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THE DIELECTRIC CONSTANTS OF CELLULOSE

AND OF

WATER SORBED THEREON

A THESIS

by

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SULLARY

It has been found that increase in bursting strength of paper is accompanied by a decrease in the dielectric constant of that paper. This is true whether the strength is increased by pressure on the wet sheet or by beater treatment. Two explanations have been made for this relationship, an increase of fibre-to-fibre bonds and increased flatness of the fibres with increased strength. It has not been possible to separate these two effects.

The anisotropy of cellulose as a dielectric has been established and a method devised whereby the axial and transverse values of the dielectric constant of the cellulose fibril could be measured. These values are:

> Axial dielectric constant 7.2 Transverse dielectric

constant 5.3.

Previous values for the dielectric constant of cellulose have been shown to agree with the above if the fibril and fibre orientations are taken into account.

These results have been interpreted in terms

of the relative freedom of groups on the cellulose chain

and it has been suggested that absorption and dispersion in cellulose is probably due to displacement of hydroxyl groups restrained by secondary and coordinate valence forces rather than to rotation of glucose anhydride rings.

A dielectric value versus water content curve has been obtained and found to agree with previous measurements. This curve definitely shows that the first water sorbed on cellulose is strongly held and has a low dielectric constant. Attempts to calculate the dielectric constant of the sorbed water from the dielectric values have shown the impossibility of such calculations on the basis of present knowledge.

GENERAL INTRODUCTION

GENERAL INTRODUCTION

For several years a series of investigations designed to increase the knowledge of the physical chemistry of cellulose and cellulose-water systems has been proceeding in this Laboratory. The necessity for such a series of coordinated researches becomes evident when one glances at the mass of data on these systems which has accumulated and received no adequate explanation. The rapidly increasing applications of cellulose in the industrial world of today make this work the more necessary.

Cellulose has two outstanding physical properties which make it the useful substance it is today. Both natural and artificial fibres have tremendous tensile strengths in the longitudinal direction, ranging from 25 to over 100 Kg. per mm²., compared to ordinary steel with a tensile strength of about 45 Kg. per mm². The nature of the forces that give such strengths to cellulose fibres is not yet fully understood, but appears to be bound up to a large extent with the nature of the second major physical property of cellulose. This second property cannot be stated so simply, but it has to do with the nature of the affinity between cellulose and water. It

is this property which forms the basis for the papermaking industry, the rayon industry and the manufacture of cellulose films such as "Cellophane." It is the general subject upon which the above-mentioned series of researches has been directed.

One important result of this attraction was recognized when the first paper was made in ancient times. These early paper-makers were able to obtain a sheet merely by pressing cellulose fibres into a mat in the presence of moisture and then removing the moisture. It has since been shown that the strength of such sheets is due mainly to an adhesion between the fibres. Other natural fibres do not form such sheets, and even cellulose fibres show no tendency to form fibre-to-fibre bonds unless the sheet is formed in the presence of water. This phenomenon is definitely connected with the cellulose-water attraction.

Until modern times little was understood about the nature of this affinity and the formation of bonds in paper. Paper-making was a true art and paper qualities were controlled by empirical rules which were learned only through long practice. At the present time the study of the cellulose-water relationship has assumed the proportions of a special branch of colloid chemistry.

The organic chemist has given a clear picture of the cellulose molecule, and X-ray analysis has given a

2.

picture of the arrangement of the molecule in the fibres.

The botanist has shown the microstructure of the fibres.

The purpose of the physical investigations is to relate the above facts with the observed properties of the cellulose and cellulose-water systems. This problem has been approached from many different angles. Among these may be mentioned: heats of wetting as a measure of the activity of cellulose surfaces, amounts and rates of adsorption and desorption by cellulose at different relative vapour pressures as a measure of cellulosewater affinity, density measurements in different media and dielectric constant measurements on the adsorbed liquid to discover the condition of the adsorbed layer.

The application of dielectric constant measurements to the problem was actually begun with two purposes in mind. It was hoped that such measurements might lead to a practical method for the measurement of moisture content of paper, preferably while still on the paper machine. If the sorbed water on cellulose actually existed as liquid water with a dielectric constant of about 80, it should be quite easy to measure small amounts of water by dielectric constant measurements on the moist paper since cellulose itself was known to have a dielectric constant of less than 10. If, however, the sorbed water existed in a changed state on cellulose, as was thought

3.

to be true at the time, it was hoped that dielectric

constant measurements might lead to an insight into just

what the condition of that water actually was. In order to show how such measurements could help solve this problem it is first necessary to discuss the nature of the dielectric constant (1).

The dielectric constant is generally familiar in the expression for the force f between two electric charges e and e', separated by a distance d :

$$f = \frac{ee'}{Ed^2}$$

where E is a constant characteristic of the medium between the charges, i.e., the dielectric constant.

This constant is also familiar in the expression

$$C = EC_{o}$$

where C_0 is the capacity of a condenser with a vacuum between its plates and E is the dielectric constant of the medium between its plates when C is measured. This latter equation forms the basis for the most common method for the measurement of the dielectric constant. This method is discussed later.

In order to form a mental picture of what happens to an insulator when it is placed in an electric field, it is necessary to discuss briefly the molecular

theory of dielectrics as developed by Debye (2).

The influence of an insulator on an electric

field is described on the assumption that every element

of volume of the insulator, dS, acts as if possessed of a certain electric moment IdS, I being the electric moment per unit volume. If we cut through the insulator a cylindrical cavity of small cross-section with its axis in the direction of the lines of force, a unit electric charge brought into the cavity will be acted upon by a force $\boldsymbol{\varepsilon}$, which is the electric intensity. If, however, a section be cut out between two planes very close together and perpendicular to the lines of force, a unit charge in the cavity thus formed will be acted upon by a different force D, which is the electric displacement. D differs from $\boldsymbol{\varepsilon}$ because of the induced charge on the two plane surfaces of the cavity, so that:

$$D = \varepsilon + 4 \pi I$$

The classical theory now gives another view of the dielectric constant in the relation:

$$E = \frac{D}{\varepsilon}$$

From this it is seen that the dielectric constant is dependent on the electric moment per unit volume, or on the amount of induced charge on the insulator. The perfect insulator must be a vacuum since then there can be no induced charge, $D = \mathcal{E}$ and therefore $\mathbf{E} = \mathbf{1}$.

5.

It is useful to picture the induced charge as a dis-

tortion of the electron orbits in the atoms of an in-

sulator, and the dielectric constant as a measure

of the amount of this distortion of the electron orbits possible in the atoms of the insulator in question. This picture, first proposed by Mosotti (3), has since been found insufficient to describe all cases.

It is customary to speak of the above induced charge as the Molar Polarization, P, a quantity which depends on the dielectric constant in the following equation:

$$P = \frac{E - 1}{E + 2} \cdot \frac{M}{d} = \frac{4\pi N \alpha_o}{3}$$

where M is the molecular weight of the substance of density d, N Avogadro's number and α_o the electric moment per molecule induced by a field of unit intensity, the induced dipole moment. This is the Clausius-Mosotti equation (82).

Maxwell (4) showed that:

 $\mathbf{E} = n^2$

where n is the refractive index, and this leads to identity between the molar polarization and the molar refraction. However the molar polarization is always larger than the molar refraction, and this fact has been explained by introducing three types of polarization.

