revealed by x-rays), cross links, and junction points that persist even when the cellulose is swollen by an amount it would swell in liquid water. The accessibility values reveal nothing about the absolute reactivity of these regions; therefore, it would be wrong to give the impression that such measurements characterize the chemical convertibility of a cellulose. The accessibility, as measured by one of the above methods, is only one of a large number of factors that may include (1) the ease of diffusing through the readily and difficultly accessible regions, (2) the presence and nature of cross links, (3) the morphology of the fiber, (4) the presence of peculiar end groups, (5) the presence

of noncellulosic components, and (6) their distribution and manner of association with the cellulose." (60)

Thus it may be seen that in all probability none of the methods so far brought to light may be considered as an exact measure of the amount of crystalline material. X-ray diffraction, being a direct method, comes the closest to being an exact measure, but even this is inexact to the extent that it cannot pick up very small regions of regularity. In general, it may be said that all such measurements are profoundly influenced by the crystalline-amorphous ratio, so much so that nearly any measurement is useful as a means of comparing various samples, provided one recognizes the limitations of the method used, and its appropriateness in view of the nature of the information desired.

THE DIELECTRIC CONSTANT OF CELLULOSE

A dielectric material is not a conductor of electricity because its electrons are bound in a space lattice from which they cannot escape. When a dielectric is placed in an electric field, however, the centers of charge may be disturbed, resulting in an opposing field within the dielectric. Such distortion is known as polarization. A dielectric becomes polarized when inserted between the plates of a charged, isolated condenser, and its field opposes that of the condenser, thus decreasing the potential difference between the plates. The charge has not changed, though, so that the ratio of the charge to the potential difference, which is known as the capacitance of the system, is increased. Such polarization is characteristic of a given dielectric under any particular conditions, and is usually expressed as the ratio of the capacitance of a condenser filled with the dielectric to its capacitance when empty. This ratio is the specific inductive capacity, which is more commonly called the dielectric constant (ϵ').

If the electric field is alternating, the polarization reverses with the applied field. Unlike the condition in a static field, not all the possible types of displacement of charge occur simultaneously, as different types of polarization take place at different frequencies. Therefore, the dielectric constant varies with changing frequency.

TYPES OF POLARIZATION

Electronic polarization (displacement of electrons) is the only type occurring at frequencies in the visible range. At such frequencies, the dielectric constant is equal to the square of the index of refraction.

Atomic polarization takes place in the infrared range, so that as the frequency decreases, the dielectric constant increases. Neither electronic nor atomic polarization is much affected by temperature.

Rotation of polar molecules in an applied field may occur at still lower frequencies. This is dipole polarization. Debye (61) derived a temperature relationship for such polarization in the form:

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

where $\underline{P}$ is the molar polarization, $\underline{A}$, $\underline{a}$, and $\underline{b}$ are constants for a particular material, and $\underline{T}$ is the absolute temperature. Debye assumed that the molecule is free to rotate, and that no interaction between molecules takes place; his relationship is quantitative when such assumptions are valid, as in the case of gases or dilute solutions of polar molecules in nonpolar solvents. In most dielectrics, the relationship has only qualitative significance, however.

If the various components of a heterogeneous material have different electrical properties, charges may build up at the interfaces and become oriented in the applied field, resulting in an increase in the dielectric constant. This is known as <u>interfacial</u> <u>polarization</u>, and, due to the relatively large size of the particles involved, usually occurs at lower frequencies than other polarizations. It decreases as the temperature is raised, because of thermal agitation.

The polarizability of a nonpolar dielectric is given by

$$\underline{P} = [(\epsilon' - 1)/(\epsilon' + 2)](\underline{M}/\rho), \qquad (2)$$

where $\underline{P}$ is molar polarizability, $\underline{M}$ is molecular weight, and ρ is density. The dielectric constant may be related to density if $\underline{P}$ is considered constant for any given molecule, by

$$(\epsilon' - 1)/(\epsilon' + 2) \propto \rho \; . \qquad (3)$$

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

DIELECTRIC LOSS

Because the movements of the various particles do not take place in a perfectly elastic medium, there is a certain amount of friction, and energy is lost as heat. This is known as the dielectric loss of the material, and is often expressed as the power factor, which is the cosine of the phase angle between the current and impressed voltage.

CELLULOSE AS A DIELECTRIC

Cellulose is a linear polymer containing many polar groups. The dielectric constant of such polymers generally increases with increasing temperature and decreasing frequency. Fuoss and Kirkwood (82-86) have shown that the dielectric behavior observed in other polymers of this type cannot be quantitatively explained by the relations discussed above. They concluded that the observed effects are due largely to the motions of dipoles in what is effectively a medium of high viscosity. The attachment of the dipoles to the polymer chain restrains them in their positions. Secondary valence forces may be operating between chains of portions thereof. The motion of any dipole affects the motion of neighboring dipoles.

Baker and Yager (87) showed that the dielectric constant was related to the interaction between the chains. In the case of polydecamethylene sebacamide, they found that decreased crystallinity and, hence, decreased hydrogen bonding, resulted in increased dielectric constant. Thus, the dielectric properties are related to the relative freedom of the polar groups.

With our knowledge of the variations in the submicroscopic structure of cellulose, it is apparent that the dielectric properties may be profoundly affected by the nature of this structure.

As Calkins (88) reviews the situation:

"When cellulose is placed in an alternating electrical field at 'power frequencies', electronic polarizations will take place. By means of the relation, $\epsilon = \underline{n}^2$, where $\underline{n}$ is the index of refraction, the contribution of this type of polarization to the dielectric constant is found to be about 2.5 or roughly a third of the accepted value of 6.1 for native cellulose. It is probable that little dielectric loss occurs.

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

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

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

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

HISTORICAL REVIEW

The literature on the dielectric properties of cellulose has been reviewed by Delevanti (89), Hansen (90), and Calkins (88), all of whom have made significant contributions.

The earliest measurements on cellulose were probably those of Albert Campbell (91), who in 1906 used a bridge circuit which followed Maxwell's design. He obtained dielectric constants of 1.7 to 2.6 for paper samples which had been dried at 110°C. without evacuation. He realized the need for a means of density correction, but did not propose one. For viscose films dried several days at 80-110°C., he obtained values ranging from 6.7 at 20°C., up to 7.5 at 70°C.

The dielectric constant of native cellulose most generally accepted today is that of De Luca, Campbell, and Maass (92), who obtained a value of 6.1 by a method of liquid mixtures.

Stoops (93) measured the dielectric properties of cellophane over a wide range of frequencies and temperatures. At 1000 cycles, he found the dielectric constant to be 7.6 at 25°C., to increase somewhat at higher temperatures, and to decrease slightly at higher frequencies. Under the same conditions, the dielectric constant of cellulose triacetate sheeting was 4.0, and it varied similarly with respect to temperature and frequency. Its dielectric loss was only slightly lower than that of cellophane, so Stoops attributed the major portion of this loss to the rotation of the cellulose chains, rather than to rotation of hydroxyl groups, since the latter are not present in the acetate. Moreover, the resonant frequency of rotation of hydroxyl groups is higher than the frequencies he used. In the light of present knowledge, Stoops' method of moisture removal (drying at 105°C. without evacuation) might be considered inadequate, so that the difference in loss between cellophane and the acetate might have been due to traces of residual moisture in the cellophane.

Shaw and Windle (94) measured the dielectric constant of cellophane at 3000 megacycles in a resonant cavity and obtained a value of 4.04 ± 0.03, with the field parallel to the surface of the film. Their method of desiccation is not clear.

Relation to Density

Hansen (90) found that the dielectric constant of kraft pulp was related to density by the Clausius-Mosetti relationship, and Calkins (88) found the same to be true of pure native fibers. Endicott (95) considered paper as a series of fiber resistances either in parallel or in series, and found that the series representation fits quite accurately the case of a particular kraft paper. Further data (not given) indicated that a combination of the series and parallel elements would be more accurate, however. Calkins (88, p. 13) calculated that such a combination would give effectively the same value as the Clausius-Mosetti relation, and claimed that Endicott's equations lose validity over a wide density range.

Effect of Moisture

The effect of moisture content on dielectric constant has been the subject of considerable study. Argue and Maass (96) measured the dielectric constant of cellulose at a series of moisture contents, and found that the dielectric constant of the water initially absorbed is less than one fourth that of liquid water, from which they concluded that as the moisture content decreased, the water was increasingly bound to the cellulose. Garton (97) likewise concluded that the polarizability of bound water was much less than that of free water. These findings indicate that the accuracy of the dielectric constant determination is little affected by the presence of small amounts of moisture.

Greenfield (98) confirmed this by measuring the equilibrium dielectric constant of kraft paper at a series of vacuums. Reduction of the pressure from 400 to 0.25 mm. caused a decrease in dielectric constant of only 3%, although the power factor decreased 80%.

Calkins (88, p. 90) found no significant difference in dielectric constant upon decreasing the pressure from 250 microns to 0.1 micron.

<u>Effect of Impurities</u>

Dielectric loss is also increased by the presence of cationic impurities, as Hansen (90) found by adding a calcium salt to a kraft paper. He was unable to show any definite effect on dielectric constant. Such an effect is probably slight if the ash content is rather small.

<u>Effect of Crystallinity</u>

Calkins (99) found that whereas cellophane had a dielectric constant comparable with that of native cellulose, the value for a fibrous regenerated cellulose was considerably higher. Pressing at moderate pressures caused the latter to decrease, and Calkins found that the moisture regain was similarly decreased, indicating the possibility of a relationship between dielectric constant and crystallinity under pressure. These findings are the subject of further investigation in the present work.

PRESENTATION OF THE PROBLEM

Calkins has discovered the possibility of a linear relationship between the dielectric constant of cellulose and its crystallinity. His observations were confined to various specimens of fibrous material precipitated from cellulose xanthate, whose crystallinity had been varied by various aftertreatments. Among his findings was the fact that the pressing of handsheets at moderate pressures decreased both the dielectric constant and the moisture regain of the samples.

Calkins' data on cellophane did not seem to fit the general relationship, the dielectric constant of this material being much lower than that of a fibrous regenerated cellulose having the same moisture regain. The possible cross linkages produced by storage in a formaldehyde solution were suggested as an explanation.

The present problem involves the extension of observations similar to those of Calkins to a wider range of materials, including native celluloses and various types of regenerated materials; to further investigate the effect of moderate pressures on both crystallinity and dielectric constant; to test the effect of formaldehyde storage on cellophane; to broaden the basis for comparison of crystallinities; and to arrive at a rational explanation of the observed phenomena.

To accomplish this, certain modifications in Calkins' apparatus were desirable. There had to be devised methods of preparation of specimens of various materials in a form suitable for measurement in the available apparatus. Comparisons were to be based on complete sorption isotherms, rather than single moisture-regain values, and measurements of the ultimate density of the various materials were to be made as an auxiliary means of comparison.

APPARATUS FOR THE MEASUREMENT OF DIELECTRIC CONSTANT

BRIDGE

A modified conjugate Schering capacitance bridge was built by Delevanti (89) along the lines of the design suggested by the American Society for Testing Materials (100) and was described in detail by him. This bridge was later rebuilt in relay rack form by the staff of The Institute of Paper Chemistry and was available for this work. It is capable of measuring the equivalent parallel capacitance of a test capacitor of suitable size over a wide frequency range. The equivalent circuit diagram of the bridge is shown in Figure 5. C_2 is a General Radio precision capacitor with a negligible power factor. The others are air capacitors of suitable sizes. The resistors (R_3, R_4, R_5, and R_6) are 10,000-ohm precision-matched noninductive resistors. S_2 is a shielded single-pole, double-throw, laminated wafer-type switch. The leads to the test capacitor are of shielded cable.

The detector (D) is a high-amplification vacuum-tube amplifier. Since a few minor changes were made in this amplifier to reduce motorboating, the present circuit is shown in Figure 6. The indicating device is a Weston Model 440 galvanometer, which measures the rectified alternating output of the amplifier.

SOURCE OF ALTERNATING VOLTAGE

A transitron-type oscillator capable of delivering sinusoidal alternating voltages ranging in frequency from 200 to 10,000 cycles

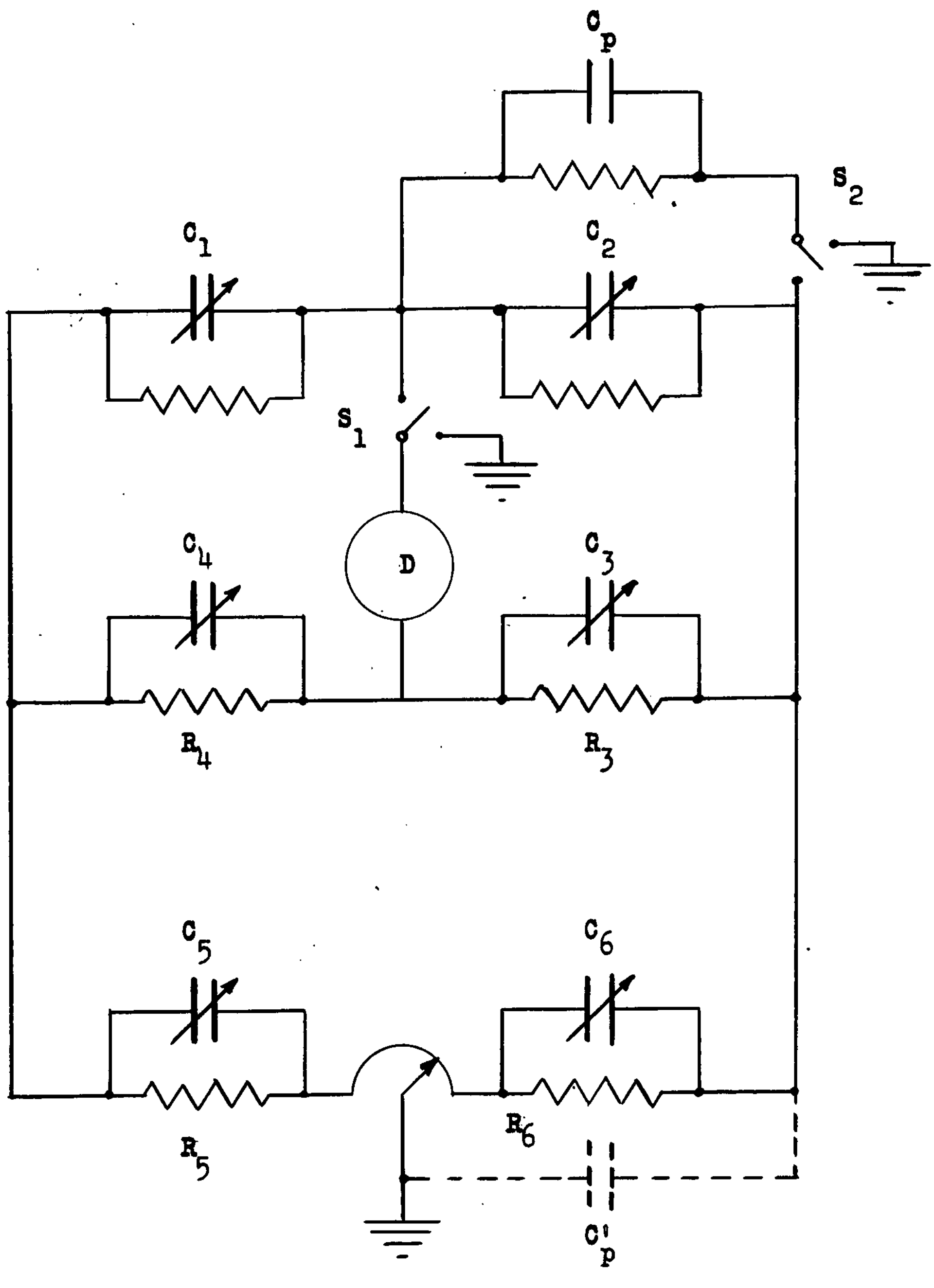


Figure 5

Electrical Circuit of Schering Bridge

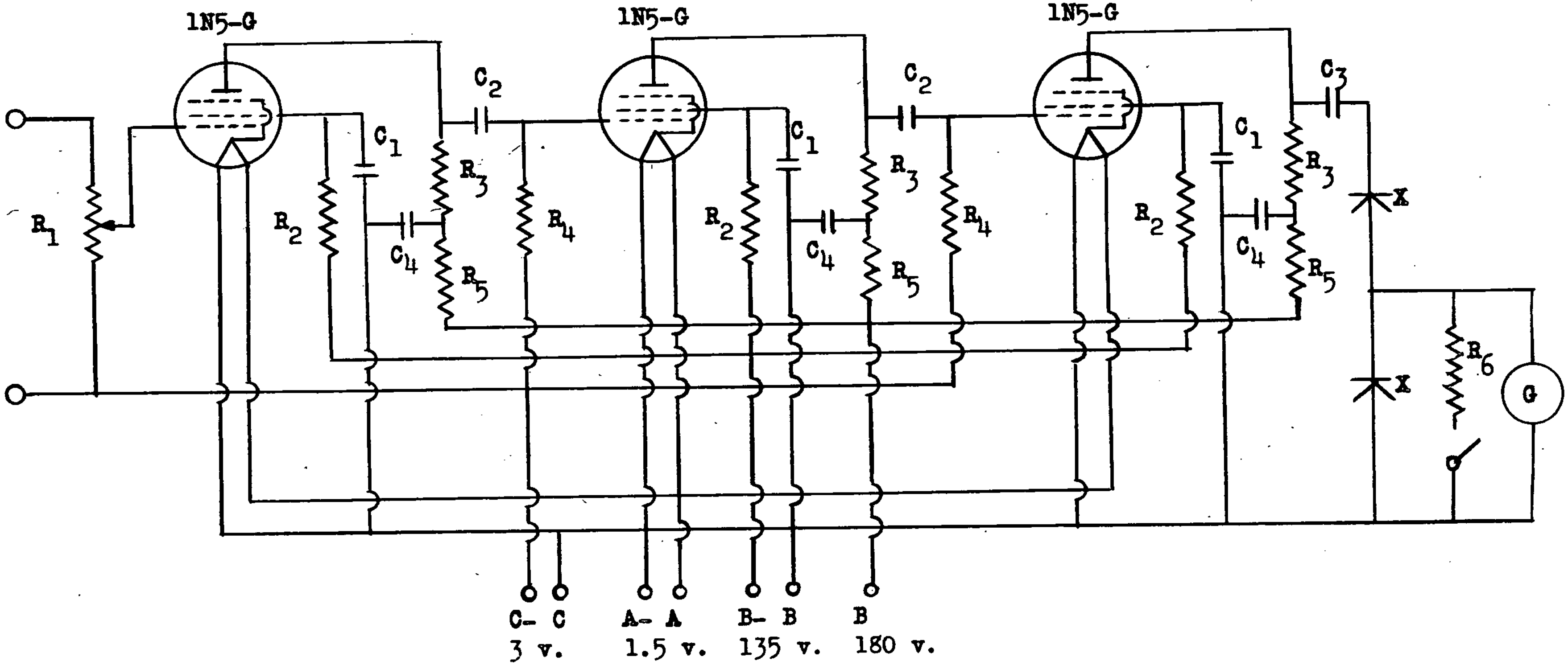


Figure 6
Circuit Diagram of the Bridge Balance Detector

Legend for Figure 6

R_1 = 0.25-megohm potentiometer gain control

R_2 = 0.25 megohm

R_3 = 0.6 megohm

R_4 = 1 megohm

R_5 = 20,000 ohms

R_6 = 800 ohms

C_1 = 0.03 mfd.

C_2 = 0.02 mfd.

C_3 = 1 mfd.

C_4 = 40 mfd., 450 v.

X = Copper-copper oxide rectifier

G = Galvanometer, Weston Model 440

per second was built by Hansen (90) and was described in detail by him. This oscillator was used as a source of alternating voltage for the Schering bridge in this work.

Because the wave form of the output of the transitron oscillator varies considerably as the amplitude is changed, an oscilloscope was used to monitor the output to the bridge.

TEST CAPACITOR SYSTEM

The test capacitor system, shown in Figure 7, was built by Calkins, and the details of its construction are given by him (86, p. 20-42). It consists of a pair of electrodes three inches in diameter, mounted in such a way that pressures up to 1000 p.s.i. can be exerted upon the sample while electrical measurements are being made. To accomplish this, the upper electrode is held rigidly by a supporting framework, whereas the lower electrode can be moved vertically by means of a hydraulic jack. The jack shaft is sealed to the base plate by a sylphon bellows, which permits the vertical movement without hindering the vacuum seal. The magnetically moved sample holder used by Calkins was considered unnecessary and was removed.

A separation gage which consists of a pair of auxiliary electrodes is used to measure the spacing between the main electrodes. The upper auxiliary electrode is held in a fixed position relative to the upper main electrode, whereas the lower auxiliary electrode moves only vertically, in unison with the lower main electrode; the latter

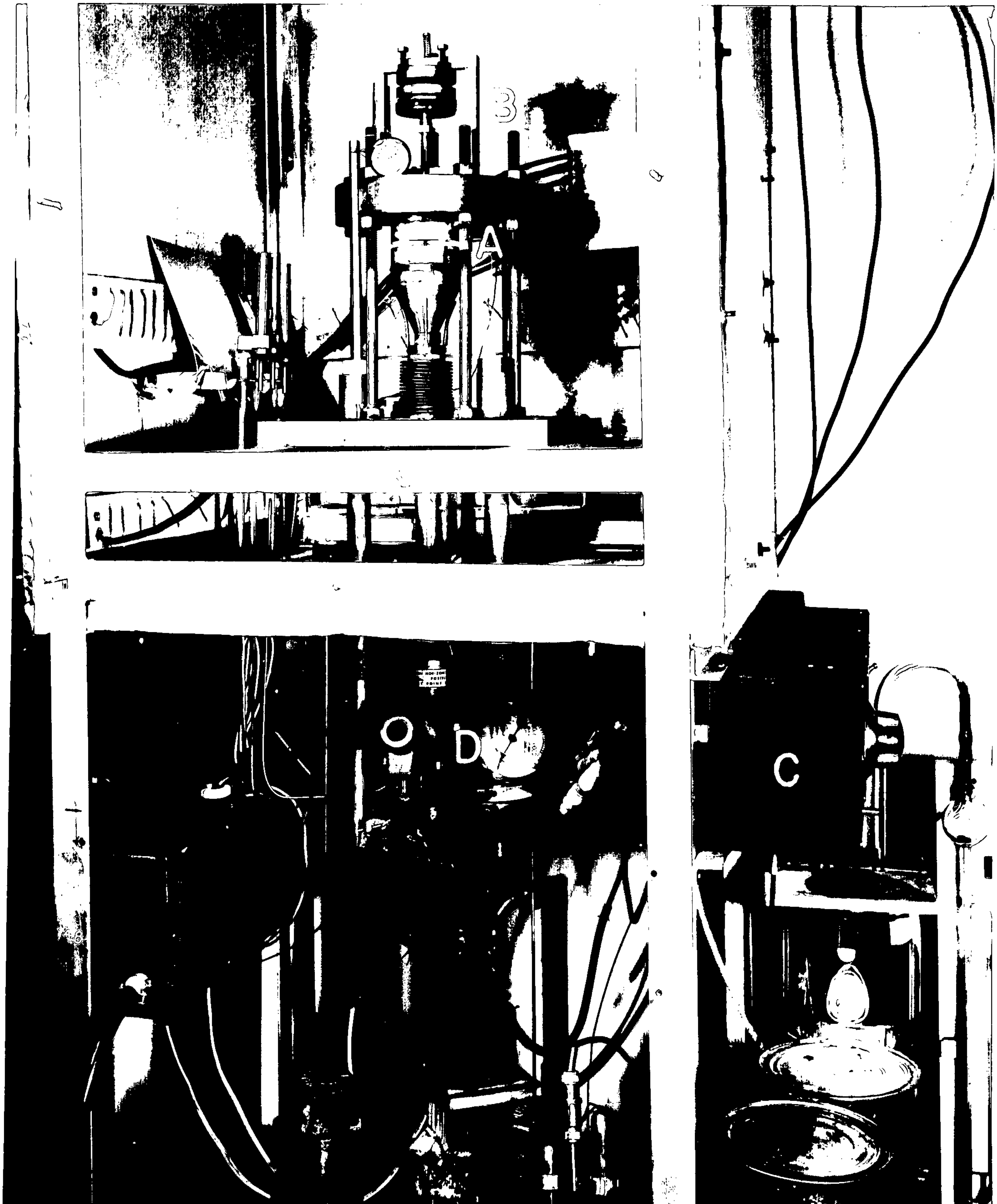


Figure 7

Test Capacitor System

A Main electrodes
B Spacing gage capacitor
C Auxiliary Bridge
D Jack

relationship is fixed by a Pyrex rod which passes through the upper main electrode and through a small hole punched in the center of the sample, so that the polished end of the rod bears against the center of the lower main electrode.