The molecules of many substances have a permanant dipole moment. Debye (5) accounted for the

moments of such molecules with the equation:

 $P_{M} = \frac{4\pi N}{3} \cdot \frac{\mu^{2}}{3kT}$

in which μ is the permanent dipole moment of the molecules, k, the Boltzmann gas constant and T the absolute temperature. This may be called the molecular polarization P_{M} . The second type of polarization is called atomic Polarization P_{A} , and arises from displacement of nuclei, atoms or groups. The third polarization, identical with the molar refraction, is, as described above, due to a shift of electrons in the electric field. It may be designated as the electronic polarization P_{π} . Thus we have the molar polarization:

$$P = P_E + P_A + P_M$$

Molecules, nuclei, atoms or groups have too great an inertia to be displaced in the rapidly alternating electric field of a light wave, and thus refractive index measurements give us a measure only of P_E , the electronic polarization. However, the frequencies of the electric fields used in dielectric constant measurements are small enough so that such displacements can take place. The dielectric constant is a measure of the molar polarization, P.

In a crystalline solid the molecular polarization P_M is usually zero because the molecules are so rigidly fixed in the lattice that orientation of the dipoles is impossible. This should be the case with cellulose. Thus, dielectric constant measurements on cellulose, in combination

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with refractive index measurements, can give important

evidence on the structure of cellulose. It should be

possible to interpret differences in dielectric constants as

differences in orientations, in freedom of movement of

polar groupings in the molecules.

In the case of the cellulose-water system dielectric constant measurements should again give important and easily interpreted results, provided that the dielectric constant for the added water can be evaluated. Water has a very high dipole moment which gives rise to a large value for the molecular polarization and thus for the dielectric constant. However, in ice, the effect of orientation of these dipoles is entirely absent except at very low frequencies and the dielectric constant drops from over 80 for water to less than 3 for ice at a temperature near the freezing point. The dielectric constant of water sorbed by cellulose will therefore be a measure of the molecular polarization of that water, of its degree of orientation and freedom.

The present work is divided into two parts, corresponding to the above discussion. The first deals with measurements of the dielectric constants of cellulose and interpretation of the results obtained. The second treats the cellulose-water system in terms of dielectric constant measurements made upon it.

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THE DIELECTRIC CONSTANT OF CELLULOSE

INTRODUCTION

THE DIELECTRIC CONSTANT OF CELLULOSE

A. - Introduction.

Cellulose is the basic constituent of all plant life and as such has attracted the interest of botanists. But, also, cellulose is supreme among organic raw materials. It not only excels in abundance but in the range of its uses. It is not to be wondered, then, that the investigation of cellulose structure has seen the concerted efforts of physicists and chemists as well as of botanists, especially in the present century. In order to facilitate discussion at the end of this work, the following few pages attempt to summarize the present state of our knowledge of cellullose structure.

This problem is actually a sub-class in a general division of colloid science, that of the structure of swelling materials. The early botanists (1860-1880) proposed the first definition of swelling. A solid is said to swell when it takes up a liquid while at the same time:

- (a) It does not lose its apparent (microscopic)homogeneity.
- (b) Its dimensions are enlarged.
- (c) Its cohesion is diminished: instead of hard

and brittle it becomes soft and flexible.

The first of these is a somewhat artificial distinction

and there exist many borderline substances. Many other

properties common to these materials have since been discovered. X-ray spectrography has shown that most substances that can swell are built up of a large number of sub-microscopic crystals and that these crystals are much longer than they are broad. The great majority of swelling substances have a high molecular weight, generally polysaccharides, albuminoids, rubber and other polymers. It has become very probable in recent years that all these substances of high molecular weight are built up from elongated micelles and that their molecules have the form of long threads (8). There are also swelling crystals which can swell without losing their crystalline properties. Examples are the albuminoid vitellin and haemoglobin. A few inorganic substances which show swelling are also known. Notable examples are certain silicates.

It is not proposed to go into the theory of swelling here, but the subject has been mentioned because it is felt that a proper perspective of the cellulose problem can only be gained by such an approach. The work done by many investigators on these swelling materials, and in particular on protein fibres, can help a great deal in the interpretation of phenomena noted in cellulose

10.

study.

The organo-chemical structure of the cellulose molecule is now fairly definitely established. It is a long chain of glucose anhydride units joined by oxygen bridges as below:



Many different measurements of the length of these chains exist, but the majority of investigators assign a length of 150 to 200 glucose groups to the cellulose molecule in the natural state. It seems quite probable that the molecule has no definite length except between these limits. Of particular interest with regard to the structure of cellulose are the hydroxyl groups on the 2, 3 and 6 carbon atoms. The hydroxyl groups on the 2 and 3 carbon atoms are secondary, while there is a primary hydroxyl group on number 6 carbon.

These long chains are deposited from water solution in the plants, from many of which we can extract practically pure cellulose in the form of fibres. The first great contribution to solving the structure of these

fibres was made by Naegeli in 1858 (7). To account for

the observed swelling properties he proposed a micellar

theory. Fibres were composed of sub-microscopic building units, probably crystalline, and separated by water films. Most of the present conceptions of the colloid chemistry of cellulose are based on this ground-work laid by Naegeli.

Cox has recently made a critical examination of the evidence for internal arrangement of cellulose in natural fibres (9). He states: "Perusal of the literature might tend to give the impression that internal arrangement of cellulose in natural fibres is known with some degree of precision. Actually, much is based on assumptions carried over from study of simple aliphatic molecules." After stating that X-ray examination of cellulose alone cannot give "detailed" information of cellulose structure, he shows that our present picture is based on:

(a) Chemical evidence (the molecule itself).

(b) X-ray data for cellulose.

(c) X-ray data for simple organic compounds. What is known of the orientation of chains and atoms is based particularly on (c) above, and at the present time such data do not include any from the "detailed" analysis of simple carbohydrates. With these reservations in mind

12.

we now go on to the picture obtained by these X-ray

measurements.

Sponsler and Dore showed that there was a regularly occurring grouping in cellulose consisting of four glucose units and showed how this could be explained in relation to the known chain structure (10). Mark and Meyer have made extensive studies on this subject and have definitely established the dimensions of this unit cell (11). The X-ray diagram does not show clearly defined spots. This broadening may be caused by the presence of small constituent particles of a crystalline nature or by lattice irregularity or distortion. Hengstenberg and Mark believe that micellar division plays the larger part because the intensity of radiation scattered diffusely by cellulose is only slight (12). On this basis they have calculated the dimensions of these micelles or crystallites to be 500Å in length and 50Å in cross-section. This corresponds to a chain length of at least 100 glucose units with about 50 chains in a bundle. They also calculated the internal area of cellulose as the surface of micelles of this size and obtained a value $7 \times 10^7 \text{ cm}^2$. This is in fairly good agreement with values per gram. obtained by direct measurement (13, 14, 15, 16), which

13.

forms very strong support for the existence of micelles

in the fibre structure.

Recently, experimental evidence has caused many investigators to believe that this simple picture of sub-microscopic micelles or crystallites piled like bricks to form the cellulose fibre does not give the true picture of the structure. Thus Neale has pointed out (17) that in order to reconcile the results from cellulose degradation and nitration it is necessary to think of a fibre as an imperfectly crystalline structure but continuous except for random breaks in the primary valence chain. A fairly satisfactory picture has now been arrived at and, although investigators still differ on minor points, there seems to be general agreement on the nature of the structure. Astbury and Woods (18) state that the bounding surfaces of micelles are not sharply defined but the micelles are to some extent entangled with one another by pseudo-crystalline growths and shared molecular chains. Freudenberg (19) from the rod double-refraction of lignin residues and other data believes the micelles are united by overlapping chain molecules into what he terms "micelle series." He states: "The micelle series may not be considered as regular or uniform. They are to be

14.

parallel micelle series." Broda and Mark (20) define

micelles as regions in the fibre where the lattice

considered as in part grown together with adjacent

structure is very marked and the residual valencies of the long chain molecules are satisfied. At the edges of these micelles the valences are not satisfied due to irregularities in the chains. It is here that the entrance or adsorption of foreign materials takes place.

Perhaps the two clearest pictures of this structure have been given in two recent papers. In the first of these Frey-Wyssling (21) considers fibres to consist of anastomosing rods or microfibrils with a chain lattice of cellulose molecules. The homogeneous portions of this lattice correspond to Naegeli's micelles, which are not independent but knit together by chain molecules. In the second, Campbell and Maass (22) picture the fibre as a network of branching crystals with many "faults" or open spaces between the solid elements. The term crystallite simply denotes this network of crystalline material. The crystalline nature of cellulose lies in the regular spacing of the glucose groups rather than in the arrangement of the chains, although some lesser degree of arrangement must follow. These authors suggest that the term "micelle" should not be used synonymously with "crystallite" in this structure, but reserved for the suspended particles in a colloidal solution. However.

15.

Staudinger (23) has stated that the crystallized com-

ponents of cellulose are crystallites with a macromolecular

lattice and that such crystallites may be termed micelles

in the Naegeli sense. This difference would appear to be one of definition and not of theory.

It will be noted from the above discussion that the modern conception of cellulose microstructure involves a less organized structure than is contained in the micellar theory of Naegeli. Cellulose consists of an open network of units consisting of bundles of molecular chains. At the points of highest orientation in these bundles there is true crystalline structure and these crystalline parts have a fairly constant diameter of about 50Å. There will thus be amorphous sections and crystalline sections separated by parts which grade from crystalline to amorphous. These latter parts are important in consideration of the entry of liquids into the fibre structure.

Katz and his associates have studied the effects of swelling by various agents on the X-ray diagram of cellulose (78, 79, 80). They have found that swelling in water alone has no effect on the X-ray pattern indicating that water does not enter the crystalline part of the structure. This indicates a radical difference in the forces holding the cellulose chains together in the amorphous as compared to the crystalline parts of the

16.

fibre. Water can break the bonds in the amorphous part

and has no effect on those in the crystalline portion.

Recent work suggests that in cellulose fibres one must consider three types of valence forces, primary valence bonds, hydrogen bonds and secondary or Van der Waals bonds. The primary bonds hold the individual chains together. They have dissociation energies of over 70,000 calories and ordinarily they have lengths of less than 2A. Hydrogen bonds are a comparatively new development and the subject is still not entirely understood. They are a type of coordinate bond in which the hydrogen accepts a share in electrons of a donor atom. They have dissociation energies varying from about 6000 to 18000 calories and bond distances of 2 to 4A. One of the strongest types of these bonds is formed by a hydrogen atom between two oxygen atoms and Huggins has shown that such bonds can be formed between a hydroxyl group on a cellulose chain and the oxygen of the glucose anhydride ring of a neighbouring chain (81). Such a bond has a definite direction and requires a definite orientation between the two chains. Many investigators today believe that these bonds are the ones which hold the cellulose chains together in the crystallites. Such bonds would explain the insolubility of the crystallites in water. The secondary valence bonds have dissociation energies of 2000 to 7000 calories and lengths of 3.5 to 4.5Å. There is no stereo-

17.

chemistry of secondary valence forces and such bonds can

therefore form in the amorphous part of cellulose fibres.

They can also form between individual fibres and are the most probable source of strength in paper. These bonds are soluble in water but can be reformed on the removal of water since the surface tension between narrow boundaries is sufficient to pull neighbouring parts within the range of the secondary valence forces.

The structure so far discussed has been submicroscopic and proposed partly from the results of X-ray examination and partly as a hypothesis to explain experimental results. Microscopic study has given a somewhat similar picture of the visible fibre structure. By means of suitable treatment, such as beating or partial hydrolysis, it is possible to make the fine structure of a fibre microscopically visible. The structural elements thus shown are called "fibrils" and were first reported by Meyer in 1838 (24). Naegeli also described lateral striations which he noted in fibres (7).

At the present time, there is some doubt as to whether or not this fine structure is actually present before treatment of the fibre. Freudenberg (19) states that fibrils are thick and thin, long and short, mechanically disintegrated pieces of the web formed by his micelle series. According to I.W. Bailey (25) the

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cellulose matrix of primary and secondary walls appears to

be composed of aggregations of threads or fibrils which

are held together by branching and interconnections. These anastomosing fibrils vary considerably in size but approach the dimensions of Freudenberg's micelle series. It seems quite probable that fibrils are formed due to the breakdown of parts of this network. The separation of these fibrils appears to take place along sections of lower density in the fibre.

In a recent paper A.J. Bailey and R.M. Brown have produced convincing experimental evidence for constancy of fibril diameter in cellulose from a number of different sources (57). They report that cellulose unit fibrils appear to have one more or less constant diameter, 0.9 to 1.0 , independent of origin, chemical treatment or mechanical processing. These unit fibrils are held together in the plant by a cementing gel, but are themselves incapable of being gelatinized in water by ordinary methods. They also believe anastomosing of fibrils highly improbable. This paper and one to be mentioned later (39) indicate a new trend in the ideas of a group of investigators. It is difficult to comment on these ideas at the present time because there is a much larger body of contrary evidence.

Microscopic study of the arrangement of fibrils

19.

in the fibre has shown that as a general rule fibrils are

arranged more or less spirally at different angles to the

fibre axis (26). Although there is a fairly typical

fibrillar orientation for all the fibres from each cellulose source, I.W. Bailey (25) states that there is a considerable element of danger in assuming, as is so frequently done, that the fibres of any specific tissue or plant are characterized by a specific structural pattern or a constant fibrillar orientation. This is particularly true for wood and cotton fibres.

In ramie and to an almost equal extent in linen the fibrils are all arranged parallel to the fibre Thus Campbell (27) has stated that linen fibres. axis. when beaten, split longitudinally along the fibre axis. This simple arrangement makes linen and ramie fibres ideal for X-ray and optical measurements. A very clear presentation of the structure of cotton fibres has recently been given by Anderson and Kerr (28). The primary wall of cotton fibres shows two opposing systems of fine spirally The spiral threads were found wound threads of cellulose. to make an angle of approximately 70° with the long axis of the fibre (29). In the secondary wall, which forms the bulk of the fibre, there are daily growth rings. These are in reality regions of dense and less dense deposition. The fibrils, which are clearly very much branched and interconnected, are again spiralled about the fibre axis

20.

but at an angle of about 30°. The first layer often shows

a complete reversal of spiral direction and it is probable

that the plan of this first layer is followed in each

subsequent layer. The structure of wood fibres is the

most variable. In general, the outside layer consists of fibrils wound in a tight spiral, almost perpendicular to the fibre axis. In the inside layers the fibrils become progressively more nearly parallel to the fibre axis as the interior of the fibre is approached (30). However, the secondary wall in wood fibres shows all combinations from concentric to radiocentric in fibres from the same tree (25).