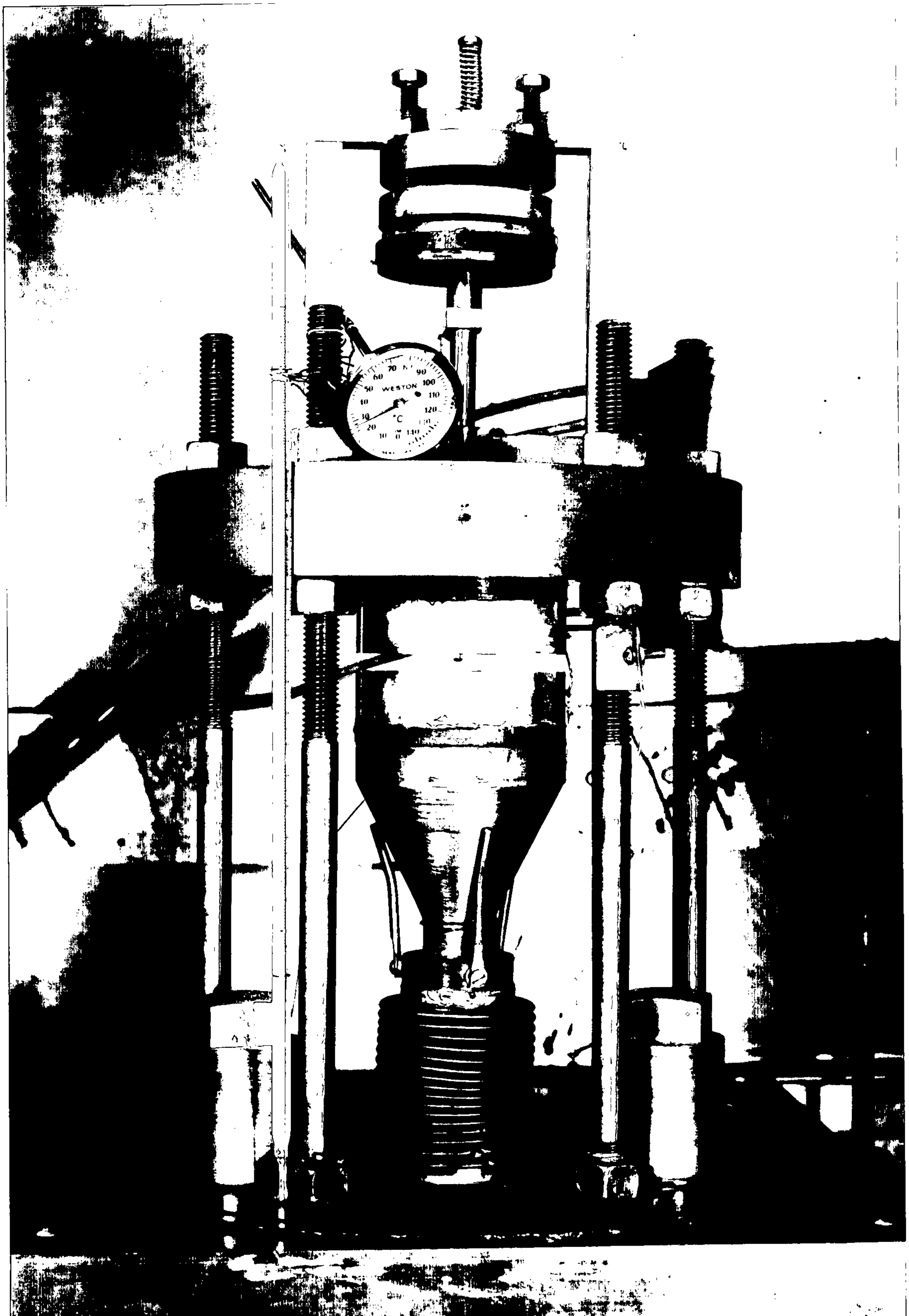
The electrode system is enclosed in a bell jar which can be evacuated to a pressure of 0.1 micron by a diffusion pump backed by a Cenco Megavac. For measuring the pressure within the system, a McLeod gage is connected through the base plate by way of a trap which is kept at -80°C. by a mixture of Dry Ice and benzyl alcohol. The electrode system, including the bell jar, is enclosed in an insulated box whose temperature can be controlled within 1°C. from 25 to 110°C.

ELECTRODE-SEPARATION GAGE

Although the remainder of the test capacitor system was used in the form in which it was built by Calkins, the separation-measuring arrangement was rebuilt to improve its stability. As shown in Figure 8, the frame supporting the upper auxiliary electrode was replaced by one constructed of heavier material than that used by Calkins. Steel bar stock 0.5 inch square, which had been well aged, was cut to the required lengths, carefully faced off on a lathe, drilled, tapped, and countersunk, and the whole assembled with two 5-40 by 1-inch brass screws in each joint. The gage was reassembled in the same manner as it had been previously assembled, except that the auxiliary electrodes were adjusted so as to be very nearly in

Figure 5

Arrangement of Electrodes


WESTON
°C

contact when the main electrode spacing was 0.010 inch. This provided greater accuracy at the wider spacings used in this work. The effective range of sample thickness was 0.010 to 0.017 inch. (Calkins was limited to thinner specimens because of his interest in loss angle, with which the present study was not primarily concerned.)

AUXILIARY CAPACITANCE BRIDGE

The auxiliary capacitance bridge used to measure the electrode spacing was completely rebuilt in the form of an equal-arm bridge, as shown in Figure 9. R_1 and R_2 are deposited metal, low-inductance resistances. C_2 and C_4 were chosen by experiment to give a suitable range and sensitivity for the desired separations. The 1000-cycle band-pass filter, F, was introduced to reduce the noise components due to the poor wave-form of the power supply, which was a 1000-cycle microphone hummer. The bridge and hummer were each mounted in steel boxes affixed to the side of the framework supporting the test capacitor system. The auxiliary bridge was connected with the hummer and with the test capacitor box by shielded cables.

CALIBRATION OF THE ELECTRODE-SEPARATION GAGE

The electrode-separation gage was calibrated in the manner described by Calkins (88, p. 43-48), who used as standards squares cut from brass shim stock and having holes etched in their centers for the passage of the separation-gage feeler rod. The thickness of these shims was measured with a Federal compressibility tester as a

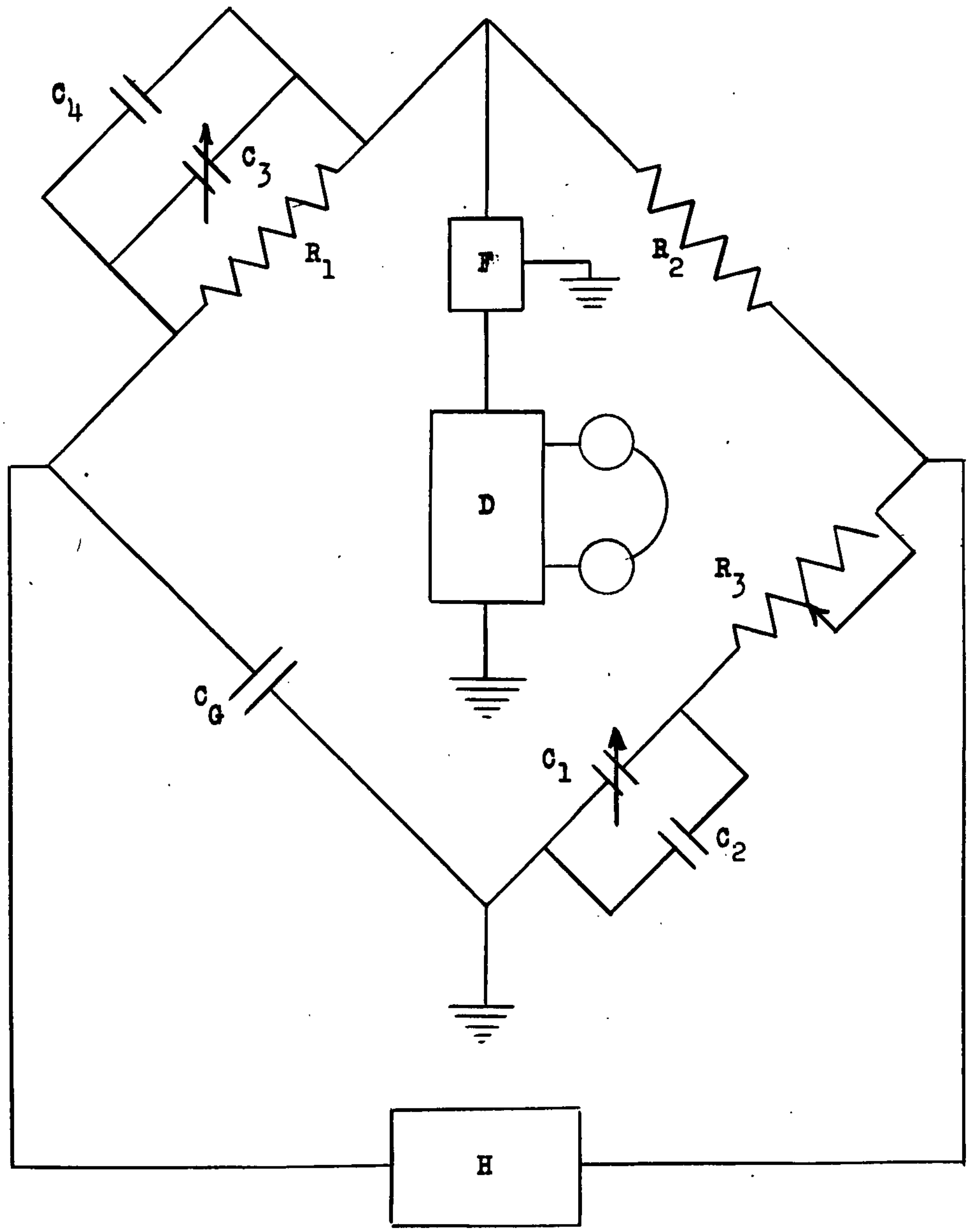


Figure 9

Electrical Circuit of Auxiliary Bridge

C_G	Spacing gage	R_1, R_2	10,000 ohm deposited metal resistors
C_1	500 mmfd. variable air capacitor	R_3	900 ohm variable resistor
C_2	210 mmfd. mica capacitor	H	1000-cycle microphone hummer
C_3	500 mmfd. variable air capacitor	F	1000-cycle band-pass filter
C_4	250 mmfd. mica capacitor	D	General Radio audio amplifier, Model 514-A

means of comparison with a feeler gage which had been calibrated by the National Bureau of Standards. More than 100 separate thickness measurements were made on each shim, and their mean was taken as the average thickness of the shim. The data on the thickness of the shims are probably accurate to 0.00005 inch. The values obtained are given in Table III.

TABLE III

THICKNESS OF STANDARD SHIMS

Nominal Thickness, 10^{-3} in.	Measured Thickness, 10^{-3} in.	Calkins' Values,[a] 10^{-3} in.
2	2.24	2.21
3	3.14	--
4	4.48	4.44
7	6.90	6.86
10	10.22	10.24
15	15.04	--

[a]The shims for which these values are given were also measured by Calkins, whose results are presented here as evidence of the precision of the method of measurement.

As has already been noted, the effective thickness range of the test capacitor system was 0.010 to 0.017 inch. In order to cover this range, combinations of two shims were used to give thicknesses not available in shim stock. The sum of the measured thicknesses of the two was used in each case as the thickness of the combination, and the shims were marked, so that the pairs would always be used in the same position relative to each other. The combinations used are shown in Table IV.

TABLE IV

THICKNESS OF SHIM COMBINATIONS USED

Nominal Thickness, 10^{-3} in.	Combination Used	Measured Thickness, 10^{-3} in.
10	10	10.22
11	7 and 4	11.38
12	10 and 2	12.46
13	10 and 3	13.36
15	15	15.04
17	10 and 7	17.12

Since errors in the standards as the result of compression and thermal expansion are of the order of 0.1%, they may be disregarded.

<u>Method of Calibration</u>

In calibrating the separation gage, the shim (or shims) and electrodes were carefully cleaned, and the shim was placed in its proper position between the main electrodes. After the bell jar was put in place, the system was evacuated and brought to 105°C. After equilibrium had been attained, the jack was set for a 940-p.s.i. electrode pressure, and the auxiliary bridge was balanced; the mean reading of three balances was recorded as the balance point. The temperature was decreased stepwise to 75, 50, and 25°C., and increased stepwise to 105°C., repeating the balancing at each temperature. It was found that it required 12 to 15 hours to attain equilibrium at each temperature.

This process was completed for each of the six shim combinations used, and the data were used in the preparation of the calibration curves shown in Figure 10. These curves were constructed and used in the manner described by Calkins (88, p. 45-48). Because it was soon found that the calibration was not entirely stable, a single point check was run at the end of each dielectric-constant run to determine the correction to be applied. To make such a check, the shim which corresponded most nearly to the thickness of the sample measured in that particular run was inserted and tested in the same fashion as in the calibration itself, except that the check was made only at room temperature. After some experience, it was found that evacuation made a negligible difference in the check calibration reading, so that, in the later runs, the check was made without evacuation.

The correction was applied by the use of the equation derived by Calkins (88, p. 47):

$$\Delta \underline{p}_{cor} = (\underline{p}_1^{\,2}/\underline{p}_2^{\,2})\Delta \underline{p}\,, \tag{4}$$

where $\Delta \underline{p}_{cor}$ = the correction to be added to $\underline{p}_1$,

$\underline{p}_1$ = apparent separation with paper specimen in place,

$\underline{p}_2$ = apparent separation with standard shim in place, and

$\Delta \underline{p}$ = $\underline{p}_s - \underline{p}_2$, where $\underline{p}_s$ = actual reciprocal thickness of standard shim,

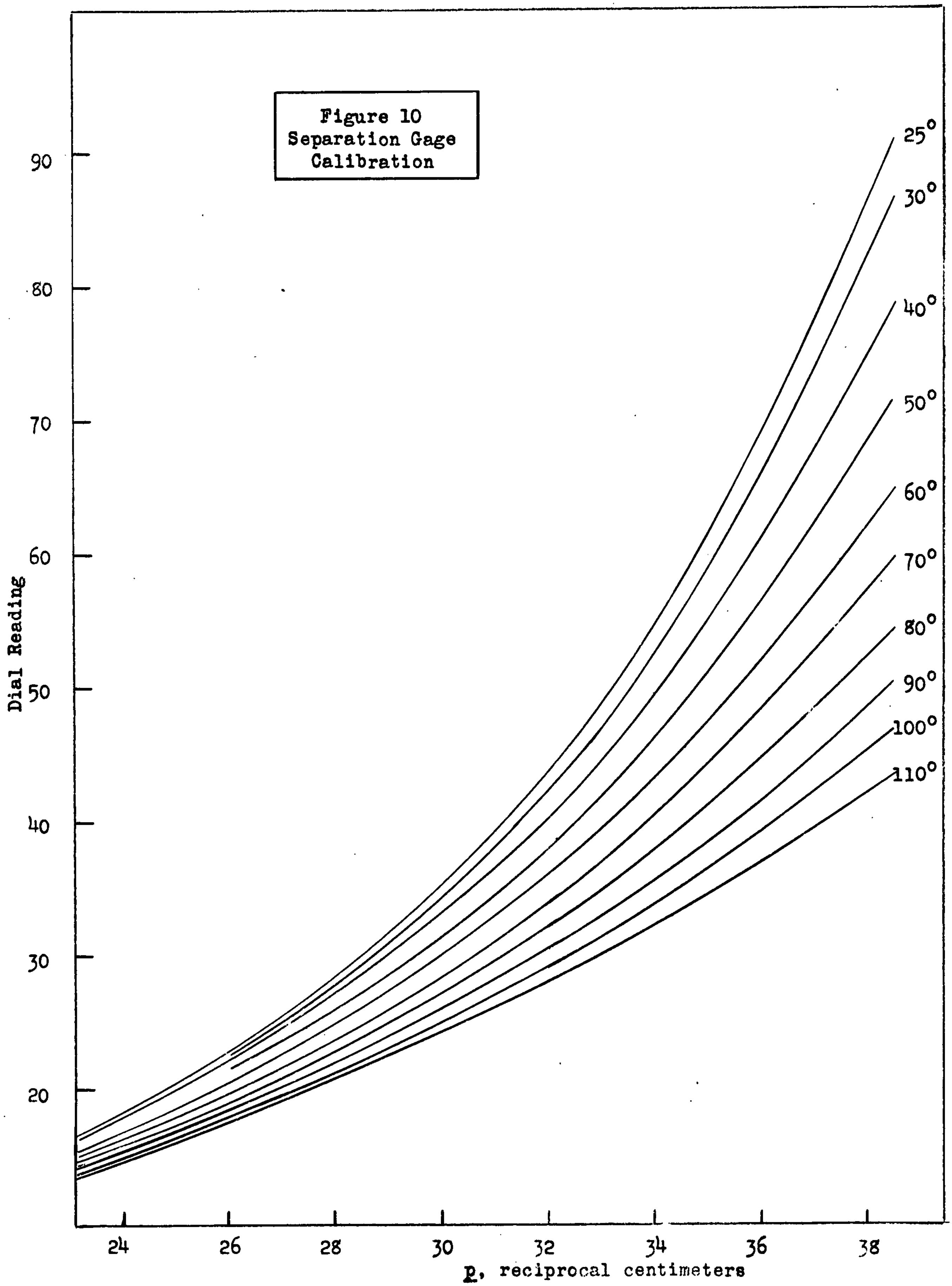


Figure 10
Separation Gage
Calibration
Dial Reading
90
80
70
60
50
40
30
20
25°
30°
40°
50°
60°
70°
80°
90°
100°
110°
24
26
28
30
32
34
36
38
p, reciprocal centimeters

where all $\underline{p}$ values are given in reciprocal centimeters. Sample calculations showed that even in extreme cases, such as in the test of the Clausius-Mosotti relationship, where $\underline{p}$ was as large as 2.4, due to the low electrode pressures employed, this equation gave the same results as the more rigorous one:

$$\Delta \underline{p}_{cor} = \Delta \underline{p}\ (\underline{p}_1 \underline{p}_{cor} / \underline{p}_2 \underline{p}_s). \qquad (5)$$

Since Equation (5) can be solved only by successive approximations, Equation (4) was used during the investigation.

Error of the Thickness Measurement

There are several factors involved in the calculated separation which may introduce errors. The auxiliary bridge can be balanced to 0.1 dial unit. However, the accuracy is limited by the calibration curve, which cannot be read closer than 0.1 $\underline{p}$ unit. This amounts to an error of 0.25 to 0.5%, depending upon the separation. A similar error occurs in making the calibration reading. The calibration correction was calculated to the nearest 0.1 $\underline{p}$ unit, which made a total of 0.75 to 1.5% possible error from these sources. The temperature was estimated to the nearest degree, which corresponds to an error in $\underline{p}_{cor}$ of about the same magnitude. Thus it is likely that the error in the separation measurement is less than 2%.

MEASUREMENT AND CALCULATION OF DIELECTRIC CONSTANT

A number of sheets of a particular cellulose sufficient for the total thickness to lie within the thickness range of the test capacitor were carefully chosen for cleanliness, good formation, and smooth surface, and placed in position on the lower electrode. The number of sheets used was normally three or four, and as high as 14 in the case of one cellophane, but never less than two. The sheets were cut to a diameter of about 3.5 inches, and a 0.25-inch hole was die-cut in the center for the passage of the spacing-gage feeler rod. The apparatus was assembled and the system evacuated and heated to 105°C. A normal minimum of 24 hours was allowed for complete desiccation to be attained, as a result of preliminary observations recounted in a later paragraph. At the end of this time, the specimen was placed under 940 p.s.i. pressure. The temperature and vacuum were noted, and the Schering bridge was balanced, immediately following which the auxiliary bridge was balanced. In cases where the effect of frequency was studied, the balances were made at 500, 1000, 2000, 4000, and 10,000 cycles per second. In all other cases, balances were made only at 1000 cycles per second.

The method of balancing the Schering bridge was as follows: the test capacitor was disconnected from its parallelism with C_2 (see Figure 5) by throwing switch S_2 to ground, whereupon the bridge was balanced by successive adjustments of capacitors C_2 and C_4, alternating with adjustments of the Wagner ground (the latter with switch S_1 to ground). When balance had been attained, the settings of C_4, in dial units, and C_2, in micromicrofarads, were recorded. Then the test capacitor was paralleled with C_2, the balancing procedure repeated (including adjustments of the Wagner ground), and the new C_2

and C_4 readings recorded.

The temperature was allowed to fall to the next desired value (if any) and, after allowing 15 hours for equilibrium to be established, the balancing process was repeated. Measurements were made at 105, 75, 50, and 25°C., and repeated at the same levels in ascending order, although in some instances the increasing temperature series was omitted, and many measurements were made only at 105°C.

At the conclusion of the run, the vacuum was broken and the specimens removed. The area between the electrodes was carefully cut out and its mean diameter measured. Ordinarily this was done by cutting to the edge of the impression left by the electrodes, but in the case of cellophanes, no such impression was discernible, since the material was already at its ultimate density, and in any case, the large number of sheets was unmanageable. Therefore, the cellophane specimens were left under jack pressure and carefully trimmed flush with the cylindrical surfaces of the electrodes with a sharp knife. The specimens were dried to constant weight at 105°C. From the data thus determined, the dielectric constant was calculated in the manner described below:

CALCULATION OF DIELECTRIC CONSTANT AT A STANDARD DENSITY

The simplified equation given by the American Society for Testing Materials (100) was used in the calculation of the capacitance of the test capacitor:

$$\underline{C}_p = \underline{C}_2 - \underline{C}'_2 , \qquad (6)$$

where $\underline{C}_p$ = the equivalent parallel capacitance of the test capacitor, in micromicrofarads,

$\underline{C}_2'$ = the capacitance of condenser C_2 when the test capacitor is in the circuit, in micromicrofarads, and

$\underline{C}_2$ = the capacitance of condenser C_2 when the test capaciter is disconnected from the circuit, in micromicrofarads.

Edge Correction

Because the electrodes were not guarded, there was a certain amount of edge capacitance. Scott and Curtis (101) have prepared an empirical equation for edge correction which is applicable, even though it was designed for thinner electrodes than were used in this work. A form of this equation adjusted to the units employed in the present study is

$$\underline{C}_e = (0.147 \log_e 1.5\underline{p}_{cor} + 0.0185\ \underline{K})\underline{P}, \qquad (7)$$

where $\underline{C}_e$ = edge correction to be subtracted from $\underline{C}_p$, in micromicrofarads,

$\underline{p}_{cor}$ = corrected reciprocal thickness of specimen, in reciprocal centimeters,

$\underline{K}$ = dielectric constant of the specimen, and

$\underline{P}$ = perimeter of electrode, inches (9.37).

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

TABLE V

ELECTRODE EDGE CORRECTIONS AT VARIOUS DIELECTRIC CONSTANTS AND SEPARATIONS

Dielectric Constant	Separation, in.	$\underline{C}$, mmfd.	$\underline{C}_e$, mmfd.	Edge Correction, %
2.75	0.010	418	6.1	1.5
	0.015	278	5.6	2.0
4.2	0.010	638	6.35	1.0
	0.015	425	5.87	1.4
7.0	0.010	1062	6.83	0.6
	0.015	708	6.36	0.9

Although these hypothetical values embrace the entire range of dielectric constants and separations encountered during the work, the edge capacitance is very nearly 6.0 mmfd. in all cases; therefore, to simplify the calculations, this value was assumed as the edge correction in all calculations. Application of this value in the assumed cases in Table V results in a maximum error of 0.17% in the calculated normal capacitance ($\underline{C}_n$, the capacitance when the electric field is perpendicular to the plane of the electrodes), which may be considered negligible. Therefore,

$$\underline{C}_n = \underline{C}_p - 6.0 \qquad (8)$$

The dielectric constant of the test capacitor was determined from the ratio of the observed capacitance ($\underline{C}_n$) to the calculated vacuum capacitance ($\underline{C}_v$) of the test capacitor:

$$\epsilon' = \underline{C}_n/\underline{C}_v \qquad (9)$$

Since $\underline{C}_v$ may be calculated from the equation,

$$\underline{C}_v = 1.11\, \underline{A}/4\pi\underline{d}, \tag{10}$$

$\underline{p}_{cor}$ is defined as $1/\underline{d}$, and $\underline{A}$, the electrode area is 43.7 sq. cm., by substitution in Equations (9) and (10) and rearrangement, the equation for dielectric constant in terms of the experimental data is

$$\epsilon' = 0.259\, \underline{C}_m/\underline{p}_{cor} \tag{11}$$

The average density of the space between the electrodes, ρ, is the weight of the specimen between the electrodes, in grams, divided by the volume of the space in cubic centimeters, or,

$$\rho = \underline{W}/\underline{dA}, \tag{12}$$

where $\underline{W}$ is the ovendry weight of material between the electrodes. A simplified form is obtained by substitution of numerical values:

$$\rho = 0.0229\, \underline{W}\underline{p}_{cor} \tag{13}$$

Since dielectric constant varies with density, and since it was not feasible to make all measurements at the same density, all results were calculated to a standard density by the use of a form of the Clausius-Mosotti relation, which has been found to hold for both native and regenerated fibers:

$$(\epsilon' - 1)/(\epsilon' + 2) \propto \rho \tag{14}$$

Since the density of most of the specimens tested was in the vicinity of 0.7, this was selected as the standard density.

SOURCES OF ERROR IN THE METHOD OF MEASUREMENT OF DIELECTRIC CONSTANT

Since the data obtained during the investigation are of such a nature as not to be amenable to statistical evaluation of the experimental errors encountered, an analysis of the experimental errors involved would be of value.

The Schering bridge is inherently quite accurate; it is limited, in the case of the measurement of capacitance, chiefly by the accuracy of the precision capacitor, which is ± 1 micromicrofarad or less. This means that the error in $\underline{C}_p$, in the range of capacitances encountered, is 0.5% or less, depending upon the capacitance of the particular sample. Delevanti has shown that no appreciable error is introduced through the use of the approximation formula for capacitance (Equation 6).

As has already been shown, an estimated edge correction of 6 mmfd. has reduced the residual error which is due to edge capacitance to less than 0.2%.

Inasmuch as the effect of frequency upon the dielectric constant was found to be very slight over the frequency range used, errors due to small frequency variations may be neglected.

Calkins has shown that the use of considerable electrode pressure effectively eliminates any "air gap" between electrodes and the surface of the specimen (<u>55</u>, p. 50).

In the calculation of dielectric constant at standard density, it has been assumed that the Clausius-Mosotti relationship holds for all the materials tested. A preliminary experiment (p. 80) showed that this is true for a regenerated fiber, with an accuracy of about 1%, which may be charged to experimental error.

A potentially serious error was encountered, particularly in the earlier runs, in the lateral misalignment of the main electrodes. It is estimated that the area under actual test could be as much as 2% smaller than the actual electrode area used in the calculations. Since the sample area was carefully cut out, measured, dried at 105°C., weighed on an analytical balance, and the weight corrected to the actual electrode area, the sample weight may be considered as correct, well within the 2% value.

The largest error involved in the measurement and calculation of dielectric constant is that of the electrode separation, since it enters into the calculation twice. For a typical sample, the measured $\underline{C}_n$ is 400 mmfd., $\underline{W}$ is 1.000 gram, and $\underline{p}_{cor}$ is 35 cm.$^{-1}$. The calculated dielectric constant at a density of 0.7 is 2.58.

If $\underline{p}_{cor}$ is in error by 2%, the error in $\epsilon'_{0.7}$ is 3.5 to 3.9%. Since the other errors are small by comparison, the experimental error of a single dielectric constant measurement should be less than 5%.

THE MEASUREMENT OF DENSITY

The method of Hermans (73), with some modifications, was used to determine the ultimate density of the various raw materials tested. In its essentials, the method involves the thorough drying of small pellets of the sample, impregnation with carbon tetrachloride vapor, and immersion in liquid carbon tetrachloride under vacuum. A sealed tube containing the sample pellets floating on carbon tetrachloride is transferred to a special water bath and its temperature slowly raised until the pellets sink. The density of carbon tetrachloride at the temperature at which the pellets are just suspended in the liquid is the density of the sample.

The apparatus used (Figure 11) is a modification of that developed by Hermans. Because of difficulties encountered in applying a vacuum from an external pump, the vacuum was attained by heating the whole apparatus to a temperature above the boiling point of carbon tetrachloride, then sealing the system from the atmosphere, and allowing it to cool. In this way, the purpose of evacuation--ensuring that only carbon tetrachloride and the cellulose sample are present in the testing tube--is achieved without the use of an external pump.

In operation, three or four sample pellets (about 0.5 mg. each) were inserted into the conditioning tube (F), and the lower bulb of the distilling flask (A) was filled with carbon tetrachloride which had been especially dried by refluxing 24 hours over fused calcium

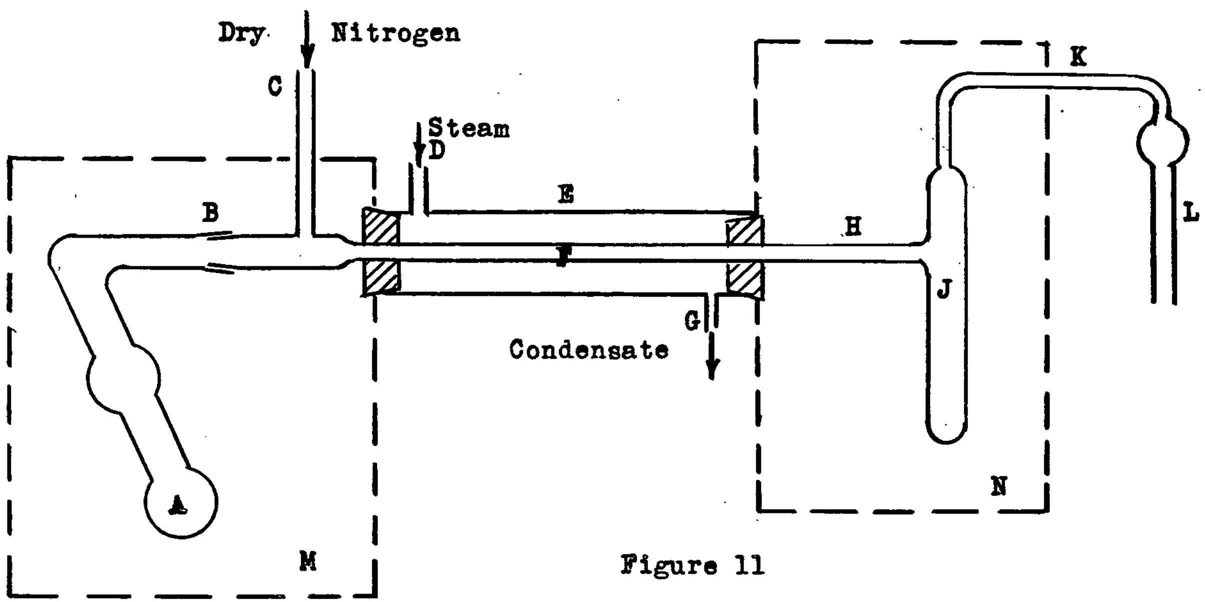


Figure 11

Density Sample Conditioning Apparatus

A Distilling flask, 50 ml.
B Ground glass joint
C Nitrogen inlet
D Steam inlet
E Steam jacket
F Conditioning tube
G Condensate outlet
H Sealing point
J Sample tube
K Sealing point
L Calcium chloride-filled drying tube
M,N Removable ovens; can be heated electrically to 80° C.

chloride and then fractionally distilling. A small amount of phosphoric anhydride was added to the flask to take up any residual moisture. The ground joint (B) was assembled and a very slow stream of dry nitrogen passed through the system from point C. The nitrogen was dried by passing it through a tall column of calcium chloride, followed by a trap kept at -80°C. by a mixture of Dry Ice and benzyl alcohol. The conditioning tube was then heated to 105°C. by passing steam from the laboratory supply through the jacket (E). As a precaution against the moisture contained in the air in the system before assembly, the two ovens (M,N) were assembled about their respective ends of the apparatus, and a small amount of carbon tetrachloride vapor was distilled through the system to sweep out the air. The nitrogen flow and steam heating were continued overnight, but the oven heat was shut off as soon as the sweeping was finished.

When the drying had been completed, the nitrogen inlet was sealed off, and the ovens again heated. This caused a slow passage of carbon tetrachloride vapor through the system, driving the nitrogen from the samples. After about 90 minutes, the heat was removed, and the system was sealed at K. After cooling, the entire apparatus was upended, causing the pellets to drop into the sample testing tube (J). The apparatus was returned to its horizontal position, J was placed in a freezing mixture of ice and salt, and oven heat was applied at A, resulting in the distillation of carbon tetrachloride into the testing tube. When the liquid level in the latter was three fourths of the way up to its inlet, the tube was sealed off from the remainder of the system at H. A new testing tube and nitrogen inlet were sealed onto the conditioning chamber, which was then ready to be re-used.

For the measurement itself, the testing tube was transferred to a special water bath whose temperature could be closely controlled over a wide range. The water bath was actually two baths, one inside the other, to avoid the effects of convection currents. The outer bath consisted of a 12-inch diameter by 12-inch high glass battery jar, equipped with a motor-driven stirrer, a Fenwal Thermoswitch, knife-type heaters, and a steam inlet for rapid temperature changes. It also had an overflow siphon to maintain a constant level during steam injection. The inner bath was a 3-liter beaker suspended within the outer bath. It, too, had a motor-driven stirrer, a special clamp which held the sample tube completely submerged, and a thermometer graduated to 0.2°C. and calibrated against a thermometer tested by the National Bureau of Standards. During the calibration, the latter was held in the position ordinarily occupied by the sample testing tube. Difficulties resulting from evaporation from the inner bath were prevented by a continuous film of mineral oil floated on the surface.

In use, the testing tube, which was insulated from the clamp by a short length of rubber tubing, was clamped in place, and the temperature of the outer bath was raised (by injection of steam) to a temperature slightly below that at which the pellets were expected to sink. After 30 minutes, the inner bath reached the same temperature, and the temperature was raised approximately 0.5° at a time until the pellets sank. To avoid convection currents, 15 to 20 minutes were allowed between each temperature change and the next reading.

The mean of the densities of carbon tetrachloride at the temperatures at which the various pellets were just suspended was taken as the density of the sample, at the temperature corresponding to that density. Following Herman's example, the density was reduced to density at 20°C., through the equation

$$\rho_{20} = \rho_t [1 + 0.00008(\underline{t} - 20)], \qquad (15)$$

where ρ_{20} = density at 20°C., g./cc., and

ρ_t = measured density at temperature $\underline{t}$ (°C.).

The densities thus determined showed fair agreement with those obtained by Hermans (73). A notable exception was Fortisan, which, although Hermans has published no density value for it, yielded values far below those expected from its other known properties (see Table VII). Microscopic examination revealed an abundance of gas occlusions within the fibers of this material, which would account for the discrepancy. The same was true to a lesser extent of the other regenerated materials.

Hermans (102) has recently pointed out a possible source of error during this determination which is due to the presence of phosphorus trioxide in the phosphoric anhydride placed in the distilling flask. A test of the material used showed that this contamination was indeed present. The magnitude of the error is not known, however, and since the usefulness of the method in the present study had proved to be somewhat limited (see below), it was not considered worth while to begin again with specially purified phosphoric anhydride.

Although the results on the cellulosic raw materials were fairly good, it was found that reproducible results could not be obtained on samples in handsheet form. Evidently during the wetting, pressing, and drying involved in the sheetmaking, the fibers had been so altered as to prohibit complete drying, or complete displacement of the nitrogen by the organic vapor. Accordingly, density determination was abandoned as a means of measuring the changes brought about by pressing, and reliance was placed on the moisture sorption measurements.

THE MEASUREMENT OF ACCESSIBILITY

The method of Wink (103) was used to measure the moisture regain of the various samples at 73°F., and at several relative humidities. The absorption isotherm was interpreted as suggested by Hailwood and Horrobin (75).

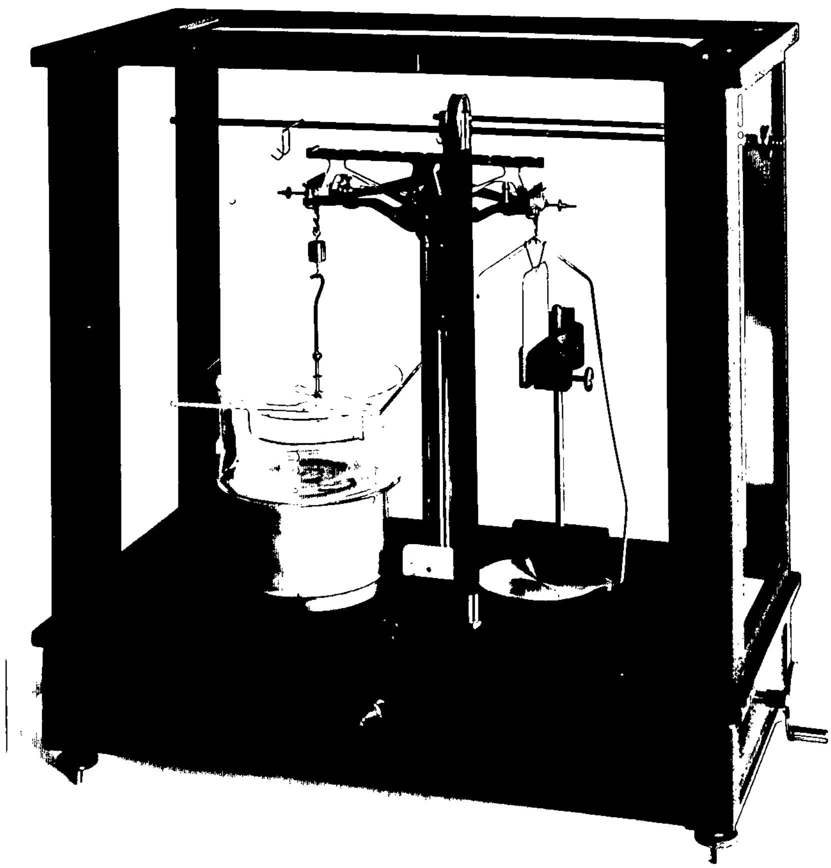
To obtain the sorption data, the samples were placed in an open glass Petri dish suspended within a covered crystallizing dish by means of a brass rod passing through a hole in the cover, and terminating in a hook. A conical collar soldered on the rod provided an effective seal for the tapered hole in the cover. A constant relative humidity was maintained within the crystallizing dish by a saturated salt solution. When the hook was suspended from the beam of an analytical balance, the sample could be weighed without changing the humidity conditions within the vessel. The apparatus is shown in Figure 12.

In use, the balance was first zeroed against a suitable counterpoise in place of the left-hand balance pan. Before any subsequent weighings, the balance was always zeroed to the same counterpoise. The weight of the empty Petri dish and its suspending device was determined, after which the sample (about 0.5 gram) was distributed over the bottom of the Petri dish.

All samples were first dried over phosphoric anhydride. Weighings were made every day until constant weight was attained. The sample, with its Petri dish, suspension device, and cover was then

Figure 12

Sorption Apparatus



transferred to the first of the salt solutions in the absorption series. The salts used and the corresponding relative humidities are given in Table VI. As each solution was prepared, its equilibrium relative humidity was checked against an electric hygrometer.

TABLE VI

SATURATED SALT SOLUTIONS AND THEIR RELATIVE HUMIDITIES

Salt	Relative Humidity (104) at 73°F., %
Lithium chloride	11.1
Potassium acetate	22.9
Magnesium chloride	32.9
Sodium nitrite	64.8
Sodium chloride	75.5

The weighings were repeated daily until constant weight was attained, after which the transfer to the next higher humidity was made. Since only the adsorption cycle was desired, at the end of the cycle each sample was dried over phosphoric anhydride, and the tare of the dish and suspension again obtained, as a check. Depending upon the size and nature of the sample, as well as the amount of the humidity change, from 4 to 14 days were required to attain equilibrium after each change. The entire operation was carried out in a room maintained at 73°F.

CALCULATIONS

The data were interpreted by fitting the isotherm derived by Hailwood and Horrobin, in its simplified form, which assumed the formation of a monohydrate only:

$$\underline{Mr}/1800 = [\alpha \underline{h}/(1 - \alpha \underline{h})] + [\alpha\beta \underline{h}/(1 + \alpha\beta \underline{h})] \qquad (16)$$

where $\underline{M}$ = "molecular weight" of the operative polymer unit,

$\underline{r}$ = moisture regain, grams per 100 grams of dry sample,

$\underline{h}$ = percentage relative humidity, and

α and β are constants.

In accordance with the suggestion of Hailwood and Horrobin, this equation was reduced to the form

$$\underline{A} + \underline{Bh} - \underline{Ch}^2 = \underline{h}/\underline{r}, \qquad (17)$$

by substituting $\underline{A} = \underline{M}/[1800\,\alpha(\beta + 1)]$,

$\underline{B} = \underline{M}(\beta - 1)/[1800(\beta + 1)]$, and

$\underline{C} = \underline{M}\alpha\beta/[1800(\beta + 1)]$.

The method of least squares was used to calculate $\underline{A}$, $\underline{B}$, and $\underline{C}$ from the five moisture regains determined experimentally. $\underline{M}$, α, and β could then be evaluated. Since $\underline{M}$ is the molecular weight corresponding to one hydroxyl group taking part in the absorption, and the actual molecular weight per hydroxyl for cellulose is 162, the inaccessible fraction is given by $(\underline{M} - 162)/\underline{M}$.

Because of the nature of the calculations involved in the interpretation of the data, it is difficult to estimate the experimental error encountered. However, the moisture regains of duplicate samples agreed generally within 0.2%, which would correspond to an absolute error of about 0.5% in accessibility at the higher relative humidities, which is where the larger errors occurred. In general, the calculated value of moisture regain fell within range of the two experimental values for each point.

It is recognised that drying over phosphoric anhydride does not result in complete dryness; however, all samples underwent the same procedure, so that the results should be comparable.

PREPARATION OF CELLULOSES FOR TESTING

The physical characteristics of the cellulosic materials tested are listed in Table VII.

COTTON LINTERS

The cotton sample used was a standard linter cotton obtained from the Hercules Powder Company. The fibers were too long for papermaking purposes, so they were beaten in a Valley one-pound beater to 435 ml. Schopper-Riegler freeness and screened with a laboratory screen. Dirt particles were settled out in the manner described by Calkins (88, p. 69). The settled stock was dewatered, pressed, and stored for sheetmaking. This material was designated Cellulose D.

WOOD PULP

A high-alpha wood pulp made by the Brown Company was obtained from the physical chemistry department of The Institute of Paper Chemistry. This material was used for sheetmaking without any further treatment, except for tearing into small pieces and soaking overnight before disintegrating. This material was designated Cellulose J.

CELLOPHANES

Samples of viscose sheet material were obtained from the Du Pont Company. One was an unplasticized 600-PUT-0 Cellophane, and has been designated Cellulose A. The other was plasticized 600 PT Cellophane, and was designated Cellulose B.

TABLE VII

PHYSICAL PROPERTIES OF VARIOUS CELLULOSES

Cellulose	Description	Degree of Polymerization	Moisture Vapor Accessibility, %	Ultimate Density in CCl_4 at 20°C., g./cc.	Ash, %
A	Unplasticized cellophane	370	59.3	1.520	0.3
B	Plasticized cellophane	270	--	--	0.04
C	Undried cellophane, stored several years in formaldehyde	250	39.2	--	--
D	Cotton linters	1000	27.1	1.544	0.06 - 0.14[a]
E	Cordura rayon	370	67.0	1.515	0.02[a]
F	Unplasticized cellophane, stored 66 days in formaldehyde solution	--	38.2	--	--
G	Fiber G	460	54.3	1.527	0.3[a]
H	Fortisan saponified acetate	365	49.4	1.508[b]	0.4[a]
J	Alpha wood pulp	915	40.0	1.541	0.12[a]
K	Bemberg rayon	485	59.5	1.520	0.5[a]

[a]Ash content of handsheets.