Much of the above information on the fine structure of cellulose fibres has resulted from double refraction studies. The double refraction of cellulosic materials was shown by Ambronn to be made up of three different double refractions, any one or all of which may be effective in a given case (31). These are:

- (a) molecular or internal double refraction due to an anisotropic arrangement of atoms in the molecule,
- (b) particle double refraction due to anisotropic arrangement of structural units, the dimensions of which are less than light,
- (c) stress double refraction, a special form of particle double refraction exhibited only when the material is under stress.

21.

Ordinarily in reporting refractive index measurements

on cellulose the three types of double refraction are

not distinguished.

When the crystalline nature of cellulose was finally confirmed by X-ray diffraction measurements it was found that cellulose belongs to the monoclinic However, only two refractive indices are measured system. because orientation in a single fibre occurs only in the structural chain direction. Examination of the fine fibrils under the microscope and between crossed Nicol prisms shows clearly that in the fibril the crystallites are lying with their long axes parallel to the fibril axis (27). Thus refractive index measurements on fibrils give the largest possible double refraction corresponding to the highest orientation. The crystallographic axis is parallel to the fibril axis and the refractive index in this direction is the axial refractive index. The transverse refractive index is measured perpendicular to the axis. Ramie and linen fibres have their fibrils parallel to the fibre axis and thus exhibit the maximum double refraction. Some investigators have calculated the angle of the spirals in cotton from the lowering of the double refraction. They obtain good agreement with experimentally determined values. (32, 33).

The picture of the structure of cellulose fibres that has been given is thought to represent

22.

majority opinion on the subject. However many in-

vestigators do not agree with it and have produced ex-

perimental evidence in support of their contentions. Various types of particles other than fibrils have been isolated from cellulose. Wiesner by acid treatment isolated dermatosomes (34). Ritter reported spindleshaped fusiform bodies obtained by dissolving out some of the carbohydrate material (35). Ritter and Seborg obtained spherical units from these fusiform bodies by treatment with phosphoric and sulphuric acids (36). However they suggested that these were not spherical in the fusiform bodies but became that shape due to swelling. Farr believes the fibrils are made up of ellipsoidal particles held together by a pectin-like substance (37). She states that the swelling and cuprammonium viscosity of cellulose may be attributed to this binding material. Anderson and Kerr have shown that all these particles can be explained as parts of the anastomosing web of the fibrils (28). It is to be noted that their isolation always requires a rather drastic treatment of the fibre.

A more serious controversy has been present, particularly in recent years, over the nature of the bonding which holds the fibres together in paper and which accounts for the stability of the fibre structure itself. One side of this problem has already been given in the

23.

discussion on secondary valence forces. Some investigators

hold an opposite view. Thus Ritter believes a cementing

material of hemicellulosic nature to exist between the layers of fibrils in the cell wall of delignified wood fibres (38). As already stated, Farr has postulated a pectin-like substance as a cementing material between the ellipsoidal particles. In a recent paper, Lewis, Brauns and Buchanan state that in paper there is a complex system of interlocking fibres held together in part by an intermeshing of fine fibrous structures resulting from the fraying of the fibre and in part by the cementatious material liberated or formed during the beating operation (39). They have isolated skin-like bodies left behind on careful swelling of cellulose fibres in cuprammonium solution, and they attempt to show that this fibre membrane is the source of the cementatious material. An analysis of this and other similar papers shows that the experimental evidence can be explained equally well on the basis of secondary valence bonds between cellulose molecules. However, until further evidence appears, there seems to be no good reason for complicating the subject of the bonding between cellulose structural units by assuming a non-cellulosic binding material.

Very few investigators have measured the

24.

dielectric constant of cellulose and none of them have applied their results to the elucidation of the structure of cellulose. There are two reasons for this fact. The

first lies in the difficulties inherent in dielectric constant measurements on fibrous materials. This led to uncertainties in the values obtained. The practical use of cellulose products as electric insulators was the chief interest in such measurements and the results were not extended to cellulose structure.

The values reported in the literature show considerable variation. The International Critical Tables state that the dielectric constant of cellulose lies between 3.9 and 7.5, but do not list the source of their data. Karo (40) in a critical review of the physical constants of cellulose assigns a value of 6.7, which is that obtained by Campbell (41) using low frequency currents. This is also the value listed in Physikalisch-Chemisch Tabellen (42). Stoops (43) measured the dielectric constant of cellophane sheets and reported values at 22°C. ranging from 6.9 to 7.7 depending on the frequency of the measuring current. The first and only previous measurement using a method which eliminated the difficulties encountered with fibrous materials was made by De Luca, Campbell and Maass (43). They report the dielectric constant of standard cellulose to be 6.1 at 25°C. and a frequency of 1,000,000 cycles. The above results will be discussed in

25.

detail in a later section of this work.
CAPACITY MEASUREMENT

B. Capacity Measurement

I. Apparatus

The principal methods for the measurement of the dielectric constant can be divided into three classes: (1) The dielectric constant can be calculated from a measurement of the electric force acting through an insulator by use of Coulomb's Law (44). Recently a new application of this method, which may be of great use in the cellulose problem, has been introduced by Doborzynski (45).

(2) Drude introduced a method based on the fact that the velocity of propagation of electromagnetic waves through a material is proportional to the square root of the dielectric constant of that material (46).

(3) By far the most common methods for the measurement of dielectric constant are based on the previously mentioned equation relating capacity to dielectric constant, $E = C/C_0$. The accuracy of such methods depends only upon the accuracy of the capacity measurement. Nernst pioneered in the use of a bridge method for capacity measurement (47); a resonance method was used by Tank (48) and others; a heterodyne beat method was investigated by Herweg (49), Isnardi (50) and Williams and co-workers (51, 52).

26.

The heterodyne beat method was used in this

Smyth has discussed the theoretical bases of this work.

method in some detail. The frequency of an oscillating

circuit, in which only the capacity is varied, is inversely proportional to the square root of the capacity. Now if we have two such oscillating circuits, one having a fixed frequency and one having two capacitances in parallel by either of which the frequency may be varied, and allow their output to feed into a common detector-amplifier system a new oscillation will be produced corresponding to the difference between the two frequencies. If this frequency difference is in the audible range a beat-note will be produced. If one of the capacitances in the variable oscillator is adjusted to give zero beat conditions then the oscillators are operating at the same frequency. The size of an unknown capacitance, introduced into the variable oscillator circuit which was previously set to zero-beat, can be measured as the change in capacity necessary in a standard capacitance in parallel with the unknown to restore zero-beat conditions.