[b]This extremely low value was apparently caused by gas occlusions within the fibers.

The original undried cellophane tested by Calkins was still available; it had been stored for several years in an aqueous formaldehyde solution. The sheets were washed in several changes of distilled water over a period of several days and dried under heavy tension upon laboratory drying frames. This was designated Cellulose C.

In an effort to reproduce any possible effects of storage in formaldehyde, a similar solution (3.2%) was prepared, and a number of sheets of Cellulose A were stored in it for a period of 66 days. At the end of this time, the sheets were washed and dried in the same manner as the undried cellophane. The resulting material was designated as Cellulose F.

REGENERATED FIBERS

In view of the fact that the peculiar nature of some of the regenerated fibers to be tested would make their preparation in the laboratory difficult or impossible, it was decided to use commercially produced rayon yarns. These yarns were cut to lengths of 1 to 5 mm., using an ordinary paper cutter. With the exception of the viscose rayon, these short lengths were used directly in the sheetmaking operation.

VISCOSE RAYON

A high-tenacity viscose tire-cord rayon, Du Pont Cordura, was chosen to represent this type of material. The yarn available was

1100 denier, 480 filament, 0 twist. The cut lengths were beaten for two hours in a Valley one-pound beater, which resulted in a negligible drop in freeness, but did shorten the fibers somewhat. The stock was settled and dewatered in the same manner as the cotton linters. This was designated Cellulose E.

FIBER G

A small quantity of Fiber G, 1100 denier, 552 filament, 1.52" twist, was obtained from the Du Pont laboratories. This is an experimental fiber and is a viscose rayon which has an unusually high crystallinity as a result of the manner in which it is spun. This was designated as Cellulose G.

SAPONIFIED ACETATE RAYON

A quantity of Fortisan was obtained from the Celanese Corporation. This is a rayon which has been spun as cellulose acetate, stretched, and then saponified. The product has a high crystallinity, and unusually high tenacity. Analysis by the modified Eberstadt method revealed that this particular sample was completely saponified. It was designated Cellulose H.

CUPRAMMONIUM RAYON

A skein of cuprammonium rayon was obtained from the American Bemberg Corporation. This sample was 75 denier, 60 filament, 0 twist. It was designated Cellulose K.

PREPARATION OF TEST SHEETS

The nature of the apparatus used required that the samples be in the form of handsheets. Several methods of sheetmaking were used in preliminary tests. In all cases, the stock was disintegrated according to Institute Method 411; it was subjected to 75,000 revolutions in the British disintegrator at 1.2% consistency.

ACID WASHING

To test the effect of ash reduction by acid washing, one batch of cotton linter stock was stirred in 1% hydrochloric acid at room temperature for one hour. It was filtered and washed repeatedly with distilled water until the washings showed no trace of chloride in a test with silver nitrate.

LOW-CONTAMINATION SHEET MOLD

The sheet mold used by Calkins (58, p. 74) was reconstructed and tested. It consisted of a Büchner funnel mounted on a ring stand. A tube of natural rubber was cemented around the inside as a gasket. A fine brass sheet-forming wire supported by a large-mesh stainless wire screen was fitted inside the gasket. Either of two deckle boxes could be used, each consisting of a glass cylinder whose ground lower edge formed a good seal with the rubber gasket. The smaller box held 3 liters of stock suspension, and the larger held 7 liters. A perforated disk of 0.25-inch Lucite mounted on a saran handle was used as an agitator. This sheetforming device was used with distilled water only, and the very small amount of metal ensured the least possible contamination.

Preliminary studies showed, however, that these precautions were unnecessary. Therefore, the sheets finally tested were formed according to Institute Method 411, using the standard British sheet mold and tap water. Because of the tendency of the long fibers to knot together, the stock for each regenerated fiber sheet was stirred in a malted milk mixer for several minutes before forming the sheet, and the agitator of the sheet mold was given 10 to 14 strokes in place of the usual seven, to ensure adequate dispersal of the fibers. Because of the lack of hydration, the drainage of these sheets was extremely rapid, and the formation was quite good.

With rare exceptions, the sheets were pressed at 50 p.s.i. for two minutes before air drying.

Calkins' difficulties in the air drying of handsheets were circumvented by the selection of a drying method to suit the material at hand. The linters and wood pulp sheets were dried on the standard British disks and rings. The sheets from regenerated fibers were left on the disks and air dried under very light tension by laying upon each sheet a brass ring consisting of a 0.5-inch length of 4- or 5-inch brass pipe. In most cases this provided sufficient tension to prevent cockling without causing the sheets to split. A certain amount of splitting did occur, but sufficient sheets were made from each sample to allow such sheets to be discarded.

Although the cellophanes were already in sheet form, only the unplasticized material could be tested in its original condition. The plasticized cellophane had cockled in storage, and was soaked overnight in distilled water and dried on the standard disks under heavy tension, with the aid of the drying frame described by Calkins (55, p. 76).

The cellophanes stored in formaldehyde were washed in distilled water and dried in the same manner.

PRESSING

Since an essential part of the study was the effect of moderate pressure on dielectric constant and accessibility, the conditions of pressing are of special significance.

Normally, each handsheet was pressed between a blotter and the standard drying disk for two minutes at 50 p.s.i. These were designated as normal sheets. A few sheets were not pressed at all (e.g., those used in testing the validity of the Clausius-Mosotti relation).

Pressing at higher pressures was done in the Elmes molding press in the Plastics Laboratory of The Institute of Paper Chemistry. Since the platens of this press were rather rough, two steel plates were procured for use as platens. The upper plate was 7 inches square, the lower one, 10 inches square. Each plate was made of 0.5-inch cold-rolled steel, ground on both sides to parallel surfaces, flat within 0.0001 inch.

WET PRESSING

For moderate-pressure wet pressing, a sandwich of disks, sheets, and blotters was taken from the British sheet press in which it had been pressed for two minutes at 50 p.s.i., placed between the two steel plates, and inserted between the unheated platens of the molding press, as nearly centered as possible. Since preliminary tests showed no crushing of the sheets as the result of high pressures, the pressure was immediately raised to 4000 p.s.i., through the action of 62.5 tons on the 31-sq. in. area of the sheets. The pressure was maintained at this value for ten minutes, then released. The blotters were removed from the sheets which were then air dried in the same manner as the corresponding normal sheets. The pressed sheets showed much less tendency to split than the normal ones.

COLD PRESSING

In cold pressing, a sufficient number of airdry sheets (three to six) to make the pressed product of suitable thickness for testing was selected for quality and laid between two carefully cleaned drying disks. This sandwich was then pressed at room temperature in the same manner as in the wet-pressing procedure.

HOT PRESSING

Hot pressing was carried out in the same way as cold pressing, except that the platens were preheated to about 110°C. and held at this temperature for the duration of the pressing.

The hot-pressed laminates were quite stiff and compact, and had acquired a surface gloss from the disks. The cold-pressed sheets delaminated much more easily and did not have the surface gloss.

Wet pressing had a distinctive effect on the regenerated sheets. The normal sheets, with the exception of Fortisan, were extremely weak and had a tendency to fall apart at the least mistreatment. The wet-pressed sheets had acquired a moderate strength, however, and could withstand considerably more handling. Normal Fortisan sheets were fairly strong and were similar to those from the unbeaten wood pulp in this respect.

Calkins found little or no effect of pressing on cotton-linter sheets, and hence these sheets were given no special pressing treatment.

ANALYTICAL PROCEDURES

ASH

Ash determinations were carried out according to Institute Method 610. The cutout specimen from the electrical testing was divided into two parts for oven drying, after which they were ashed and ignited. As a result, the sample size was usually about 0.5 gram.

DEGREE OF POLYMERIZATION

The degree of polymerization (D.P.) was estimated from the intrinsic viscosity of the nitrated derivatives in acetone by means of the modified Staudinger equation,

$$D.P. = (\eta)/\underline{K}_m, \qquad (18)$$

where (η) = intrinsic viscosity

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

The samples were nitrated, and their viscosities were measured according to the method described by Heuser (105).

PRELIMINARY EXPERIMENTS

ATTAINMENT OF EQUILIBRIUM

The earliest experiments were directed toward the establishment of a time schedule by which to carry out the succeeding tests. During the separation-gage calibration work, it was found that it required 12 to 15 hours for mechanical equilibrium to be established after a temperature change. Since each sample was to be desiccated at 105°C., it was certain that no measurements could be made before about 15 hours had elapsed. Whether desiccation would be complete by this time was still to be learned. Calkins found that desiccation was sufficient after 15 hours; however, his samples were much thinner than those used in the present work.

Table VIII shows part of the data from a typical run; the samples in this case were Cordura rayon handsheets.

These data indicate that equilibrium was established by the end of 18 hours. As a precaution, all samples were conditioned for 22 to 24 hours prior to making the first measurement. In the cases of some cellophanes, even this was not enough, as was apparent from the excessive loss angle, which prevented a complete balance of the bridge. In such cases, 36 hours proved to be sufficient.

TABLE VIII

DATA ON ATTAINMENT OF EQUILIBRIUM

Time, hr.	Temp., °C.	Vacuum, mu	Frequency, cycles/sec.	p_{cor}	C_x, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
0	27	10	1000	28.7	291	2.67	0.697	2.63
12	102	0.1	1000	28.8	299	2.68	0.701	2.67
18	103	0.1	1000	28.7	302	2.72	0.697	2.73
24	103	0.1	1000	28.7	302	2.72	0.697	2.73
82[a]	103	0.1	1000	28.7	302	2.72	0.697	2.73

[a] After cooling to room temperature, releasing vacuum, re-evacuating, and reheating under vacuum for 17 hours.

EFFECT OF METHOD OF SHEET FORMATION

Handsheets were made under a variety of conditions, in order to try to learn what precautions regarding contamination and quality of sheet formation had to be observed. Sheets were made in the low-contamination mold previously described, and in the British sheet mold; with distilled water and with city water; and with and without acid-washing of the stock. The results of these tests are given in Table IX.

TABLE IX

EFFECT OF METHOD OF SHEET FORMATION ON DIELECTRIC CONSTANT OF COTTON LINTERS

	Ash, %	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
Effect of Sheet Mold Used (acid-washed stock, distilled water):				
Glass mold, 3 l.	0.18	2.49	0.746	2.36
Glass mold, 7 l.	0.27	2.48	0.726	2.37
British mold	0.38	2.42	0.750	2.29
Effect of Water Used (acid-washed stock, British mold):				
Distilled water	0.38	2.42	0.750	2.29
City water	0.02	2.45	0.730	2.37
Effect of Acid-Washing (British mold, city water):				
Acid washed	0.02	2.45	0.730	2.37
Not acid-washed	0.24	2.51	0.724	2.43

Inspection of these data reveals a certain amount of relationship between the precautions taken and the ash content of the resulting sheet, but very little between the ash content and the dielectric constant. In the absence of any definite indication of an effect beyond the experimental error, it was apparent that unusual precautions were unnecessary. As a result, the sheets to be tested were made in the standard British mold, using city water.

EFFECT OF QUALITY OF SHEET FORMATION

It was feared that in testing cellulosic materials in the form of handsheets, an error might be introduced by the variations in quality of formation. To test this, sheets were made in the British mold at various consistencies. Sheets made with the mold full were of good, even formation, whereas those made with lesser dilutions were correspondingly less uniform. The results obtained on these sheets are shown in Table X.

TABLE X

THE EFFECT OF FORMATION ON DIELECTRIC CONSTANT OF COTTON LINTERS

	Ash, %	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
(British mold, city water, stock not acid-washed)				
Mold full	0.24	2.51	0.724	2.43
	negligible	2.50	0.725	2.43
Mold half full	0.18	2.43	0.719	2.37
	0.14	2.50	0.753	2.35
Mold quarter full	0.06	2.50	0.716	2.45
	0.52	2.51	0.716	2.46

As can be seen, the pairs were consistent within themselves, but there was no definite trend of variation of dielectric constant with formation quality. Accordingly, it was concluded that formation has a negligible effect upon the results.

THE RELATION BETWEEN APPARENT DENSITY AND DIELECTRIC CONSTANT

Since it was obviously impossible to make all electrical measurements at the same density, some sort of density correction was necessary before any comparisons among results could be made. Hansen and Calkins showed that the dielectric constants of a kraft paper and of purified native cellulose were related to apparent density by the Clausius-Mosotti relationship, $(\epsilon' - 1)/(\epsilon' + 2) \propto \rho$.

It remained to be ascertained whether this relation could also be applied to regenerated fibers. A test was made, using handsheets made of Cordura viscose rayon fiber. The sheets were not wet-pressed, and thus retained a high degree of compressibility. These sheets were placed in the test capacitor and desiccated in the usual manner, after which the temperature of the system was reduced to that of the room. The first measurement of dielectric constant was made under only sufficient electrode pressure to bring the electrode separation within the range of the auxiliary bridge. Succeeding measurements were made at progressively higher pressures, until the end of the auxiliary bridge range had been reached. After releasing the vacuum, the sample was removed, cut out, measured, dried, and weighed in the usual manner, and a calibration check was made. In doing this, a separate calibration was made for each measurement of dielectric constant made, each under the same electrode pressure as the corresponding measurement, and with the standard shim nearest in thickness to the separation measured. Calibration corrections were then applied in the usual manner. The results of this experiment are shown in Table XI and Figure 13.

TABLE XI

TEST OF VALIDITY OF CLAUSIUS-MOSOTTI RELATION FOR REGENERATED FIBERS

Electrode Pressure, p.s.i.	P_{cor}	ρ, g./cc.	ϵ'	$\frac{\epsilon' - 1}{\epsilon' + 2}$
120	25.0	0.322	1.58	0.162
155	27.3	0.351	1.63	0.174
275	31.0	0.399	1.76	0.202
410	33.3	0.428	1.83	0.217
510	34.7	0.447	1.91	0.233
565	36.3	0.467	1.95	0.240
685	37.9	0.488	2.01	0.252
700	38.7	0.498	2.03	0.255
760	39.2	0.505	2.04	0.258

The line in Figure 13 is the least-squares regression line, $(\epsilon' - 1)/(\epsilon' + 2) = 0.513\rho - 0.0014$, which was calculated from these data. The maximum deviation of the experimental points from this line is 2.6%; the average is 1.1%; and the correlation coefficient is 0.998. Since, in this range of ϵ' values, transformations to $(\epsilon' - 1)/(\epsilon' + 2)$ tend to increase errors in ϵ', it may be concluded that the relationship is truly linear within the experimental error of the determinations. The intercept ordinate is negligible. It may therefore be concluded that the Clausius-Mosotti relationship is valid for regenerated materials as well as for native fibers.

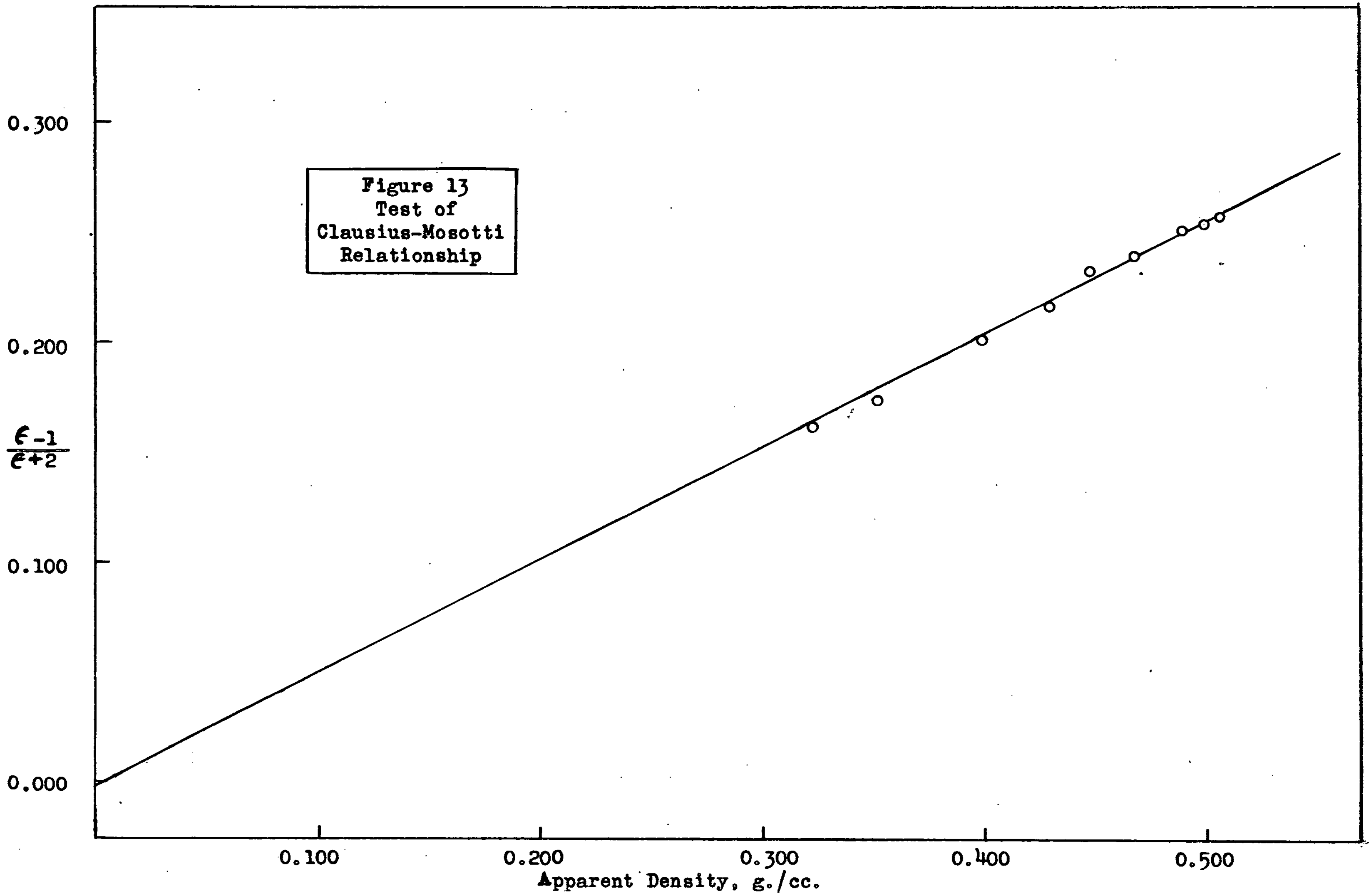


Figure 13
Test of
Clausius-Mosotti
Relationship

It is of interest to note that extrapolation of this line to a density of 1.52 suggests that the dielectric constant of viscose rayon at its ultimate density is in the range of 11 to 12. The possible implications of this will be discussed later.

EXPERIMENTAL RESULTS

THE DIELECTRIC CONSTANT OF NATIVE FIBERS

COTTON LINTERS

The dielectric constant of linter cotton is tabulated in Table XIV (see Appendix). Figure 14 shows the relation to temperature, whereas Figure 15 shows the very small effect of frequency.

The values of $\epsilon'_{0.8}$ listed in Table XIV show fair agreement with the findings of Calkins. Although somewhat higher than his mean values, they are still below his extremes.

Extrapolation to a density of 1.547 yields a dielectric constant of 6.5, compared with De Luca's 6.1 for the solid substance.

The variation of dielectric constant with temperature, as seen in Figure 14, shows the increase observed by Calkins and others. However, the slight minimum reported by Calkins was not observed. In this connection, it must be noted that in the present work, the temperature was not varied in as small steps as Calkins used. Thus, the minimum may exist without having been observed.

The frequency effect, shown in Figure 15, is very slight, but is in the direction previously reported, i.e., ϵ' decreases as frequency increases.

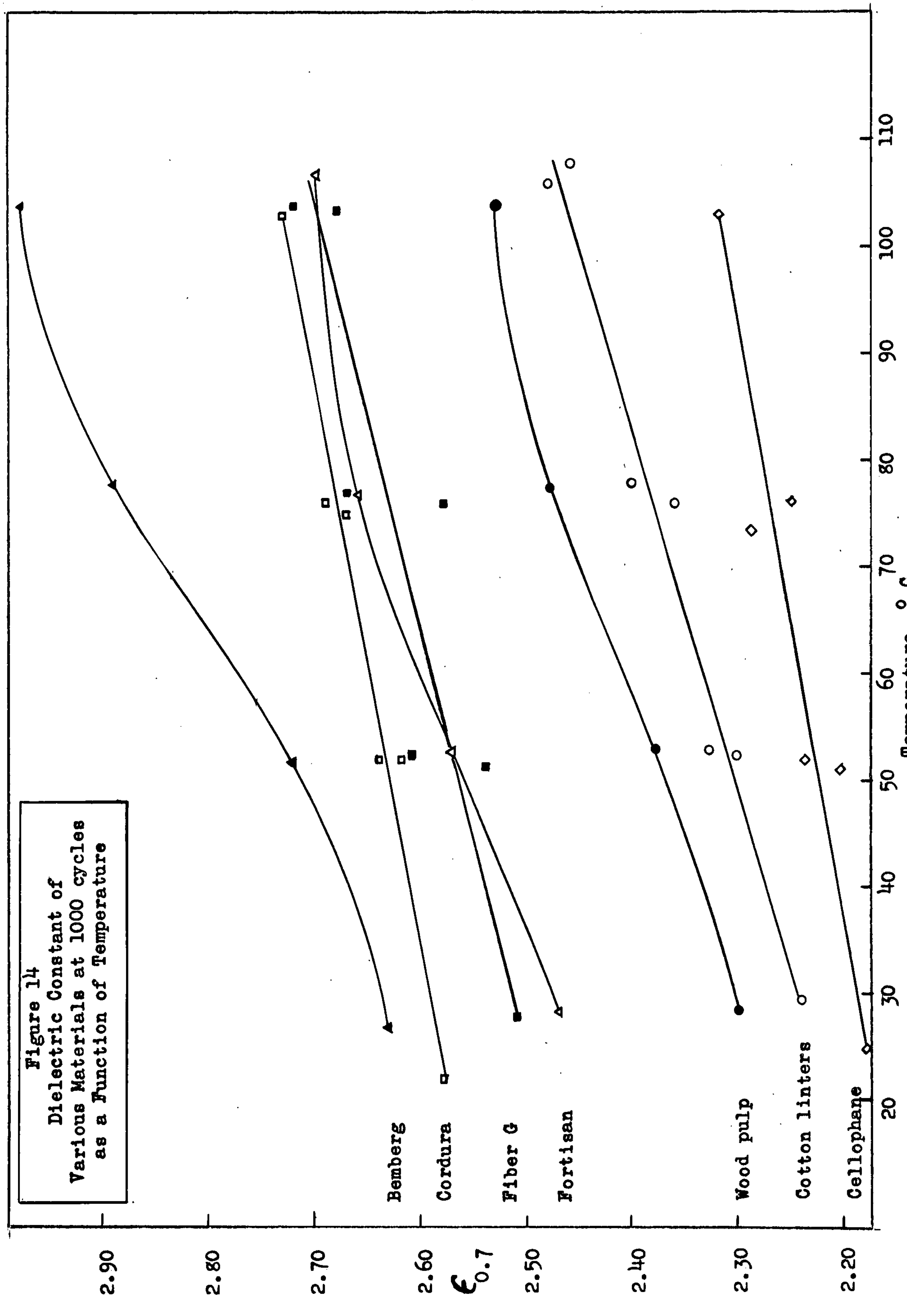


Figure 14
Dielectric Constant of
Various Materials at 1000 cycles
as a Function of Temperature

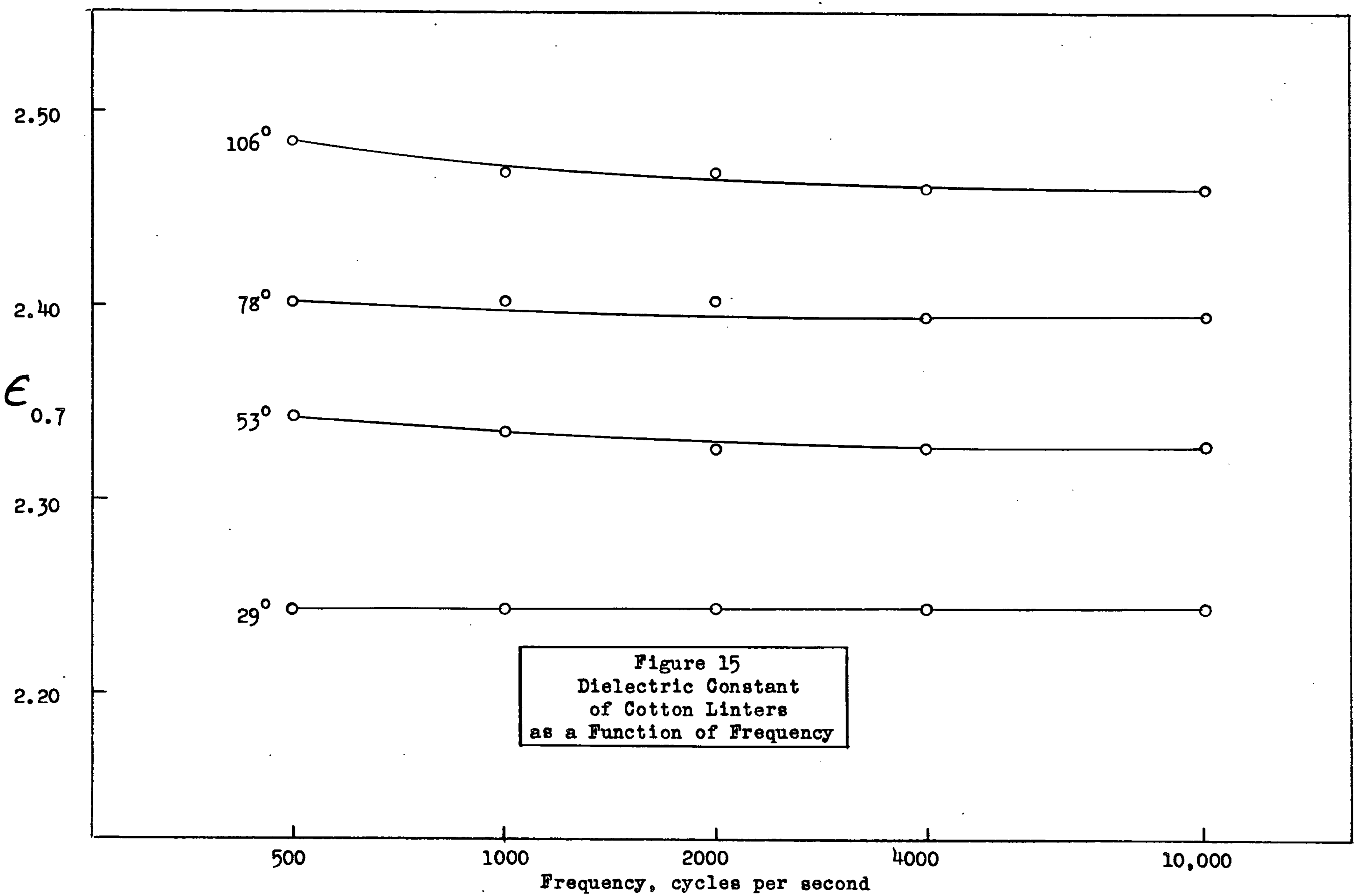


Figure 15
Dielectric Constant
of Cotton Linters
as a Function of Frequency

There was a very small hysteresis effect upon cooling to room temperature and reheating. An examination of the data reveals that the measured capacitance shows no such hysteresis; the difference is due to the decreased sample thickness during the ascending temperature series. This decrease may be real, or may be due to failure of the separation-gage assembly to assume the same proportions upon heating as it did upon cooling. The latter situation seems more likely. In any case, the values obtained are within the estimated experimental error.

WOOD PULP

The dielectric constant of wood pulp (Appendix, Table XV) was found to behave in a quite similar manner. The frequency effect was not measured, but the temperature effect was about the same as in the case of the cotton linters (Figure 14).

The dielectric constant of wood fiber was seen to be higher than that of cotton.

THE DIELECTRIC CONSTANT OF REGENERATED FIBERS

These same trends relative to temperature and frequency were also observed in the cases of all the regenerated fibers tested (Appendix, Tables XVI - XIX, Figures 14, 16, and 17). The only remarkable feature is the exaggerated temperature effect noticeable in the case of the cuprammonium rayon.

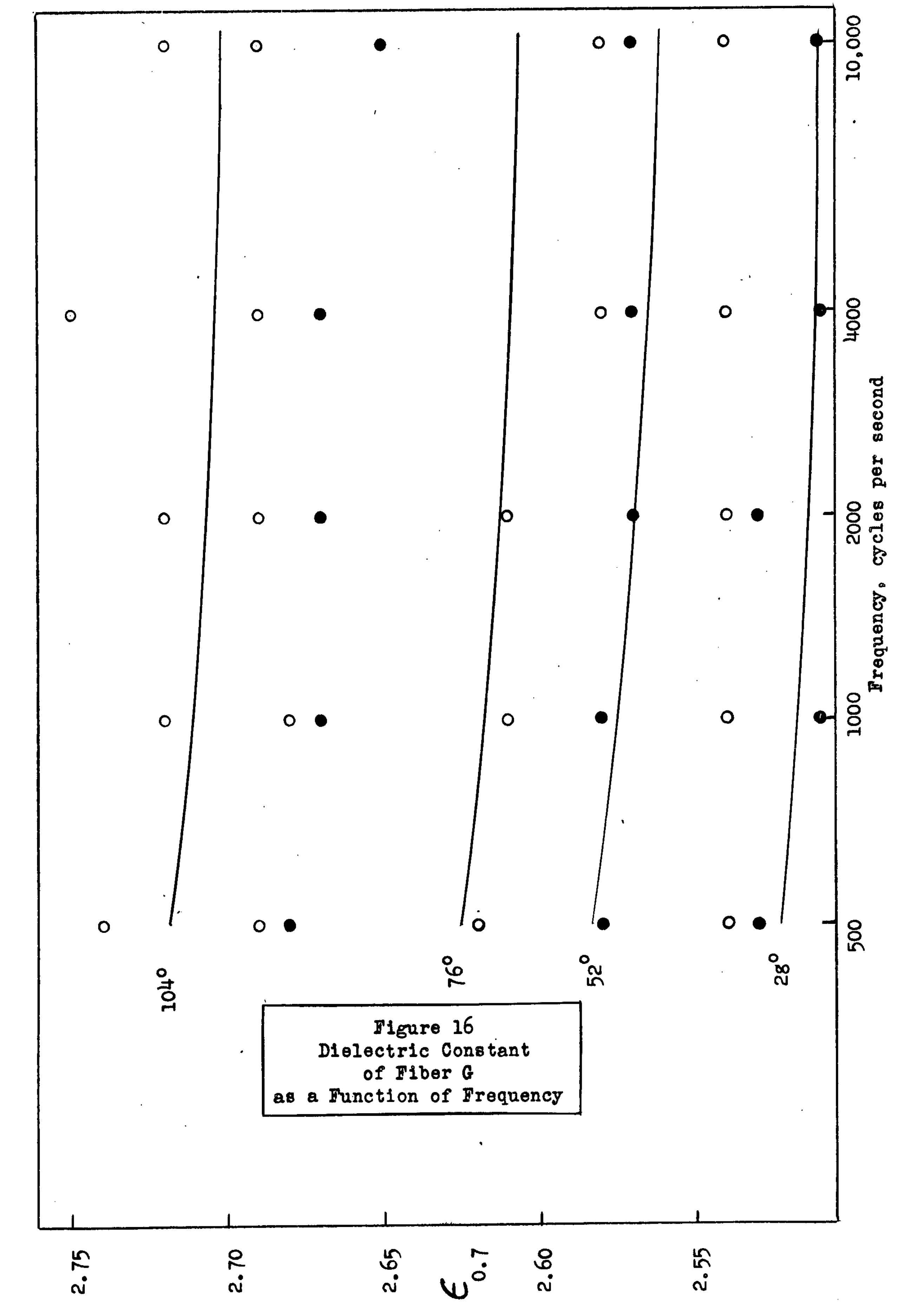


Figure 16
Dielectric Constant
of Fiber G
as a Function of Frequency

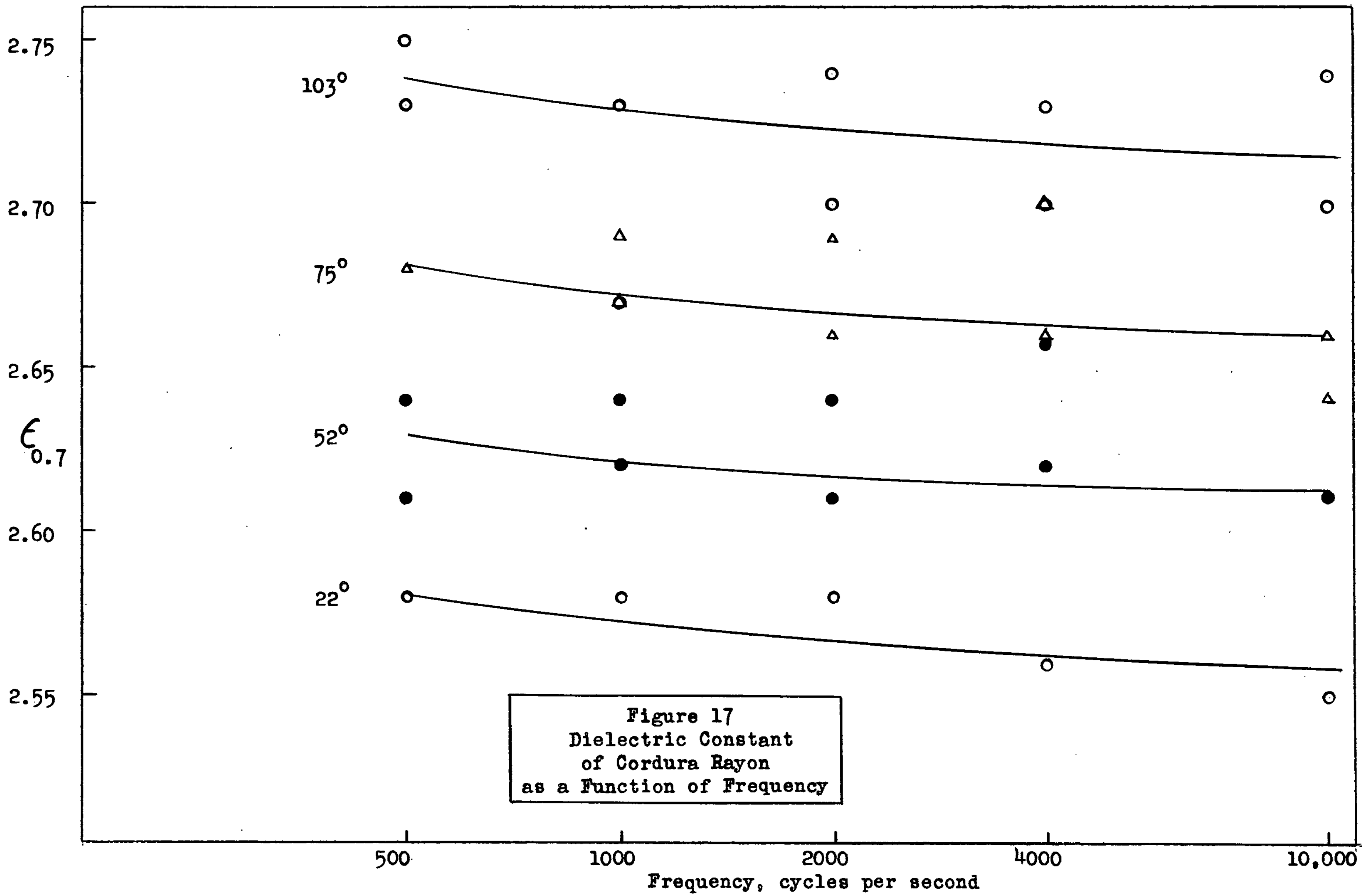


Figure 17
Dielectric Constant
of Cordura Rayon
as a Function of Frequency

The effect of frequency is more marked in the case of regenerated fibers than in native fibers. However, this is largely due to the higher dielectric constant; percentagewise, there is little difference. In all cases, the frequency effect increases as temperature increases.

All these observations are adequately explained by the theory advanced by Calkins that cellulose behaves as a linear polymer having many polar groups, in which both frequency and temperature effects are caused by the activity of the polar groups and the partial rotation of the cellulose chains. Since there are not sufficient data to establish a minimum in the dielectric constant vs. temperature relation, Calkins' views regarding interfacial polarization can be neither confirmed nor denied.

THE DIELECTRIC CONSTANT OF CELLOPHANE

The dielectric constant of regenerated films cannot be explained as readily. The general behavior is similar to that of regenerated fibers, but certain incongruities exist.

The values obtained (Appendix, Tables XX- XXIII, Figures 18 and 19) agree rather well with those of Stoops, although they are somewhat lower. This may be due to the better contact obtained by Stoops's mercury electrodes. However, the electrode pressure applied in the present case should rule out any large amount of air space; indeed, the apparent density measured was in all cases very close to the known density of this material. Stoops's method of desiccation (oven drying without evacuation) may have been responsible, particu-

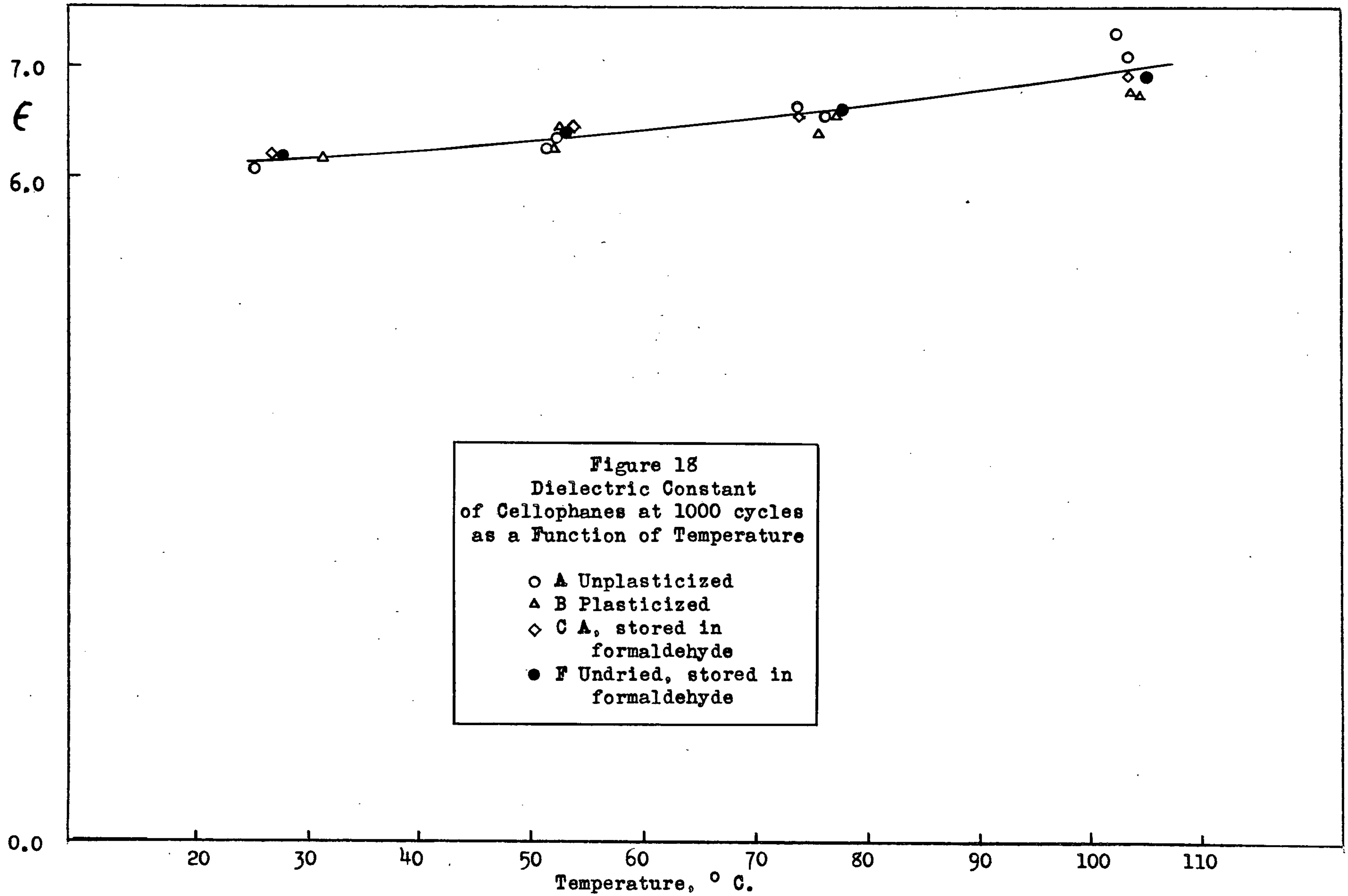


Figure 18
Dielectric Constant of Cellophanes at 1000 cycles as a Function of Temperature

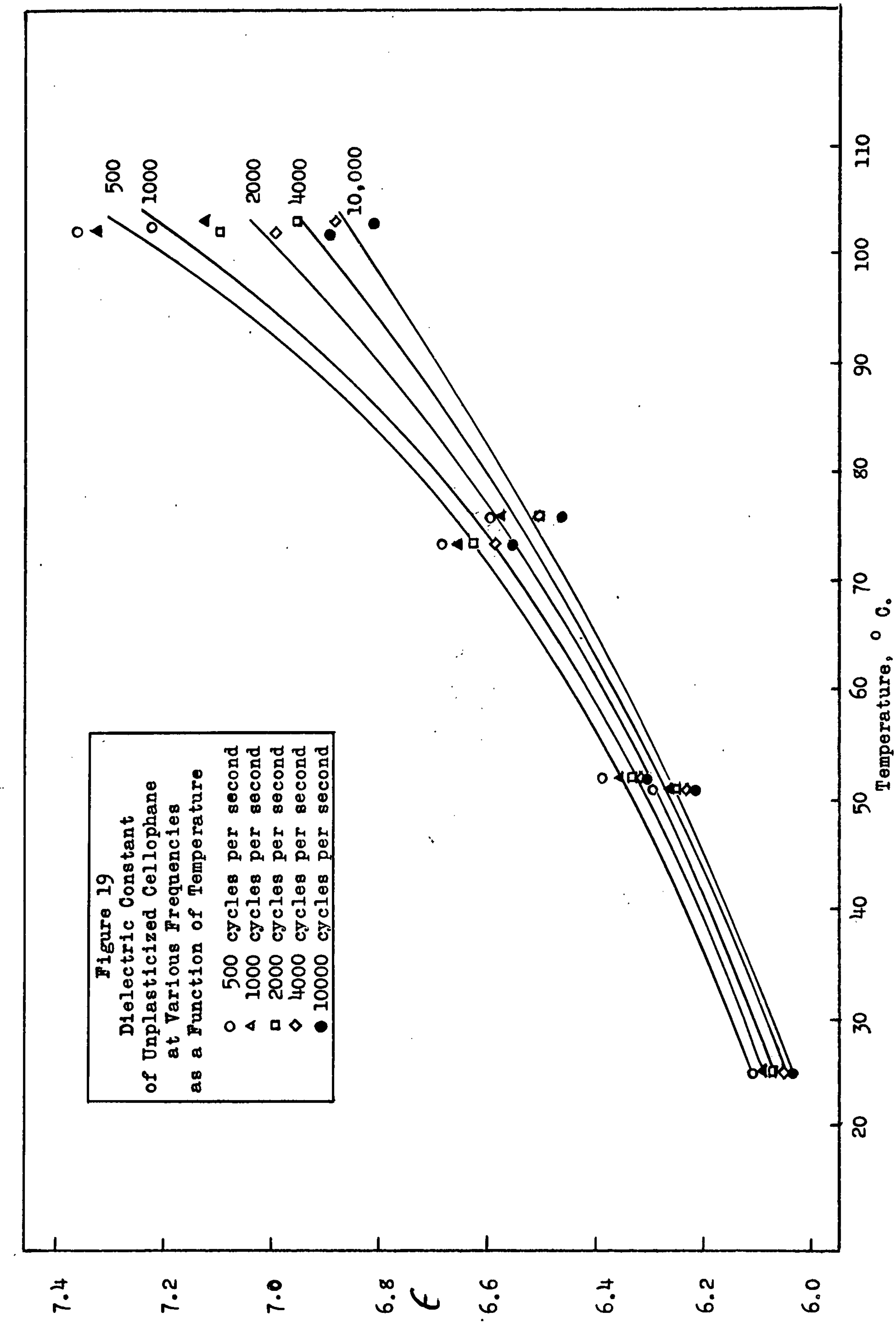


Figure 19
Dielectric Constant
of Unplasticized Cellophane
at Various Frequencies
as a Function of Temperature

larly because the compactness of cellophane makes complete drying a slow process.

In any case, the values obtained are much higher than those of Calkins. He suggested that the low ϵ' of his material may have been due to cross linkages formed during storage of the cellophane in formaldehyde. The present data indicate that this was not the case, since the dielectric constants of the several samples were about the same, regardless of age and method of storage. The difference was probably due to Calkins' method of measurement, in which only a slight electrode pressure was applied.