The apparatus used in this research was originally described by Smyth (1), but has been considerably modified by several workers in this laboratory (53, 54, 55, 56). A schematic diagram of the apparatus is shown in Fig. I. The two oscillator circuits are

27.

respectively at the top and bottom, separated by the

detector-amplifier circuit. These circuits are almost



exactly the same as described by De Luca (56). They are described in full below and any changes are indicated.

The most important factor in the design of the oscillators was their stability. Several precautions were taken to ensure the constancy of their frequencies. A heavy bus bar was used in wiring the oscillators since vibrations in the wiring can cause capacity changes. A more constant filament source, E_1 , was obtained by using four 1.5 volt dry cell batteries in series-parallel.

A fixed resistor R_2 rather than a rheostat was used to drop this voltage to 2 volts. Heavy duty 45 volt dry batteries provided the plate voltages E_2 , E_6 and E_7 . For purposes of shielding, both oscillators and the detector-amplifier unit were separately housed in sheet metal boxes which were grounded. All external leads consisted of shielded microphone cable, the shield being grounded. The microphone cable was used in preference to De Luca's copper wire in copper tubing because of its flexibility without loss of stability. The variable condensers were included in the circuit in such a way that their rotors were grounded. The precision condenser, which of necessity had to be

28.

outside the shielding box, was moved by remote control.

Even with these precautions there was a

small frequency drift in the oscillators. The effects

of this were minimized in two ways. Some of the drift was undoubtedly due to temperature changes. For this reason the oscillators were always allowed to warm up for at least fifteen minutes before using. It was not necessary to warm up the detector-amplifier circuit. In fact it was found more advantageous to charge the storage battery supplying the filament voltage to this circuit during the warm up period. The effect of the drift which still remained was more or less cancelled by the method used in taking readings. This is described later.

The capacitance C_1 was the standard condenser. It was a 500 micromicrofarad precision condenser (General Radio Type 247E). In order to increase the accuracy with which this capacitance could be read it was placed at the mid-point of the diameter of a semi-circular table. The diameter of this table was five feet. A small mirror attached to the rotor shaft of C_1 reflected a line image on to a millimeter scale fastened to the circumference of the table. The line image was formed by one of the supports for the filament in a 500 watt projection lamp. With this arrangement capacity readings could be estimated to 0.1 millimeters, equivalent to about 0.022 micro-

microfarads. As previously mentioned, this condenser was turned by remote control. Its rotor was connected by a pulley arrangement to a vernier dial at the circumference of the table. It was important that a constant tension

29.

be applied in this pulley system since the capacity of the condenser was sensitive to changes in the tension. For this reason the cord used by De Luca, in which the tension was dependent on the humidity, was replaced by a leather belt.

The capacitance C_2 was the experimental condenser containing the substance whose dielectric constant was to be measured. It is described in detail in a later section. C_3 was approximately equal to C_1 and C_4 was a variable condenser to balance the capacity of the long leads used in conjunction with C_1 and C_2 . During an actual measurement the value of C_4 is not varied so that the oscillator including it is termed the "fixed oscillator." On the other hand, the value of C_1 is changed, so that the oscillator containing it is termed the "variable oscillator."

Extraneous oscillations picked up by the long leads were blocked by resistance R_3 and condenser C_{10} . A further extraneous oscillation was present when this work was first started. This was caused by too high a value for the grid bias on the '30 tube of the variable oscillator. This was corrected by putting

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a 500 ohm resistor \mathbb{R}_7 in parallel with \mathbb{C}_5. This was
not necessary in the fixed oscillator.
The inductances \mathbf{L}_1 and \mathbf{L}_2 consisted respectively
of sixty-four and seventy turns of number fourteen insulated
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copper wire wound on cylindrical forms three and onequarter inches in diameter. The inductances L_3 and L_4 , consisting respectively of thirty-two and thirty-five turns of wire, were wound over L_1 and L_2 . The inductances L_5 and L_6 were contained within the metal boxes of the oscillators and were connected to the detector amplifier unit by means of short shielded leads passing through holes in the boxes. Originally both L_5 and L_6 consisted of four turns of number 22 copper wire wound on a bakelite form two and one-half inches in diameter and placed about one-quarter to one-half inch away from ${\tt L}_3$ and ${\tt L}_4$ respectively. It was found, however, that the sensitivity of the circuit could be greatly increased by increasing the coupling between the oscillators and the amplifier. Twelve turns of enamelled copper wire were added in parallel to and wound on top of L_5 . Fourteen turns of this wire were added in parallel to L_6 and two of these were wound on top of L_4 . This, of course, greatly increased the coupling. When the batteries were fully charged it was not necessary to have the coupling so close, but it was found to be an advantage to increase the coupling as the batteries discharged.

During this work the tube line-up in the

detector-amplifier unit was changed. At first a **x** 240

tube was used as detector followed by a similar tube as

voltage amplifier. In the output stage a U x 171 was used. These are shown in Fig. I. Approximately the same results were obtained later when a 201A tube was used as voltage amplifier and a 112A as final amplifier. In the latter case it was necessary to reduce the bias voltage E_8 to $13\frac{1}{2}$ volts.

De Luca made several improvements in this circuit in order to increase the amplification factor. The circuit including L_5 , L_6 and C_7 was made into a tuned circuit by the addition of the radio frequency choke RFC. The detection voltage E_7 was set at 45 volts. In this work a potential of $67\frac{1}{2}$ volts was found to give most efficient detection. These improvements gave sufficient volume to warrant the use of a loudspeaker, which was improvised by using the bottom of a."tin can" as the diaphragm of an earphone.

As described by De Luca, the output of this stage acted as a vacuum tube voltmeter, so that visual indication of zero beat could be obtained. This voltmeter is marked V in Fig. I and was a triple range Weston model 280. The voltage in the output stage oscillates with the frequency of the beat note. As zero beat is approached these oscillations become slower until at zero

beat the voltage drops to a minimum value and remains

stationary as long as zero beat obtains. By proper

adjustment of the bias voltage E_8 , the minimum may be

set at any value. It was found to be preferable to set this value at zero volts and use the three volt range of the voltmeter. In this way a maximum oscillatory movement of the voltmeter needle is obtained.

The switch S was a rocker-type, mercury contact switch. In order to reduce the lead correction at the experimental condenser it was necessary that this switch be close to that condenser. De Luca constructed a remote control so that the switch could be opened or closed from the operating position for the standard condenser. It was found that the remote control apparatus did not always open the switch to the same position. This introduced a variable capacity effect and for this reason the remote control was eliminated.

The frequency used in preliminary measurements was approximately 1,000,000 cycles as measured by De Luca. In all other measurements the frequency used was approximately 300,000 cycles. This figure was calculated from the dimensions of the inductance and capacitance in the variable oscillator. It was checked by beating against the carrier of a local broadcast station which operates on a frequency of 600 kilocycles.

33.

II Method of Operation

To determine capacity with the above apparatus the following was the procedure adopted. About fifteen minutes before the measurement was to be made the filament currents in the oscillators were turned on. At the same time the storage battery supplying the filament voltage E_4 for the oscillator-amplifier circuit was placed on a charging current of about one ampere. In this way a static effect which was traced to this battery could be entirely eliminated unless the measurements occupied an exceptionally long time. In that case it was sometimes necessary to give the battery a short charge between some of the measurements of a series.