However, even the new values, when reduced to standard density for the sake of comparison, are lower than might be expected; they are still not quite as high as those for native fibers, and are much lower than those for fibrous materials of similar origin to that of cellophane. The significance of this fact remains for later discussion.

THE RELATION BETWEEN DIELECTRIC CONSTANT AND CRYSTALLINITY

Examination of Figure 14 shows that whereas the dielectric constants of various materials each behave according to known concepts of the structure of cellulose, the dielectric constant at any particular temperature and frequency depends upon the nature of the material. It is known that the effect of small amounts of residual moisture which are possibly present is not serious. It has been shown that the sheet structure has little effect; all values were converted to a standard density by a relation shown to be valid for such materials. Therefore the differences must be due to differences in the submicroscopic structure of the materials.

Calkins has shown that the dielectric constant is not influenced appreciably by the type of crystal lattice.

At first glance, there may be a seeming correspondence between dielectric constant and degree of polymerization, in that the degraded regenerated products (except for the cellophanes) have higher dielectric constants than the more highly polymerized native fibers. However, there is no theoretical basis for such a relationship, *per se*, and indeed, in the discussion of the work on pressed materials it will be seen that such an effect is impossible, since hot pressing, which most certainly would reduce the degree of polymerization, causes a decrease in dielectric constant. Any apparent relation of dielectric constant to degree of polymerization is only coincidental and is due to the degradation taking place during the manufacture of the regenerated materials.

A comparison of dielectric constant with ultimate density reveals a much more striking correspondence, as shown in Table XII and Figure 20.

TABLE XII

RELATIONSHIP BETWEEN DIELECTRIC CONSTANT, DENSITY, AND ACCESSIBILITY

Cellulose	$\epsilon'_{0.7}$ (at 30°C., 1000 cycles/sec.)	ρ_{20}, g./cc.	Accessibility, %
D Cotton linters	2.24	1.544	41.8
J Wood pulp	2.31	1.541	38.5
G Fiber G	2.51	1.527	59.9
H Fortisan	2.48	1.508	49.9
K Bemberg	2.64	1.520	60.0
A Cellophane	2.19	1.520	59.3
B Cordura	2.59	1.515	67.0

With the exception of cellophane, and of Fortisan, whose density value is erroneously low, as has been mentioned, the correspondence is quite good. If Hermans' theory is valid, that density is closely related to sorptive power, and therefore to crystallinity, there must be a fairly definite relationship between crystallinity and dielectric constant.

A comparison of dielectric constant with accessibility (Figure 21) reveals a very similar correspondence. Since this is the case, we might expect density and accessibility to be closely related, which is also true, as may be seen from Figure 22. This bears out Hermans' theory.

It may be seen from these considerations that there definitely is a relationship between dielectric constant and crystallinity.

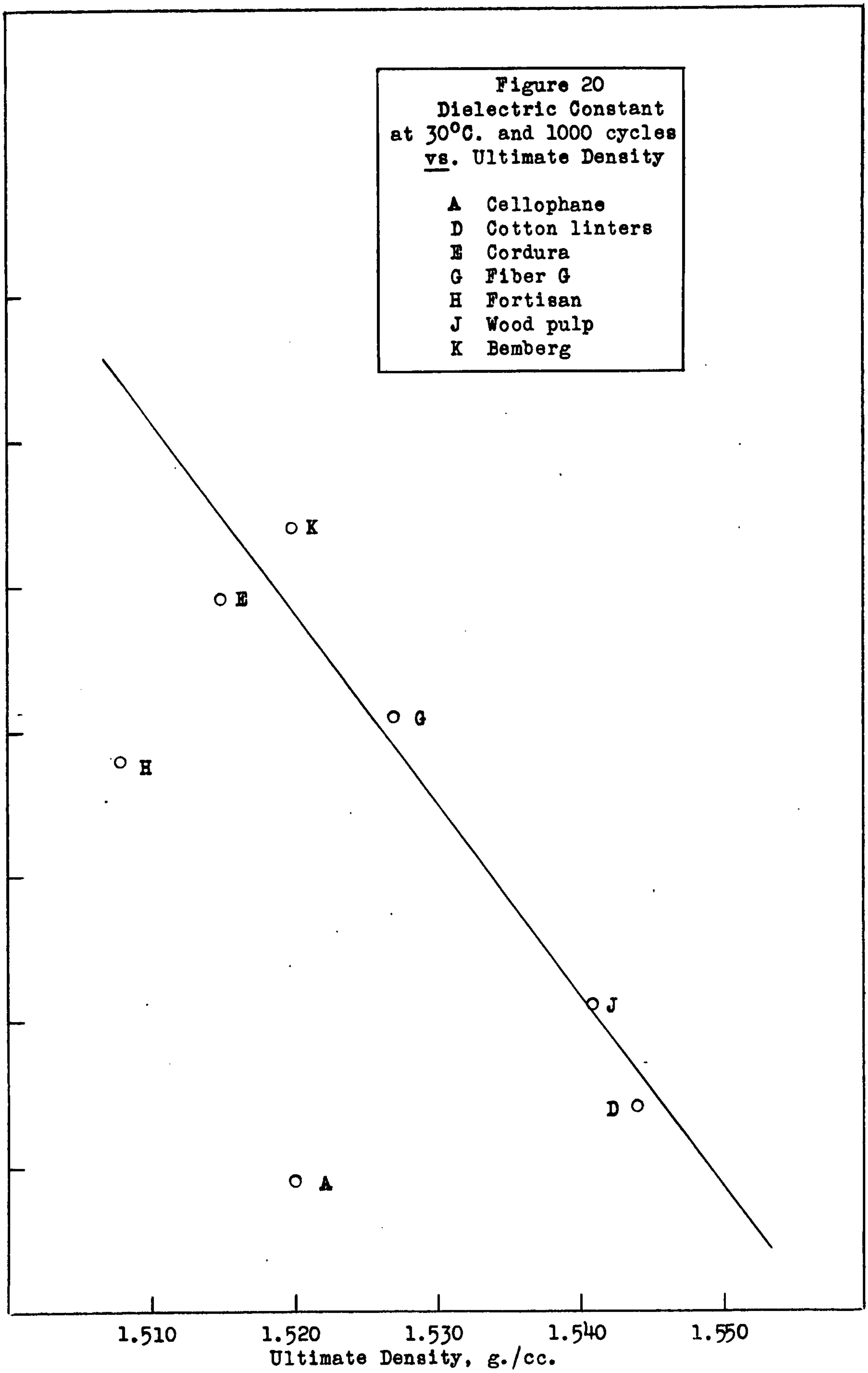


Figure 20
Dielectric Constant
at 30°C. and 1000 cycles
vs. Ultimate Density
A Cellophane
D Cotton linters
E Cordura
G Fiber G
H Fortisan
J Wood pulp
K Bemberg
2.80
2.70
2.60
2.50
2.40
2.30
2.20
ε0.7
K
E
G
H
J
D
A
1.510
1.520
1.530
1.540
1.550
Ultimate Density, g./cc.

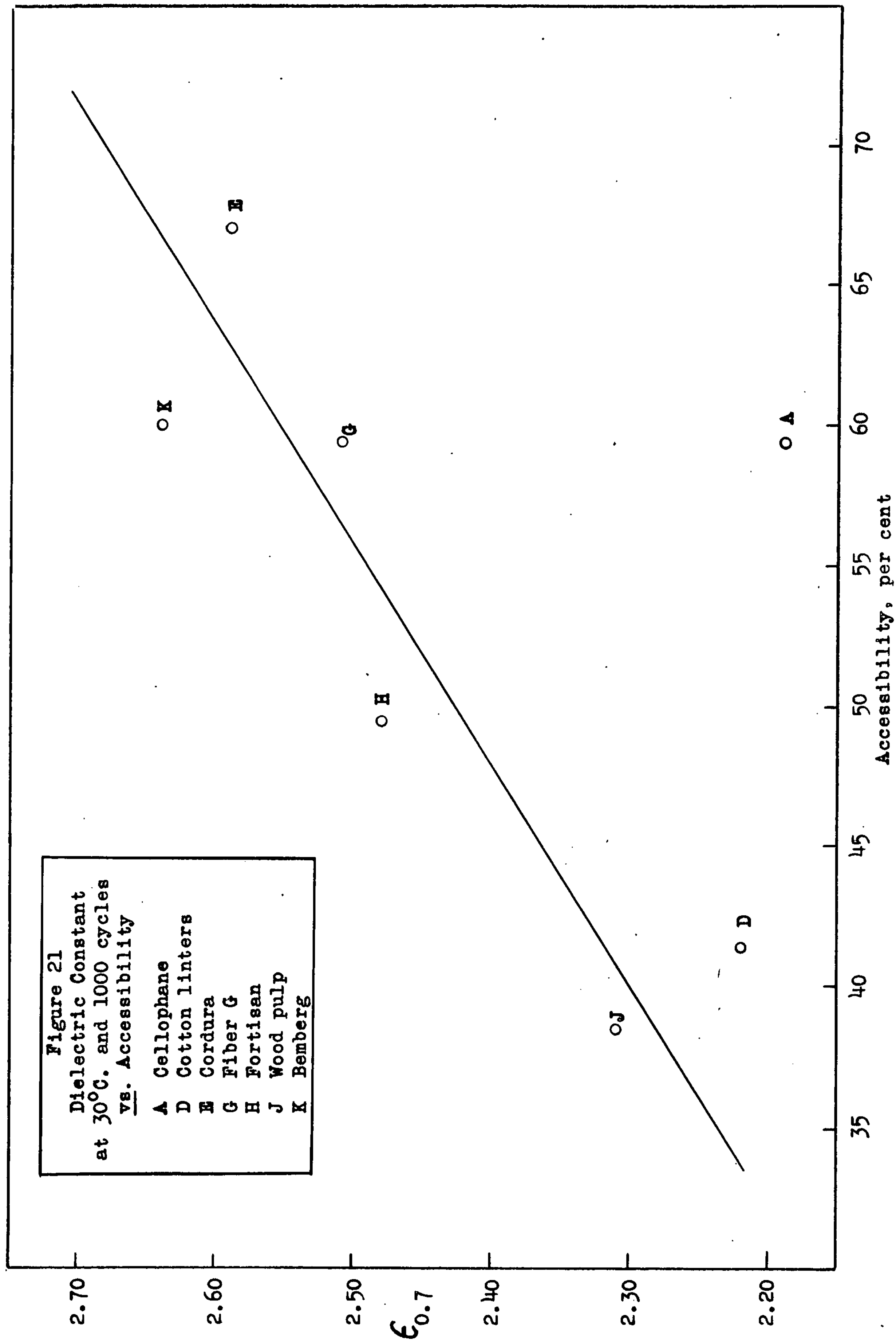


Figure 21
Dielectric Constant
at 30°C. and 1000 cycles
<u>vs.</u> Accessibility

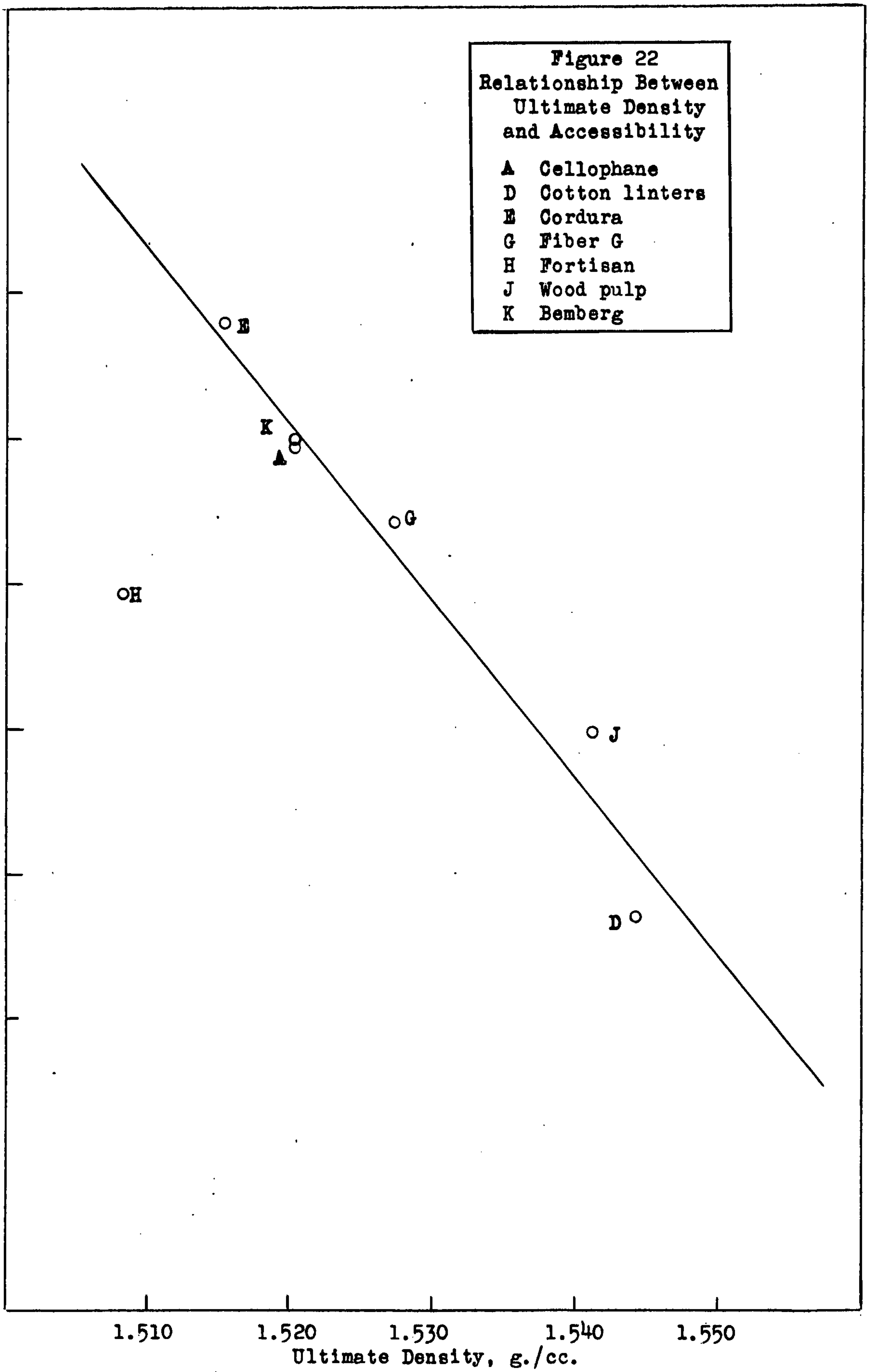


Figure 22
Relationship Between
Ultimate Density
and Accessibility
A Cellophane
D Cotton linters
E Cordura
G Fiber G
H Fortisan
J Wood pulp
K Bemberg
Accessibility, per cent
70
60
50
40
30
20
E
K
A
G
H
J
D
1.510
1.520
1.530
1.540
1.550
Ultimate Density, g./cc.

This is readily understandable--a large part of the polarization in cellulose is due to the motion of free hydroxyl groups and to the rotational vibration of portions of the cellulose chains. Such motions cannot occur within the crystallites. Therefore, the more highly crystalline a cellulose is, the smaller the amount of such motions, and the polarization and, consequently, the dielectric constant must be lower.

STUDIES ON THE EFFECTS OF PRESSING

EFFECT OF PRESSING UPON ACCESSIBILITY

Figure 23 presents the sorption isotherms of the various cellulosic materials tested. The detailed data are given in Table XXV (Appendix).

Although it was found impracticable to present the effect of pressing upon moisture sorption in graphic form, it may be seen from the data (Tables XIII, XXIV, and XXV) that the amount of absorption was generally reduced by pressing, which is indicative of increased crystallinity. The effect was not regular--some curves were lowered at low humidities but raised slightly at the higher humidities; others were lowered throughout their lengths. The net effect, however, is that of decreasing the amount of sorption, and thus lowering the accessibility calculated therefrom.

The nature of the pressing had considerable influence upon the results. In general, the pressing of wet sheets had little or no

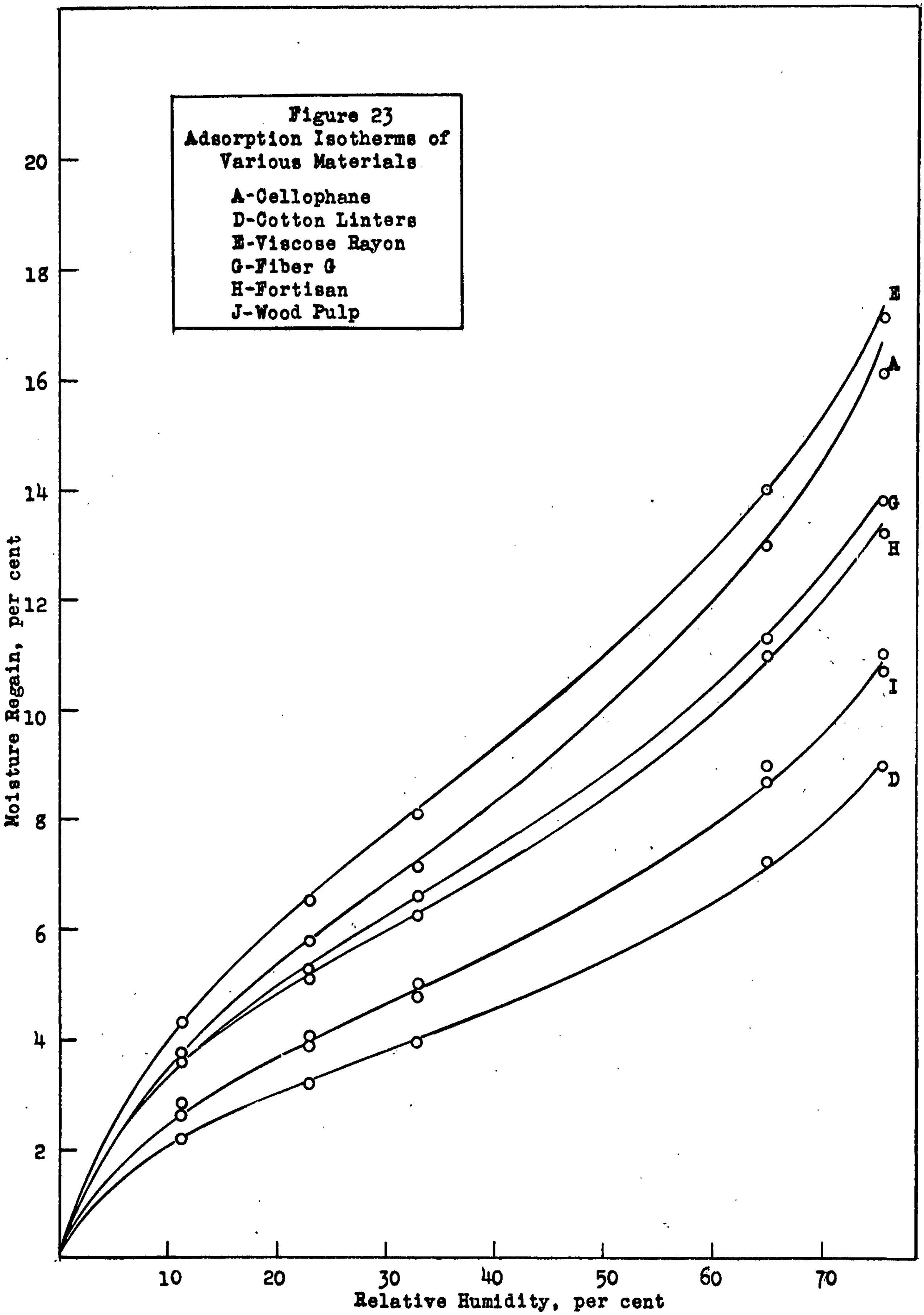


Figure 23
Adsorption Isotherms of
Various Materials
A-Cellophane
D-Cotton Linters
E-Viscose Rayon
G-Fiber G
H-Fortisan
J-Wood Pulp
E
A
G
H
I
D
Moisture Regain, per cent
Relative Humidity, per cent
20
18
16
14
12
10
8
6
4
2
10
20
30
40
50
60
70

TABLE XIII

EFFECTS OF PRESSING[a]

	Cellulose Description	ϵ'[b]	ρ, g./cc.	$\epsilon'_{0.7}$	Accessibility, %
J	Wood pulp, normal	2.60	0.721	2.53	38.5
J	Wet pressed	3.39	0.996	2.35	40.1
J	Cold pressed	3.14	0.894	2.45	37.5
J	Hot pressed	3.82	1.066	2.40	35.6
E	Cordura, normal	2.67	0.627	3.00	67.0
E	Wet pressed	3.03	0.787	2.68	67.2
E	Cold pressed	2.91	0.717	2.84	62.5
E	Hot pressed	3.50	0.882	2.69	60.3
H	Fortisan, normal	2.41	0.619	2.70	49.9
H	Wet pressed	2.74	0.723	2.65	50.1
H	Cold pressed	2.78	0.730	2.66	51.5
H	Hot pressed	3.37	0.917	2.52	42.4
K	Bemberg, normal	2.40	0.561	2.98	60.0
K	Wet pressed	2.78	0.753	2.59	57.4
K	Cold pressed	2.72	0.671	2.84	59.8
K	Hot pressed	4.14	1.058	2.54	49.2
K	Hot pressed (new sample)	4.03	1.036	2.54	----
G	Fiber G, normal	2.26	0.577	2.68	59.9
G	Wet pressed	2.59	0.698	2.60	56.1
G	Cold pressed	2.52	0.662	2.72	52.7
G	Hot pressed	2.96	0.801	2.58	53.5

[a]More detailed data are given in Table XXIV.

[b]At 1000 cycles per second, and approximately 105°C.

effect; in fact, there were some slight increases (which may have been due to experimental error).

Cold pressing generally produced some degree of decrease in accessibility, whereas hot pressing brought about a considerable decrease.

The nature of the events which take place during such pressing is fairly obvious. Since the crystalline lattice of cellulose is more dense than the amorphous structure, the effect of pressure is to cause the structure to yield by making itself as compact as possible. This is accomplished by cellulose chains in amorphous areas joining crystallites already present, where possible, or coalescing to form new crystallites which are probably quite small.

Fuller (106) found that the crystallinity of linear polyamides was increased by heating, which through thermal agitation accelerated the rotation of the chains, thus enabling new crystalline linkages to form. A similar effect was observed in cellulose acetate (107). It is very likely that the same effect brought about the increased recrystallization when the pressing was done while hot.

When pressing wet sheets, the fine structure is not subjected to an external pressure alone. Since water has permeated the entire amorphous structure, the amorphous regions are, in effect, suspended within a liquid at high pressure. Thus, there is no tendency for such chains to be brought together, and since the crystallites are already at their maximum density, the total effect is one of little or no change in the crystalline structure.

The greater or lesser changes in crystallinity upon cold pressing may well depend upon the amount of moisture in the sheet at the time of pressing, a factor which was not controlled.

EFFECT OF PRESSING UPON DIELECTRIC CONSTANT

All of the experimental points obtained in the work on pressing are plotted in Figure 24, and lines are drawn connecting the various samples of the same material, so that the effects of pressing may be seen more readily.

As may be seen from this illustration, and the data in Tables XIII and XXIV, the general effect of pressing was to decrease the dielectric constant. Since, in most cases, the accessibility was similarly reduced, the basic theory of dependence of dielectric constant upon crystalline structure would seem to be borne out.

It will be recalled that the technique used in the measurement of dielectric constant involved a hot-pressing operation, at about one fourth the pressure applied in the pressing experiments. This would have the effect of diminishing the apparent effect of hot pressing; the latter was, therefore, actually more acute than observed.

However, in the cases where the sheets were pressed while wet, the accessibility was only slightly affected, but the dielectric constant was still considerably decreased. This phenomenon is not readily explained. It might be thought that it is due to a failure of the Clausius-Mosotti relationship to hold for the higher densities of the pressed sheets. However, in no case was the apparent density of a wet-pressed sample as high as that of the hot-pressed specimen

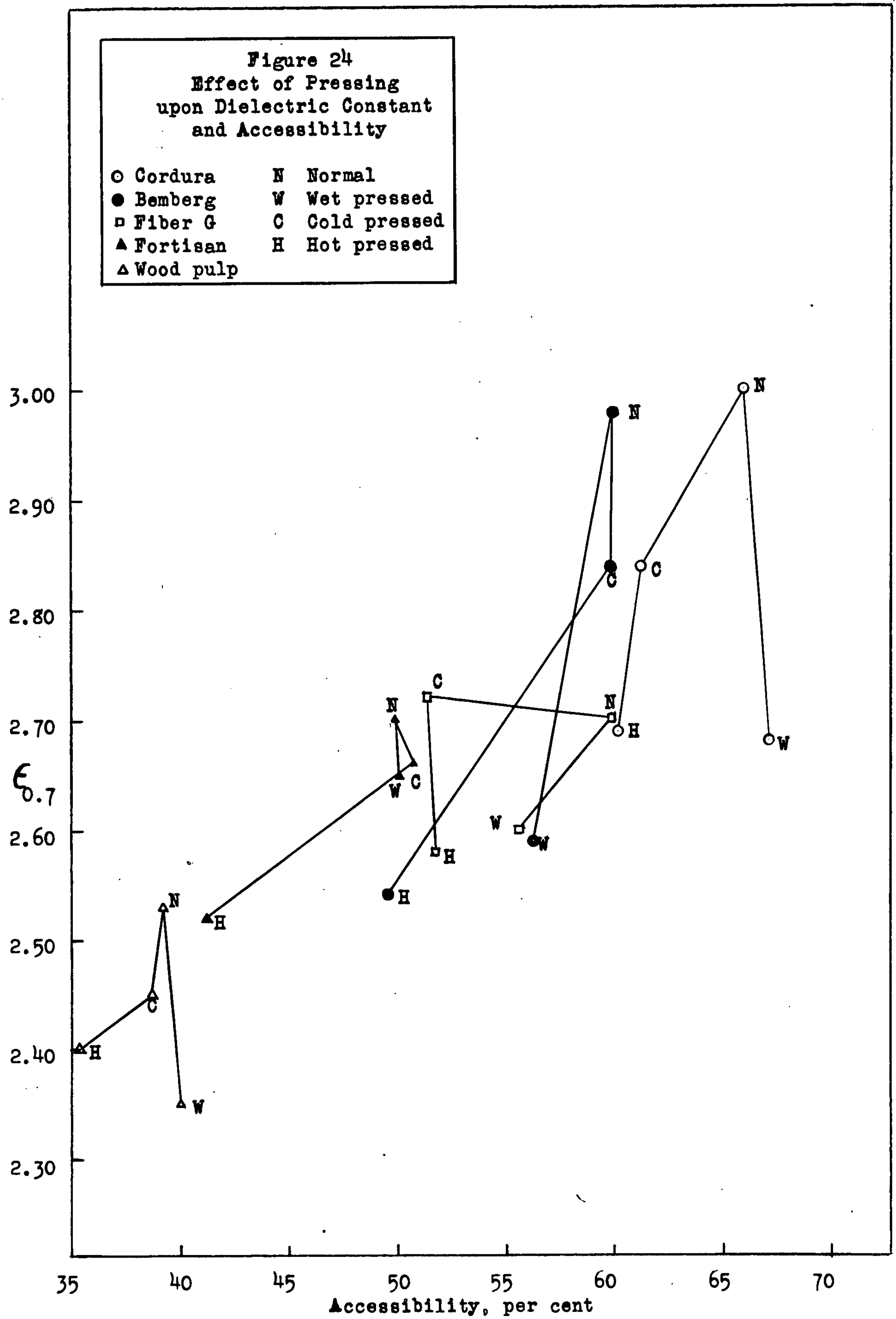


Figure 24
Effect of Pressing
upon Dielectric Constant
and Accessibility
○ Cordura
● Bemberg
□ Fiber G
▲ Fortisan
△ Wood pulp
N Normal
W Wet pressed
C Cold pressed
H Hot pressed
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
$\epsilon_{0.7}$
35
40
45
50
55
60
65
70
Accessibility, per cent

of the same material, and the dielectric constants of the hot-pressed samples exhibited a reduction appropriate to their reduced accessibility.

There is a plausible explanation, however. When a sheet is pressed while wet, the water tends to be displaced toward a zone of less pressure--i.e., it is gradually forced outward toward the periphery of the sheet. (When wet-pressed sheets were removed from the press after 10 minutes, a definite line of demarcation was visible between dry and wet areas, always near the outer edge of the sheet. It seems likely that in sheets pressed for shorter periods of time, this borderline would be nearer the center.) During the initial period of pressing, which, according to Calkins, is the interval when any possible recrystallization would occur, there was sufficient water present to "pad" the chain molecules from each other and prevent their meeting to form new zones of crystallinity. As the moisture receded, a dual phenomenon occurred: the molecular chains were brought into closer contact, and the gel-like structure began to set. Under such circumstances, many points of secondary junction could be formed between the still-kinked molecular chains in the amorphous zones. In the dried product, these junctions would greatly hinder the rotation of the chains, and correspondingly reduce polarization of this sort, and consequently reduce the dielectric constant.

Such junction points, which are "merely new points of contact between chains, of varying attractive energy" (105) do not involve a noticeable increase in amount of crystalline substance, and hence do not alter the measured accessibility. In sheets pressed while dry, the gel structure is already established, and few, if any, new secondary junction points are produced.

If this explanation is correct, it may at least partially explain the failure of cellophane to have a dielectric constant as high as chemically similar rayon fibers. Calkins (88, p. 130) compares a regenerated fiber to a sponge, in that it is filled with small voids. Cellophane, on the other hand, is a continuous homogeneous film. In such a material, the network of molecular chains, with its primary and secondary points of junction, is essentially indefinite in extent, whereas in the void-filled structure of the regenerated fiber, the network structure must be more or less discontinuous. Thus there would be less freedom of molecular motion, particularly rotational vibration, in cellophane, and its dielectric constant would therefore be lower.

The influence of junction points upon the polarisation would seem to rule out an absolute relation between dielectric constant and crystallinity. In any case, the interpretation of dielectric constant as a measure of crystallinity must necessarily be different from that of present methods, just as no two of the present methods may be considered to measure exactly the same aspect of crystallinity. Polarisation is uniquely determined by the structure of a system, in that all of the molecules within the system make their contributions to the polarization. It is conceivable that small disordered regions may exist which are so completely surrounded by crystalline regions that they are inaccessible to the usual reagents and are thus not apparent to the usual accessibility methods. It is well-known that x-ray diffraction techniques are insensitive to crystalline regions of very small extent. Each of these types of submicroscopic structure makes its characteristic contribution to the observed dielectric constant. In view of these considerations, perfect correlation with any present method cannot be expected. In Figure 25, the relationship with accessibility is illustrated. The wet-pressed cases have been eliminated because they are influenced by other factors, and the case of cellophane, which remains to be explained satisfactorily, was also omitted. The remaining data show a coefficient of correlation between dielectric constant and accessibility of 0.883.

There are indications that the dielectric constant of regenerated cellulose may be as high as 10 or 12 at its ultimate density. A measurement of this quantity could be made by the liquid mixture technique of De Luca, Campbell, and Maass (92), and would be of definite interest. Measurements on completely amorphous cellulose, as produced by Hermans' dry grinding technique would also be interesting, as would measurements on completely crystalline cellulose. The product obtained by Morehead (26) by partial hydrolysis and ultrasonic disintegration is probably almost completely crystalline. Both of these products are powders, and could not be measured in the present test capacitor system. De Luca's liquid mixture technique could

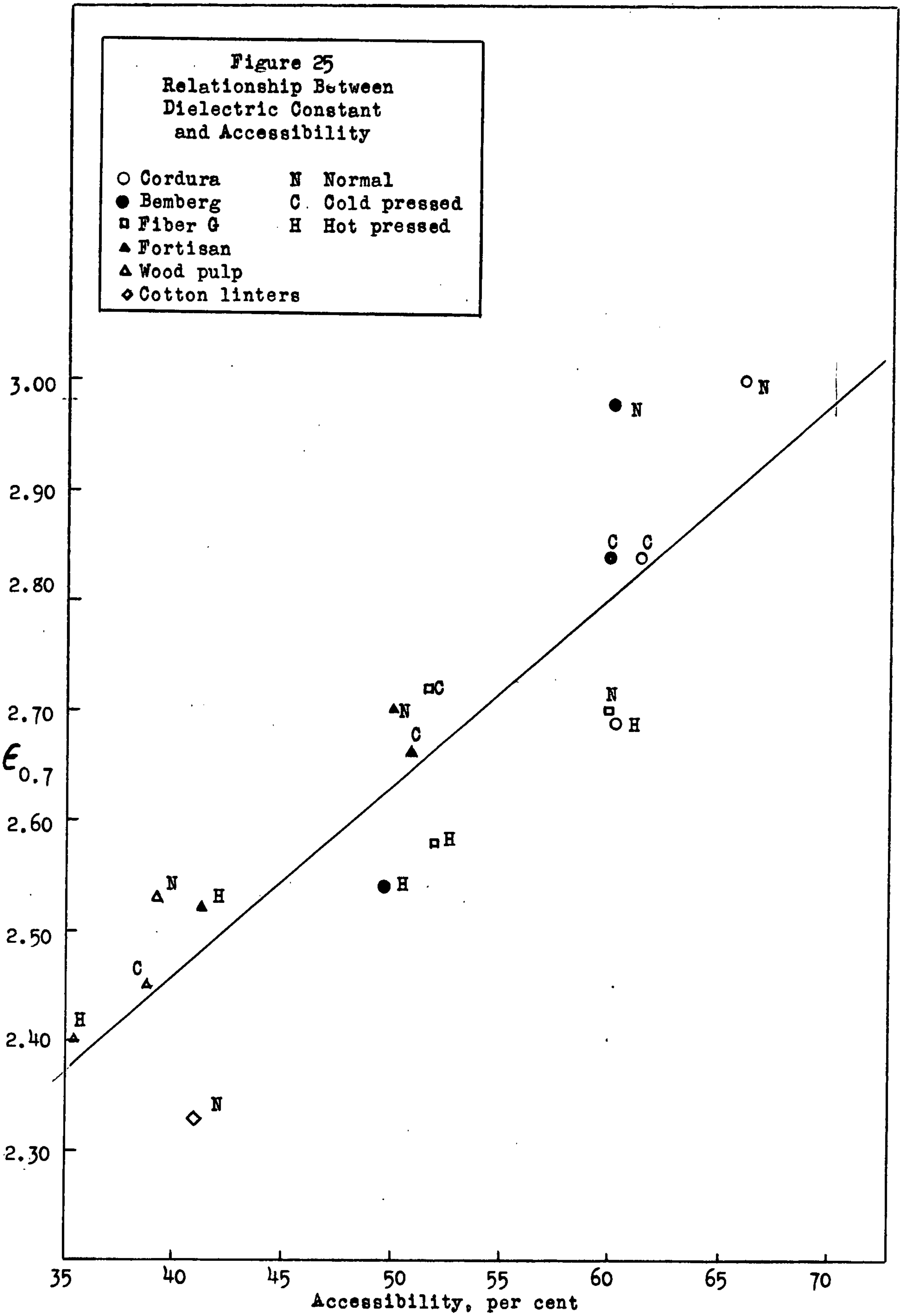


Figure 25
Relationship Between
Dielectric Constant
and Accessibility
○ Cordura
● Bemberg
□ Fiber G
▲ Fortisan
△ Wood pulp
◇ Cotton linters
N Normal
C Cold pressed
H Hot pressed
3.00
2.90
2.80
2.70
$\epsilon_{0.7}$
2.60
2.50
2.40
2.30
35
40
45
50
55
60
65
70
Accessibility, per cent

also be adapted to such measurements.

Dielectric-constant measurements may find particular value in the evaluation of rapid changes in crystallinity, because the polarisation reacts instantaneously to a change in structure, and proper experimental techniques would reveal any such change in polarization.

SUMMARY AND CONCLUSIONS

The test capacitor system of Calkins has been adapted to the measurement of dielectric constant with a reasonable degree of accuracy.

Such measurements were made at temperatures from 25 to 105°C., over a frequency range of 500 to 10,000 cycles per second, on purified cotton and wood fibers, cellophane, and regenerated fibers, including a high-tenacity viscose rayon, cuprammonium rayon, Fortisan saponified acetate, and Fiber G.

The Clausius-Mosotti relation was found to be valid for relating the dielectric constants of regenerated fibers to their densities.

It was found that the wet pressing of handsheets of regenerated fibers, as well as wood pulp, at pressures of about 270 atmospheres, caused considerable reduction in dielectric constant with little or no effect upon crystallinity, as measured by moisture vapor accessibility. It is proposed that this reduction was due to secondary cross linkages between cellulose chain molecules within the amorphous zones.

The pressing at 270 atmospheres of dry handsheets at room temperature produced a reduction in both dielectric constant and accessibility, and such pressing at about 110°C. resulted in similar but larger changes.

It was shown that the failure of cellophane to have as large a dielectric constant as chemically similar regenerated fibers is due to the structure of the material itself, rather than to the manner in which it had been stored. It is possible that this failure is due to the relative rigidity of the gel structure in cellophane.

The dielectric constant of cellulose has been shown to be profoundly influenced by its crystallinity, as evidenced by comparison with measurements of ultimate density and moisture vapor accessibility. At least a certain amount of the polarization seems to be due to the rotational vibration of cellulose chains within the amorphous zones, but since all amorphous material may not possess the same freedom of such motion (vide the restraints caused by secondary junctions), this component of the polarization is not necessarily uniquely dependent upon the amount of amorphous material present.

An interpretation of dielectric constant as a measure of crystallinity must be different from that placed on existing methods, since polarization is uniquely determined by the molecular structure. Dielectric-constant measurements may find particular value in evaluating rapid changes in crystallinity.

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APPENDIX

TABLE XIV

DIELECTRIC CONSTANT OF NATIVE CELLULOSE--COTTON LINTERS

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$	$\epsilon'_{0.8}$
24	106	0.25	500	33.8	331	325	2.49	0.703	2.48	2.82
40	78	0.4		33.9	324	318	2.43	0.706	2.40	2.72
59	53	1.0		34.1	318	312	2.37	0.710	2.34	2.65
73	29.5	190		34.6	314	308	2.30	0.721	2.24	2.51
24	106	0.25	1000	33.9	334	328	2.50	0.706	2.48	2.82
40	78	0.4		33.9	324	318	2.43	0.706	2.40	2.72
59	53	1.0		34.2	318	312	2.36	0.712	2.33	2.62
73	29.5	190		34.6	314	308	2.30	0.721	2.24	2.50
88	52.5	1.9		34.5	318	312	2.34	0.718	2.30	2.57
106	76	0.5		34.3	324	318	2.40	0.713	2.36	2.66
121	108	0.3		34.1	334	328	2.49	0.710	2.46	2.79
24	106	0.25	2000	34.0	334	328	2.50	0.708	2.47	2.82
40	78	0.4		34.0	325	319	2.43	0.708	2.40	2.71
59	53	1.0		34.2	318	312	2.36	0.712	2.33	2.62
73	29.5	190		34.6	313	307	2.30	0.721	2.24	2.50
24	106	0.25	4000	34.1	335	329	2.50	0.710	2.46	2.80
40	78	0.4		34.0	324	318	2.42	0.708	2.39	2.71
59	53	1.0		34.2	318	312	2.36	0.712	2.33	2.62
73	29.5	190		34.6	313	307	2.30	0.721	2.24	2.50
24	106	0.25	10,000	34.1	336	330	2.50	0.710	2.46	2.80
40	78	0.4		34.0	324	318	2.42	0.708	2.39	2.71
59	53	1.0		34.2	319	313	2.37	0.712	2.33	2.62
73	29.5	190		34.6	312	306	2.29	0.721	2.24	2.50

TABLE XV

DIELECTRIC CONSTANT OF NATIVE CELLULOSE--WOOD PULP

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
23	104	0.2	1000	33.2	339	333	2.60	0.721	2.53
41	77.5	0.24	1000	33.3	328	322	2.50	0.723	2.48
55	53	0.35	1000	33.4	322	316	2.45	0.725	2.38
70	28.5	0.5	1000	33.8	317	311	2.38	0.734	2.30

TABLE XVI

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--FORTISAN

Time, hr.	Temp., °C.	Vacuum, micron	Frequency cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
23	106	0.12	1000	35.1	333	327	2.41	0.619	2.70
39	77	0.2	1000	34.5	318	312	2.34	0.608	2.66
53	53	0.33	1000	34.6	310	304	2.28	0.610	2.57
68	28.5	0.4	1000	34.9	305	299	2.22	0.615	2.47

TABLE XVII

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--HIGH-TENACITY VISCOSE RAYON

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm.$^{-1}$	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	103	0.1	500	28.5	305	299	2.72	0.692	2.75
38	76	0.1		28.5	298	292	2.65	0.692	2.68
53	52	0.1		28.4	292	286	2.60	0.690	2.64
71	22	0.1		28.4	285	279	2.54	0.690	2.58
95	52	0.1		28.6	292	286	2.59	0.695	2.61
110	75	0.1		28.5	298	292	2.65	0.692	2.68
125	103	0.1		28.7	308	302	2.72	0.697	2.73
24	103	0.1	1000	28.7	308	302	2.72	0.697	2.73
38	76	0.1		28.5	299	293	2.66	0.692	2.69
53	52	0.1		28.4	293	287	2.61	0.690	2.64
71	22	0.1		28.4	285	279	2.54	0.690	2.58
95	52	0.1		28.6	293	287	2.60	0.695	2.62
110	75	0.1		28.6	297	293	2.65	0.695	2.67
125	103	0.1		28.7	308	302	2.72	0.695	2.67
24	103	0.1	2000	29.0	311	305	2.72	0.703	2.70
38	76	0.1		28.5	299	293	2.66	0.692	2.69
53	52	0.1		28.4	292	286	2.61	0.690	2.64
71	22	0.1		28.4	285	279	2.54	0.690	2.58
95	52	0.1		28.6	292	286	2.59	0.695	2.61
110	75	0.1		28.6	299	293	2.64	0.697	2.66
125	103	0.1		28.7	309	303	2.73	0.697	2.74

TABLE XVII (continued)

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--HIGH-TENACITY VISCOSE RAYON

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}', cm.$^{-1}$	C_p', mmfd.	C_m', mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	103	0.1	4000	28.8	310	304	2.72	0.701	2.70
38	76	0.1		28.5	300	294	2.67	0.692	2.70
53	52	0.1		28.5	288	282	2.56	0.692	2.66
71	22	0.1		28.5	285	279	2.53	0.692	2.56
95	52	0.1		28.6	293	287	2.60	0.695	2.62
110	75	0.1		28.7	299	293	2.64	0.697	2.66
125	103	0.1		28.8	310	304	2.73	0.701	2.73
24	103	0.1	10,000	29.0	310	304	2.72	0.703	2.70
38	76	0.1		28.6	298	292	2.64	0.695	2.66
53	52	0.1		28.5	277[a]	271[a]		0.692	
71	22	0.1		28.5	284	278	2.52	0.692	2.55
95	52	0.1		28.6	292	286	2.59	0.695	2.61
110	75	0.1		28.7	298	292	2.63	0.697	2.64
125	103	0.1		28.8	311	305	2.74	0.701	2.74

[a]This value unreliable because of electrical difficulties with bridge.