The capacitance C_1 was then set to read zero on the scale with C_2 out of the circuit (Switch S in position 1). C_4 was then rotated until approximate zero beat conditions obtained. The exact null point setting was obtained by turning C_1 to a negative scale reading and returning to the null point by turning C_1 . Because, even with the voltmeter indicator, there was still a dead space at zero beat of about 0.15 cm. it was the rule in this work always to approach zero beat by turning C_1 from the low or negative value side to the null point. If the null point was

34.

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passed it was necessary to repeat<sup>t</sup> the procedure. The scale
reading thus obtained was then the zero point. This point
was not necessarily at zero in the scale, but it was made
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to fall quite close to zero.

The switch S was then closed to position 2, thus bringing the unknown capacitance C₂ into the variable oscillator circuit. The standard condenser was then rotated to give zero beat conditions again, observing the usual precautions. Ordinarily one would expect that the difference between the new reading and the zero point reading would be the value for the capacitance C2. However, as has previously been mentioned, there was always some drift in oscillator frequency during a measurement. TO detect this drift it was necessary at once to repeat all readings at least twice. This procedure showed up and allowed elimination of errors due to frequency drift. In the majority of cases the amount of such drift was too small to require correction, but unless the above procedure was followed it was impossible to tell whether or not a large drift had occurred.

III Calibration of the Standard Condenser.

It was shown by Linton (58) and again by De Luca (56) that it is not justifiable to assume that there is a straight-line relationship between capacity of the standard condenser and scale readings. It was therefore necessary to apply a correction to the scale readings before

35.

using them in calculations. Linton applied a correction

but does not indicate the method used. In this work the

calibration was carried out in approximately the same

manner as employed by De Luca.

The aberration from linearity may arise from several causes. It was partly due to the construction of the condenser, It was also partly due to the fact that the condenser was probably not quite at the centre of the diameter of the table. The relation between capacity and scale reading was very sensitive to slight movements of the projection lamp used to produce a line image on the scale. For this reason the lamp was firmly fixed to brackets which were fastened to the table itself. Thus any motion of the table did not affect the relation of the lamp to the table.

The following was the procedure adopted for this calibration. A small capacity was introduced in the circuit of the variable oscillator in place of the experimental condenser C_2 . The displacement of the null point produced by this condenser over successive parts of the scale was measured. The lowest value was arbitrarily chosen as the unit value and the differences between this and the remaining readings were calculated. Then a calibration curve was drawn plotting the correction to be subtracted to give this unit value against the displacement whe from zero.

The value of the small capacity chosen by De Luca

36.

was about 20 cm. on the measuring scale. Actually the

smaller this capacity the more accurate will be the correction

obtained from the calibration curve. However, it was found

that too small a value introduced errors due to the length of time necessary to cover the entire scale of 200 cm. An optimum value of between 12 and 13 cm. was chosen for this work.

The largest correction in De Luca's calibration occurred in the first 50 cm. of the scale. This was due to end effects in the standard condenser when its plates were almost fully meshed. Since, to cover the entire measuring scale, only half the total capacity change possible in the standard condenser was used, this large end effect was eliminated by setting the rotor plates so that they were one-quarter unmeshed at zero on the scale. They were then three-quarters unmeshed at about 200 cm. on the scale.

It was necessary to repeat the calibration several times during this work, due to various factors such as insertion of a new projection lamp and rebuilding of the entire apparatus. No two-calibrations gave exactly the same curve but they were always very similar. A sample calibration is shown in the table below. All readings are means of three or more repetitions and a correction has been applied for drift when necessary.

37.

Zero Reading	Final Reading	Dif- ference	Devia- tion	Displace- ment from Zero	Cor- rection
0.05				رت رت	
-0.03	12.16	12.19	0.01	12.19	0.01
12.19	24,46	12.27	0.09	24,46	0.10
24.40	36.58	12.18	0.00	36.64	0,10
36.62	48. 84	12.22	0.04	48,86	0.14
48.87	61. 25	12.38	0.20	61.24	0.34
61.29	73.78	12,49	0.31	73,73	0.65
73.70	86.15	12.45	0.27	86.18	0.92
86.13	98,48	12.35	0.17	98.53	1.09
98,60	110,99	12.39	0.21	110.92	1.30
110,89	123.29	12.40	0.22	123.32	1.52
123.32	135.89	12.57	0.39	135.89	1.91
135,95	148.46	12.51	0.33	148.40	2.24
148.38	160,92	12.54	0.36	160.94	2.60
160.96	173.33	12.39	0.21	173.33	2.81
173.22	185.62	12.40	0.22	185.73	3,03
185.62	197,98	12.36	0.18	198.09	3.21

It was necessary to check each calibration immediately on completion and periodically throughout the work. This was the only way of knowing whether any change had occurred. This was done by measuring the capacity of a given condenser over different parts of the scale. A deviation in the corrected values of not more than ± 0.05 cm. from the mean was allowable. It is to be noted that, as now arranged, the correction is valid over the It is no longer necessary to avoid measureentire scale. ments where the final readings fall at the ends of the scale. A sample calibration check applied to the above calibration appears in the table below.

38.

Original	Final	Cor	Corrections			Cor-
(a)	(b)	(a)	(b)	Total	ference (b-a)	rected Dif- ference
						_
-0.01 -	40.51	0.00	0.11	0.11	40.52	40.41
20.15	60.83	0.07	0.33	0.26	40.68	40.42
60, 59	101.77	0.33	1.14	0.81	41.18	40.37
AT 47	82.59	0 12	0.84	0.72	41,12	40.40
89 06	193 00	0.85	1 54	0.69	41.03	40.34
02020	TYO 32	0.00		0.05		

IW Calculation of the Dielectric Constant

The dielectric constant is given by the ratio C/C_o , where C is the capacity of the condenser filled with the material whose dielectric constant is being measured and C_o is the capacity of the condenser in vacuum or in air. However, the capacity measurements under experimental conditions include the capacity of the leads connecting the switch S to the experimental condenser and also the end correction for this condenser.

We may write:

(a) for the condenser when empty $L+C_0 = Kd_1$

- (b) for the condenser when filled $L+C = Kd_2$
- (c) for the leads and end correction $L = Kd_3$

where L is the lead and end capacity d_l is the measured deflection for the empty condenser

plus leads.

d₂ is the measured deflection for the filled condenser

plus leads.

- d₃ is the measured deflection for leads and end correction.
- K is a proportionality constant relating capacity to scale reading.

The dielectric constant E will then be given in terms of scale readings by the relation:

$$E = \frac{Kd_2 - Kd_3}{Kd_1 - Kd_3}$$
$$= \frac{d_2 - d_3}{d_1 - d_3}$$

It is therefore possible to express capacity measurements in terms of scale readings as corrected by the calibration previously described.

SPECIAL METHOD FOR FIBROUS MATERIALS

C. Special Method for Fibrous Materials.

I. Theoretical Considerations.

The measurement of the dielectric constant of a solid is complicated by the difficulty encountered in filling the condenser completely with the solid. For those solids which can be liquefied Smyth (1) has described a method in which the liquid is solidified between the condenser plates. Even this method is sometimes inaccurate due to contraction of the solid, and of course it could not be used for a material like cellulose which has no melting point. Stoops (59) and Campbell (41) have both measured

the dielectric constant of regenerated cellulose by placing the sample between mercury electrodes which acted as the condenser plates. This is subject to limitations due to the necessity of calculating the true capacity of an air condenser of this shape. Also, in the case of the regenerated cellulose, the mercury cannot be said to fill the pore spaces which undoubtedly exist in such a material. Campbell also used a method by which the condenser plates could be pressed onto the solid. This is subject to the same limitation with regard to pores mentioned above.

There are three equations which have been applied

41.

to fibrous materials, powders and porous substances. The first of these was derived from theoretical considerations by Campbell (41) and independently by Argue and Maass (60). $\times \frac{1906}{1935}$

If the solid dielectric is in regular layers parallel to the condenser plates with air spaces between the layers, the following relationship holds:

$$E_{m} = \frac{1}{\frac{V_{1}}{V} + \frac{V_{2}}{VE}}$$
 ----- (1)

where $\mathbf{E}_{\mathbf{m}}$ is the measured dielectric constant of the solid plus air.

E is the dielectric constant of the solid.

$$\frac{V_1}{V}$$
 is the volume ratio of air.
 $\frac{V_2}{V}$ is the volume ratio of solid.

It was also shown by Argue and Maass (60), that if the solid dielectric is arranged in regular layers perpendicular to the surfaces of the condenser plates with alternate layers of air, the following relationship holds:

$$E_{m} = \frac{V_{1}}{V} + \frac{V_{2}}{V} E ----- (2)$$

where the symbols have the same significance as above. Lichtenecker (61) has empirically found an equation which may be applied to the case of a dielectric consisting of very small particles distributed at random in the air space in the condenser. This is his Logarithmic

Mixture Rule:

$$\log E_{m} = \frac{V_{2}}{V} \log E \quad ---- \quad (3)$$

where again the symbols have the same significance.

All of the above equations are ideal cases. They have been applied by some investigators, and for arrangements approaching the ideals they give fairly good results. Thus Tausz and Rumm (62) applied equation (3) to the case of powders and obtained fairly consistent results. But none of them give, or can be expected to give, reliable results with a fibrous material such as cellulose. This is due to the fact that it is not possible to give cellulose fibres an ideal orientation in the condenser. The use of these equations in connection with water on cellulose is discussed in a later section.

The method used in this work is the only known method which gives accurate values for the dielectric constants of fibrous materials. It is equally applicable to other solid forms. This procedure was discovered by Starke (63) and independently by De Luca, Campbell and $\frac{2897}{1932}$ Maass (43). It was shown in both these papers that the $\frac{1932}{1932}$ effect of random orientation of isotropic fibres relative to the condenser plates could be eliminated if the air space between the fibres is filled instead with a liquid having the same dielectric constant as the cellulose itself. The method, then, consists essentially in finding the liquid mixture which is isodielectric with the cellulose.

43.

It can be applied to insulating solids so long as the conductivity of the liquid mixture is not too much greater than that of the solid material. Leowe (64) determined

the limits of the permissible differences in conductivity.

In the work of De Luca, Campbell and Maass the composition of a liquid mixture having the same dielectric constant as the cellulose was the point of intersection of two liquid-composition versus dielectric constant curves, one with and one without the cellulose sample in place in the condenser. The dielectric constant of a liquid of this composition was then determined directly or from a curve showing the relation between percentage composition and dielectric constant.

In practice these curves were very difficult to plot accurately due to their small degree of curvature. The point of intersection was also uncertain because of the small angle at which the two curves crossed. If straight line plotting could be used, or if where a curve was necessary its shape were better defined by more points in the range of the expected dielectric constant, a greater degree of precision could be obtained. Accordingly, in this work, the dielectric constant of a liquid mixture having the same dielectric constant as the cellulose sample was determined in the following manner.

Two completely miscible liquids, A and B, were chosen such that the dielectric constant of the cellulose

44.

lay between the values for the two liquids. From previous work (43, 56) the relation between composition and dielectric constant of mixtures of these two liquids was known. The approximate dielectric constant of cellulose was also known. It was therefore possible to make up a series of ten mixtures of A and B with dielectric constants ranging from about 15% below to 15% above the expected value for cellulose. The dielectric constants of these liquid mixtures were then measured and a curve drawn showing the relationship between dielectric constant and composition. The condenser used for these measurements was then partly filled with the fibrous material.

In the previous method it was then necessary to determine the resultant dielectric constant when each of the liquids in turn occupied the space in the condenser not filled by the fibres. These results were then plotted on the same graph as the above curve and the point of intersection of the two curves was determined. Inspection of the curves thus obtained led to the fact that both have the same curvature but different slopes. It was therefore possible to assume the curvature of the second curve after once establishing the one for the liquid mixtures alone. Then only two points were necessary in all other curves to establish their slope and position. It was further possible to use straight lines for the plots, if, instead of plotting

dielectric constant versus composition, the difference

between the dielectric constants for the pure liquid mixture

and the liquid mixture plus cellulose was plotted against

composition. The dielectric constant of the liquid of composition shown by the intersection of this line with the composition axis may then be picked off on the established dielectric constant versus composition curve for the liquid mixtures alone. This was then the dielectric constant of the cellulose sample.

II. Apparatus

In order to carry out the procedure described above it was necessary to introduce the liquid mixtures into the experimental condenser under vacuum. The glass apparatus required to do this is illustrated in Fig. II. It was almost exactly the same as used by De Luca and the functions of its component parts are described in a succeeding section on experimental procedure. However, the experimental condenser, the cell containing it, the leads connecting it to the measuring apparatus and the method of temperature control are described below in some detail.

The Experimental Condenser: The experimental condenser described by De Luca was used in preliminary measurements in this work. Due to its method of construction it was difficult to insert paper into this condenser. Accordingly, a new one, eliminating this difficulty, was

46.

designed and constructed. This latter condenser was used

in this work for all but the preliminary results on



standard cellulose paper. It consisted of two concentric brass cylinders, the outside one having a length of 17.7 cm. and the inside one having a length of 16.9 cm. The inside diameter of the outside cylinder was 2.55 cm. and the outside diameter of the inside cylinder was 1.76 cm., thus giving an annular space with a width of 0.40 cm. These cylinders were held in their concentric position by two Pyrex rings, 0.5 cm. in thickness and 1.0 cm. in height. A vertical section 0.7 cm. wide was cut out of each ring to allow rapid penetration of liquids into the intercylinder space. The ends of the outer cylinder were slightly expanded and of the inner cylinder slightly cut away so that the Pyrex rings, one at the top and one at the bottom, held the cylinders firmly in place. A nickel plated binding post was soldered to a projection one cm. in length and 3 mm. in width at the top of each cylinder.

The Dielectric Cell: The condenser stood upright in a Pyrex cylinder of 3.1 cm. inside diemeter and 38 cm. in length (C in Fig. II). The purpose of this cell was, of course, to include the experimental condenser in the vacuum system. However, its special feature was a ground glass seal at the top which allowed the removal of the condenser at any time. This was a distinct advantage for

47.

it was formerly necessary to remove the cell from the

system and to cut it open in order to remove the condenser.