TABLE XVIII

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--FIBER G

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm.$^{-1}$	C_p, mmfd.	C_m, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	104	0.22	500	35.7	318	312	2.26	0.565	2.74
50	77	0.3		35.6	311	305	2.22	0.564	2.68
65	52.5	1.5		35.6	305	299	2.18	0.564	2.62
82	28	3		35.9	301	295	2.13	0.568	2.53
97	51.5	--		36.1	304	298	2.14	0.572	2.54
112	76	--		36.1	310	304	2.18	0.572	2.58
136	103.5	17		36.3	325	317	2.26	0.575	2.69
24	104	0.22	1000	36.0	322	316	2.27	0.570	2.72
50	77	0.3		35.6	312	306	2.22	0.565	2.67
65	52.5	1.5		35.7	305	299	2.17	0.565	2.61
82	28	3		35.9	300	294	2.12	0.568	2.51
97	51.5	--		36.2	305	299	2.14	0.573	2.54
112	76	--		36.2	311	305	2.18	0.573	2.58
136	103.5	17		36.4	324	318	2.26	0.577	2.68
24	104	0.22	2000	36.1	324	318	2.28	0.572	2.73
50	77	0.3		35.7	312	306	2.22	0.565	2.67
65	52.5	1.5		35.7	305	299	2.17	0.565	2.61
82	28	3		35.9	301	295	2.13	0.568	2.53
97	51.5	--		36.2	305	299	2.14	0.573	2.54
112	76	--		36.3	312	306	2.18	0.575	2.57
136	103.5	17		36.4	325	319	2.27	0.577	2.69

TABLE XVIII (continued)

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--FIBER G

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	104	0.22	4000	36.2	326	320	2.29	0.573	2.75
50	77	0.3		35.7	312	306	2.22	0.565	2.67
65	52.5	1.5		35.8	305	299	2.16	0.567	2.58
82	28	3		35.9	300	294	2.12	0.568	2.51
97	51.5	--		36.2	305	299	2.14	0.573	2.54
112	76	--		36.3	312	306	2.18	0.575	2.57
136	103.5	17		36.5	326	320	2.27	0.578	2.69
24	104	0.22	10,000	36.3	326	320	2.28	0.575	2.72
50	77	0.3		35.8	312	306	2.26	0.567	2.65
65	52.5	1.5		35.8	305	299	2.16	0.567	2.58
82	28	3		35.9	300	294	2.12	0.568	2.51
97	51.5	--		36.2	305	299	2.14	0.573	2.54
112	76	--		36.3	312	306	2.18	0.575	2.57
136	103.5	17		36.5	326	320	2.27	0.578	2.69

TABLE XIX

DIELECTRIC CONSTANT OF REGENERATED CELLULOSE--CUPRAMMONIUM RAYON

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	$\underline{P}_{cor}$, cm.$^{-1}$	$\underline{C}_p$, mmfd.	$\underline{C}_x$, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
23	104	0.15	1000	30.5	288	282	2.40	0.561	2.98
37	78	0.25	1000	30.4	280	274	2.34	0.559	2.89
52	52	1.0	1000	30.6	272	266	2.25	0.563	2.72
70	27	1.8	1000	30.9	268	262	2.20	0.568	2.63

TABLE XX

DIELECTRIC CONSTANT OF UNPLASTICIZED CELLOPHANE (A)

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm.$^{-1}$	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	102	0.15	500	27.2	780	774	7.37	1.514	--
40	73.5	0.1		27.3	712	706	6.69	1.520	--
75	52	0.1		27.6	687	681	6.39	1.536	--
96	25	0.15		27.9	664	658	6.11	1.553	--
111	51	0.15		27.9	684	678	6.30	1.553	--
130	76	0.15		27.7	712	706	6.60	1.542	--
144	103	0.15		27.6	776	770	7.23	1.536	--
24	102	0.15	1000	27.2	776	770	7.33	1.514	2.54
40	73.5	0.1		27.3	708	702	6.66	1.520	2.29
75	52	0.1		27.6	684	678	6.36	1.536	2.24
96	25	0.15		27.9	662	656	6.09	1.553	2.18
111	51	0.15		27.9	682	676	6.27	1.553	2.21
130	76	0.15		27.7	710	704	6.58	1.542	2.25
144	103	0.15		27.6	766	760	7.13	1.536	2.32
24	102	0.15	2000	27.2	752	746	7.10	1.514	--
40	73.5	0.1		27.3	705	699	6.63	1.520	--
75	52	0.1		27.6	682	676	6.34	1.536	--
96	25	0.15		27.0	661	655	6.08	1.553	--
111	51	0.15		27.9	680	674	6.26	1.553	--
130	76	0.15		27.7	705	699	6.51	1.542	--
144	103	0.15		27.6	747	741	6.96	1.536	--

TABLE XX (continued)

DIELECTRIC CONSTANT OF UNPLASTICIZED CELLOPHANE (A)

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$
24	102	0.15	4000	27.2	741	735	7.00	1.514	--
40	73.5	0.1		27.3	701	695	6.59	1.520	--
75	52	0.1		27.6	680	674	6.33	1.536	--
96	25	0.15		27.9	659	653	6.06	1.553	--
111	51	0.15		27.9	678	672	6.24	1.553	--
130	76	0.15		27.7	702	696	6.51	1.542	--
144	103	0.15		27.9	741	735	6.89	1.536	--
24	102	0.15	10,000	27.2	731	725	6.90	1.514	--
40	73.5	0.1		27.3	698	692	6.56	1.520	--
75	52	0.1		27.6	678	672	6.31	1.536	--
96	25	0.15		27.9	656	650	6.04	1.553	--
111	51	0.15		27.9	676	670	6.22	1.553	--
130	76	0.15		27.7	698	692	6.47	1.542	--
144	103	0.15		27.9	732	726	6.82	1.536	--

TABLE XXI

DIELECTRIC CONSTANT OF PLASTICIZED CELLOPHANE (B)

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.
42	103.5	0.1	1000	36.0	951	945	6.80	1.514
56	77	0.08		36.0	921	915	6.58	1.514
72	52	0.07		36.2	896	890	6.37	1.522
89	31	0.06		36.4	872	866	6.16	1.531
104	51	0.1		36.6	892	886	6.27	1.540
120	75.5	0.1		36.6	912	906	6.41	1.540

TABLE XXII

DIELECTRIC CONSTANT OF UNDRIED CELLOPHANE (C)

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.
24	103	1.4	1000	32.1	867	861	6.95	1.471
41	104	1.7		32.2	868	862	6.93	1.476
55	73.5	1.0		32.4	840	834	6.67	1.485
71	53.5	1.2		32.8	824	818	6.46	1.503
88	26.5	152		33.3	806	800	6.22	1.526

TABLE XXIII

DIELECTRIC CONSTANT OF FORMALDEHYDE-STORED UNPLASTICIZED CELLOPHANE (F)

Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm.$^{-1}$	C_p, mmfd.	C_m, mmfd.	ϵ'	ρ, g./cc.
24	104	0.22	1000	29.7	799	793	6.92	1.480
39	77.5	0.5		30.0	775	769	6.63	1.494
44	52.5	3		30.3	757	751	6.42	1.516
62	27.5	160		30.7	741	735	6.20	1.528

TABLE XXIV

EFFECTS OF PRESSING AT 4000 P.S.I. FOR TEN MINUTES

	Cellulose	Time, hr.	Temp., °C.	Vacuum, micron	Frequency, cycles/sec.	P_{cor}, cm^{-1}	C_p, mmfd.	C_n, mmfd.	ϵ'	ρ, g./cc.	$\epsilon'_{0.7}$	Accessibility, %
J	Wood pulp, normal	23	104	0.2	1000	33.2	339	333	2.60	0.721	2.53	38.5
J	Wet pressed	24	105	0.3	1000	31.1	413	407	3.39	0.996	2.35	40.1
J	Cold pressed	24	104.5	0.2	1000	31.5	388	382	3.14	0.894	2.45	37.5
J	Hot pressed	24	104	0.3	1000	34.0	508	502	3.82	1.066	2.40	35.6
E	Cordura, normal	24	103.5	0.1	1000	35.2	369	363	2.67	0.627	3.00	67.0
E	Wet pressed	24	105	0.7	1000	30.9	368	362	3.03	0.787	2.68	67.2
E	Cold pressed	24	103.5	0.2	1000	25.0	287	281	2.91	0.717	2.84	62.5
E	Hot pressed	29	104	0.15	1000	31.9	437	431	3.50	0.882	2.69	60.3
H	Fortisan, normal	23	106	0.12	1000	35.1	333	327	2.41	0.619	2.70	49.9
H	Wet pressed	24	104.5	0.2	1000	28.6	308	302	2.74	0.723	2.65	50.1
H	Cold pressed	42	105.5	0.4	1000	32.4	353	347	2.78	0.730	2.66	51.5
H	Hot pressed	23	105	0.18	1000	28.9	382	376	3.37	0.917	2.52	42.4
K	Bemberg, normal	23	104	0.15	1000	30.5	288	282	2.40	0.561	2.98	60.0
K	Wet pressed	23	105	0.15	1000	35.4	386	380	2.78	0.753	2.59	57.4
K	Cold pressed	24	105	0.25	1000	27.0	289	283	2.72	0.671	2.84	59.8
K	Hot pressed	24	105	0.25	1000	37.2	589	583	4.14	1.058	2.54	49.2
K	Hot pressed[a]	28	104.5	0.3	1000	33.2	522	516	4.03	1.036	2.54	--
G	Fiber G, Normal	24	104	0.22	1000	36.0	322	316	2.27	0.570	2.72	59.9
		136	103.5	17	1000	36.4	324	318	2.26	0.577	2.68	
G	Wet pressed	24	103.5	0.3	1000	27.8	284	278	2.59	0.698	2.60	56.1
G	Cold pressed	23	104	1.0	1000	37.3	368	362	2.52	0.662	2.72	52.7
G	Hot pressed	24	104	1.2	1000	35.0	406	400	2.96	0.801	2.58	53.5

[a] A different specimen

TABLE XXV

SORPTION ISOTHERMS

	Cellulose	Relative Humidity, % 11.1	22.9	32.9	64.8	75.5
D	Cotton linters, as received		Moisture Regain, g./100 g.			
	1	2.21	3.20	3.99	7.22	8.95
	2	2.14	3.16	3.96	7.25	9.00
	Average	2.18	3.18	3.97	7.24	8.98
	Calculated	2.15	3.22	3.98	7.15	9.06
D	Cotton linters, beaten stock		Moisture Regain, g./100 g.			
	1	2.30	3.41	4.43	8.69	10.53
	2	2.31	3.46	4.51	8.61	10.68
	Average	2.30	3.44	4.48	8.65	10.60
	Calculated	2.24	3.54	4.48	8.41	10.82
D	Cotton linters, acid washed stock		Moisture Regain, g./100 g.			
	1	2.37	3.59	4.48	8.51	10.84
	2	2.38	3.60	4.54	8.57	10.49
	Average	2.38	3.59	4.51	8.54	10.67
	Calculated	2.35	3.61	4.51	8.23	10.46
D	Cotton linters, unwashed sheets		Moisture Regain, g./100 g.			
	1	2.42	3.56	4.95	8.52	10.24
	2	2.38	3.54	4.56	8.37	9.91
	Average	2.40	3.55	4.76	8.44	10.08
	Calculated	2.33	3.72	4.69	8.30	10.21
D	Cotton linters, acid washed sheets		Moisture Regain, g./100 g.			
	1	2.43	3.61	4.50	8.34	10.40
	2	2.54	3.77	4.69	8.38	10.30
	Average	2.48	3.69	4.59	8.36	10.35
	Calculated	2.46	3.73	4.62	8.32	10.52
E	Cordura rayon, normal sheets		Moisture Regain, g./100 g.			
	1	4.39	6.47	8.08	14.01	17.13
	2	4.36	6.54	8.13	14.03	17.12
	Average	4.38	6.54	8.10	14.02	17.12
	Calculated	4.34	6.56	8.08	13.96	17.18
E	Cordura rayon, unpressed sheets		Moisture Regain, g./100 g.			
	1	4.53	6.65	8.23	14.77	17.53
	2	4.54	6.62	8.26	14.73	17.74
	Average	4.53	6.64	8.24	14.45	17.63
	Calculated	4.45	6.73	8.29	14.45	17.88

TABLE XXV (continued)

SORPTION ISOTHERMS

	Relative Humidity, %				
Cellulose	11.1	22.9	32.9	64.8	75.5
E Cordura rayon, wet pressed	Moisture Regain, g./100 g.				
1	4.42	6.47	8.20	14.77	17.95
2	4.27	6.33	8.06	14.75	17.93
Average	4.34	6.40	8.13	14.76	17.94
Calculated	4.26	6.54	8.13	14.51	18.16
E Cordura, cold pressed	Moisture Regain, g./100 g.				
1	3.94	5.86	7.59	14.09	17.01
2	4.20	6.12	7.58	14.37	17.30
Average	4.07	5.99	7.58$_5$	14.23	17.15$_5$
Calculated	3.97	6.12	7.63	13.84	17.49
E Cordura, hot pressed	Moisture Regain, g./100 g.				
1	4.08	5.81	7.45	14.24	17.31
2	4.01	5.77	7.54	14.31	17.27
Average	4.04	5.79	7.49	14.27	17.29
Calculated	3.91	6.00	7.49	13.82	17.70
G Fiber G, as received	Moisture Regain, g./100 g.				
1	3.62	5.27	6.60	11.30	13.80
2	3.59	5.26	6.61	11.36	13.74
Average	3.60	5.26	6.60	11.33	13.77
Calculated	3.56	5.35	6.57	11.27	13.83
G Fiber G, normal sheets	Moisture Regain, g./100 g.				
1	3.91	5.58	7.14	12.45	14.93
2	3.87	5.68	7.11	12.10	14.24
Average	3.89	5.63	7.12	12.27	14.58
Calculated	3.81	5.77	7.10	12.09	14.74
G Fiber G, wet pressed	Moisture Regain, g./100 g.				
1	3.83	5.57	6.79	12.31	14.77
2	4.00	5.80	7.07	12.37	14.88
Average	3.91	5.69	6.93	12.29	14.82
Calculated	3.87	5.72	6.99	12.41	14.98
G Fiber G, cold pressed	Moisture Regain, g./100 g.				
1	3.99	5.58	6.97	12.22	14.78
2	3.82	5.36	6.75	11.97	14.50
Average	3.91	5.47	6.86	12.10	14.64
Calculated	3.83	5.57	6.78	11.85	14.86

TABLE XXV (continued)

SORPTION ISOTHERMS

	Cellulose	Relative Humidity, % 11.1	22.9	32.9	64.8	75.5
G	Fiber G, hot pressed	Moisture Regain, g./100 g.				
	1	3.60	5.16	6.54	11.88	14.46
	2	3.78	5.27	6.78	12.06	14.38
	Average	3.69	5.22	6.66	11.97	14.42
	Calculated	3.59	5.39	6.64	11.72	14.66
H	Fortisan, as received	Moisture Regain, g./100 g.				
	1	3.02	4.52	5.61	9.53	11.37
	2	2.96	4.41	5.42	9.41	11.46
	Average	2.99	4.46	5.52	9.47	11.41
	Calculated	2.91	4.51	5.59	9.46	11.40
H	Fortisan, normal sheet	Moisture Regain, g./100 g.				
	1	3.60	5.20	6.34	11.14	13.34
	2	3.60	5.08	6.16	10.86	13.10
	Average	3.60	5.14	6.25	11.00	13.22
	Calculated	3.55	5.18	6.30	10.81	13.38
H	Fortisan, wet pressed	Moisture Regain, g./100 g.				
	1	3.56	5.10	6.21	10.72	12.86
	2	3.61	5.12	6.25	10.81	12.96
	Average	3.58	5.11	6.23	10.76	12.91
	Calculated	3.53	5.16	6.26	10.61	13.03
H	Fortisan, cold pressed	Moisture Regain, g./100 g.				
	1	3.63	5.16	6.23	11.12	12.88
	2	3.54	5.13	6.15	10.95	12.85
	Average	3.58	5.14	6.19	11.04	12.86
	Calculated	3.51	5.17	6.30	10.70	13.12
H	Fortisan, hot pressed	Moisture Regain, g./100 g.				
	1	3.21	4.44	5.52	10.17	12.30
	2	3.16	4.42	5.49	10.06	12.35
	Average	3.18	4.43	5.50	10.11	12.33
	Calculated	3.10	4.53	5.53	9.86	12.55
J	Wood pulp, as received	Moisture Regain, g./100 g.				
	1	2.56	3.92	4.79	8.40	10.29
	2	2.62	3.86	4.84	8.42	10.26
	Average	2.59	3.89	4.82	8.41	10.28
	Calculated	2.57	3.91	4.82	8.37	10.32

TABLE XXV (continued)

SORPTION ISOTHERMS

	Cellulose	Relative Humidity, % 11.1	22.9	32.9	64.8	75.5
J	Wood pulp, normal sheet	Moisture Regain, g./100 g.				
	1	2.64	3.87	4.82	8.68	10.69
	2	2.84	4.08	5.08	8.98	11.02
	Average	2.74	3.98	4.87	8.82	10.86
	Calculated	2.71	4.00	4.90	8.69	10.69
J	Wood pulp, wet pressed	Moisture Regain, g./100 g.				
	1	2.91	4.12	5.14	9.04	11.00
	2	2.67	3.87	4.92	8.87	10.88
	Average	2.79	4.00	5.03	8.95	10.94
	Calculated	2.74	4.08	5.02	8.83	11.05
J	Wood pulp, cold pressed	Moisture Regain, g./100 g.				
	1	2.75	3.89	4.81	8.76	10.76
	2	2.78	3.94	4.84	8.70	10.58
	Average	2.77	3.91	4.82	8.73	10.67
	Calculated	2.72	3.97	4.84	8.56	10.82
J	Wood pulp, hot pressed	Moisture Regain, g./100 g.				
	1	2.55	3.63	4.52	8.44	10.27
	2	2.57	3.69	4.54	8.40	10.29
	Average	2.56	3.66	4.53	8.42	10.28
	Calculated	2.51	3.72	4.57	8.21	10.46
K	Bemberg, as received	Moisture Regain, g./100 g.				
	1	4.10	4.97	7.30	12.66	15.37
	2	3.95	6.03	7.21	12.77	15.57
	Average	4.02	6.00	7.25	12.72	15.47
	Calculated	4.01	5.97	7.32	12.61	15.56
K	Bemberg, normal sheet	Moisture Regain, g./100 g.				
	1	4.31	6.09	7.52	13.36	16.15
	2	4.31	6.13	7.60	13.48	16.30
	Average	4.31	6.11	7.56	13.42	16.22
	Calculated	4.23	6.22	7.58	13.18	16.42
K	Bemberg, wet pressed	Moisture Regain, g./100 g.				
	1	4.21	5.91	7.32	13.29	16.12
	2	4.22	5.99	7.40	13.33	16.34
	Average	4.22	5.95	7.36	13.31	16.23
	Calculated	4.14	6.05	7.39	13.05	16.46

TABLE XXV (continued)

SORPTION ISOTHERMS

Cellulose	Relative Humidity, % 11.1	22.9	32.9	64.8	75.5
K Bemberg, cold pressed	Moisture Regain, g./100 g.				
1	4.12	5.88	7.32	13.33	16.24
2	4.23	6.04	7.56	13.41	16.41
Average	4.18	5.96	7.44	13.37	16.33
Calculated	4.10	6.07	7.45	13.15	16.53
K Bemberg, hot pressed	Moisture Regain, g./100 g.				
1	4.11	5.65	6.80	12.51	15.66
2	3.98	5.47	6.59	12.37	15.50
Average	4.05	5.56	6.69	12.44	15.58
Calculated	3.99	5.60	6.76	12.18	15.81
A Unplasticized cellophane	Moisture Regain, g./100 g.				
1	3.71	5.71	7.11	12.86	16.05
2	3.77	5.80	7.19	13.00	16.17
Average	3.74	5.75	7.15	12.93	16.11
Calculated	3.73	5.77	7.22	13.17	16.70
C Cellophane, undried for several years	Moisture Regain, g./100 g.				
1	4.25	6.12	7.79	13.85	17.13
2	3.98	5.78	7.42	13.48	16.67
Average	4.12	5.95	7.61	13.67	16.90
Calculated	4.04	6.11	7.56	13.53	17.05
F Unplasticized cellophane, stored in formaldehyde for 66 days	Moisture Regain, g./100 g.				
1	3.91	5.96	7.43	13.39	16.38
2	3.86	5.84	7.29	13.31	16.30
Average	3.89	5.90	7.36	13.35	16.35
Calculated	3.85	5.92	7.36	13.97	16.09

TABLE XXV (continued)

SORPTION ISOTHERMS

SORPTION ISOTHERM CONSTANTS

	Cellulose	A	B	C	α	β	$\alpha\beta$	M	$\frac{M-162}{M} \times 100$
D	Cotton linters, as received	2.78	0.239	0.00220	0.00837	11.31	0.0946	514	68.7
D	Cotton linters, beaten stock	3.06	0.191	0.00184	0.00848	8.36	0.0709	437	62.9
D	Cotton linters, acid washed stock	2.74	0.200	0.00186	0.00834	9.75	0.0813	442	63.4
D	Cotton linters, unwashed sheets	3.09	0.168	0.00147	0.00774	8.09	0.0626	388	58.2
D	Cotton linters, acid washed sheets	2.52	0.201	0.00183	0.0083	10.65	0.0884	436	62.9
J	Wood pulp, as received	2.45	0.186	0.00160	0.00799	10.45	0.0836	405	60.0
J	Wood pulp, normal sheet	2.11	0.199	0.00180	0.00830	12.38	0.1028	421	61.5
J	Wood pulp, wet pressed	2.16	0.189	0.00168	0.00814	11.73	0.0955	404	59.9
J	Wood pulp, cold pressed	2.02	0.206	0.00186	0.00834	13.24	0.1104	432	62.5
J	Wood pulp, hot pressed	2.29	0.214	0.00197	0.00844	12.09	0.1020	456	64.4

TABLE XXV (continued)

SORPTION ISOTHERMS

SORPTION ISOTHERM CONSTANTS

	Cellulose	A	B	C	α	β	$\alpha\beta$	M	$\frac{M-162}{M} \times 100$
E	Cordura rayon, normal sheet	1.43	0.112	0.00096	0.00781	11.03	0.0862	242	33.0
E	Cordura rayon, unpressed sheet	1.39	0.110	0.00096	0.0079	10.96	0.0866	237	31.6
E	Cordura rayon, wet pressed	1.52	0.109	0.00098	0.00809	9.91	0.0802	241	32.8
E	Cordura rayon, cold pressed	1.63	0.117	0.00108	0.00827	9.72	0.0804	259	37.5
E	Cordura rayon, hot pressed	1.63	0.122	0.00115	0.00848	9.80	0.0831	269	39.7
G	Fiber G, as received	1.73	0.139	0.00118	0.00774	11.38	0.0881	298	45.7
G	Fiber G, normal sheet	1.65	0.125	0.00105	0.00761	10.95	0.0833	496	40.1
G	Fiber G, wet pressed	1.50	0.136	0.00118	0.00798	12.33	0.0984	288	43.9
G	Fiber G, cold pressed	1.43	0.147	0.00131	0.00823	13.53	0.1114	307	47.3
G	Fiber G, hot pressed	1.69	0.141	0.00126	0.00813	11.25	0.0915	303	46.5

TABLE XXV (continued)

SORPTION ISOTHERMS

SORPTION ISOTHERM CONSTANTS

	Cellulose	A	B	C	α	β	$\alpha\beta$	M	$\frac{M-162}{M} \times 100$
H	Fortisan, as received	2.32	0.148	0.00121	0.00731	9.75	0.0713	328	50.6
H	Fortisan, normal sheet	1.57	0.155	0.00134	0.00799	13.36	0.1067	324	50.1
H	Fortisan, wet pressed	1.59	0.155	0.00131	0.00783	13.43	0.1052	323	49.9
H	Fortisan, cold pressed	1.65	0.150	0.00127	0.00778	12.71	0.0989	317	48.9
H	Fortisan, hot pressed	1.76	0.182	0.00167	0.00845	13.29	0.1123	382	57.6
J	Bemberg, as received	1.49	0.128	0.00110	0.00788	11.90	0.0938	272	40.5
J	Bemberg, normal sheet	1.34	0.128	0.00113	0.00810	12.83	0.1039	270	40.0
J	Bemberg, wet pressed	1.34	0.134	0.00121	0.00831	13.01	0.1081	282	42.6
J	Bemberg, cold pressed	1.41	0.130	0.00116	0.00823	12.20	0.1004	275	41.2
J	Bemberg, hot pressed	1.16	0.163	0.00152	0.00879	16.89	0.1485	330	50.8

TABLE XXV (continued)

SORPTION ISOTHERMS

SORPTION ISOTHERM CONSTANTS

	Cellulose	A	B	C	α	β	$\alpha\beta$	M	$\frac{M-162}{M} \times 100$
A	Unplasticized cellophane	1.75	0.123	0.00114	0.00831	9.44	0.0785	273	40.7
C	Cellophane, undried for several years	1.52	0.123	0.00112	0.00825	10.79	0.0890	266	39.2
F	Unplasticized cellophane, stored in formaldehyde for 66 days	1.69	0.119	0.00105	0.00792	9.86	0.0781	262	38.2