This required the construction of a new cell after each measurement. The ground glass seal was made vacuum-tight by means of stopcock grease and a mercury seal. The mercury was contained in a glass jacket surrounding the seal and the mercury level could be controlled by means of a reservoir (See Fig. II). The dielectric cell was connected to the vacuum system by means of a tube from the bottom and a tube issuing from the side. Twofurther side tubes served to bring out the condenser leads. These latter tubes were on opposite sides of the cell.

The Leads: A short piece of #22 bare copper wire was attached to each of the contacts on top of the condenser and brought out of the dielectric cell via the two side tubes provided for that purpose. It was not necessary to have a platinum to glass seal in these tubes even under high vacuum. Perfectly satisfactory seals were made around the copper wires at constrictions in the side tubes by means of De Khotinsky cement. These two wires were connected to the switch S by #18 gauge copper wire with wax-impregnated cotton covering. In order to prevent capacity changes due to changing humidity,

48.

around these wires they were enclosed in separate glass

tubes which were sealed by De Khotinsky cement at both

The outside cylinder of the experimental condenser ends.

was connected to the ground side of the switch S. This lead was run down the front side of the dielectric cell and the high potential lead was run down the rear side. These last precautions were necessary to avoid stray capacity effects.

Temperature Control: All measurements in this work were made at a temperature of $25.0^{\circ} \pm 0.1^{\circ}C.$ This control was obtained by means of a water bath surrounding the dielectric cell. A Pyrex cylinder, 6 cm. in diameter and 30 cm. in height, was employed as the container for the bath fluid. This cylinder was sealed at the bottom by a rubber stopper and litharge cement. The temperature of the bath was hand controlled. A tube was arranged at the bottom of the bath so that air, steam, hot or cold water could be introduced. For stirring compressed air was introduced. For large temperature changes the steam or water was used. Small temperature changes were controlled by adding small amounts of cold water at the top of the bath or by passing the flame from a hand, glass-blowing torch over the outside of the bath. Actually most temperature changes were made in the latter manner. The room temperature was kept in the vicinity of 24°C during measurements, so that the bath was always

slowly cooling. An occasional shot with the flame served

to keep the temperature well within the limits named above.

The samples were always kept at constant temperature

equilibrium before any capacity measurements were made.

III Preparation of Liquids

The liquids chosen by De Luca for his work were benzene (dielectric constant 2.27) and ethylene dichloride (dielectric constant 10.2). Mixtures of these liquids gave a wide range of dielectric constants, which was necessary for there was considerable doubt as to the value to be expected for cellulose. Such a wide range of dielectric constants was not necessary in this work, but the same liquids were used since they had proved very satisfactory for the purpose. However, the mixtures were made up in a much narrower range of dielectric constants.

In preliminary measurements the benzene used was Merck's C.P. grade and the ethylene dichloride was a technical grade supplied by Chemicals Ltd. It was shown that impurities present in the liquids were not absorbed by the cellulose, so no purification was carried out. However, difficulties were encountered in duplicating these liquid mixtures or in attempting to prepare a mixture having a specific dielectric constant. This was due to the fact that each new shipment of liquid had different

50.

amounts of impurities and therefore different dielectric constants. After the preliminary measurements a new set of mixtures was made up from properly purified liquids. These were used throughout the remainder of the work. The benzene was first stored for twenty-four hours over sodium wire. There was a noticeable evolution of hydrogen for about one hour after introduction of the sodium. The benzene was then distilled over sodiumpotassium alloy with special precautions taken to keep moisture from the distillate. The fraction taken came over between 79.9° and 80.0° C on the thermometer used. The distillate was stored over sodium wire until needed.

The ethylene dichloride was washed by shaking in a 1,000 ml. separatory funnel, first with a 5% aqueous solution of sodium hydroxide and then twice with distilled water. The ethylene dichloride layer was cloudy after the alkali treatment, but the successive water washings removed this cloudiness. The product of this treatment was then stored for twenty-four hours over dry calcium chloride. The dry ethylene dichloride was distilled using glass beads to promote boiling and taking proper precautions.against the entry of moisture. The fraction taken distilled at 83.0° to 83.2°C.

Examination of the curve showing variation of dielectric constant with composition, which was obtained by De Luca and again in preliminary results of this work, allowed the calculation of the compositions

51.

which would give a dielectric constant range of about

4 to 7. This range was made as small as possible but had

to include the expected dielectric constant of cellulose,

which was made somewhat uncertain by preliminary results in this work.

Approximately 300 ml. of each of ten mixtures of benzene and ethylene dichloride having dielectric constants within the above range were prepared gravimetrically. The percentage composition by weight of these solutions is given below:

<u>% Benzene</u>	<u>% Ethylene Dichloride</u>
53 04	17 76
00.24	40,10
52 . 42	47.58
47.55	52 . 45
45.84	54.16
43.63	56.37
39.09	60,91
34.02	65.98
31.82	68.1 8
28.27	71,73
25.11	74.89
	<u>56.24</u> 52.42 47.55 45.84 43.63 39.09 34.02 31.82 28.27 25.11

IV Experimental Procedure

(a) Liquids

It was necessary first to measure the dielectric constants of the ten liquid mixtures described above. In the description of the procedure which follows all symbols refer to Figure II.

The combined capacity of the leads and the

condenser filled with liquid was measured at least twice for each of the ten liquid mixtures. The tip T_1 was broken off and a beaker containing about 300 ml. of one of the liquids was placed under it. Application of a slight vacuum through S_2 served to draw this liquid about 10 cm. up the right side of the U -tube. With S_2 closed stopcock S_1 was carefully opened to vacuum and the liquid drawn up the left side of the U -tube into the dielectric cell. By experiment it was found that two introductions were sufficient to thoroughly wet the condenser with the liquid used. Further introductions did not change the capacity reading obtained.

The liquid level used for all measurements in this work was a line on the binding post attached to the outside cylinder of the experimental condenser. This line was formed by a constriction in the binding post. First the liquid level was adjusted to about 4 mm. above this line. At this time the oscillator filaments were turned on for their warm-up period and the liquid was allowed to come to temperature equilibrium with the bath maintained at 25°C. Fifteen to twenty minutes were found to be sufficient for the attainment of equilibrium. By this time the liquid level had fallen to the vicinity of the correct level due to evaporation into the space The level was then accurately adjusted above the surface. to the binding post mark by slightly opening S_1 either to

air or to vacuum and the capacity measurements made. The

liquid level adjustment was quite critical and care had to

be taken that the level was correct at the time of measure-

ment.

After completion of the capacity measurements the liquid was removed by opening S_1 to air. The tip T_1 was then closed by means of a short piece of rubber tubing and a pinch clamp. The residual liquid was removed to the "dry ice" trap R_2 by evacuation through S_2 . This residual liquid was later recovered. The drying was followed by capacity measurements. When a constant empty condenser capacity had been reached, S_2 was closed and the system brought back to atmospheric pressure by slow introduction of dry air through S_1 .

Each of the ten liquid mixtures was measured in In order to calculate the dielectric constants this way. from the above capacity measurements it was necessary to evaluate the lead and end correction d_3 . The method for doing this is described in a following section on calculation of the dielectric constant. However, this calculation required capacity measurements using pure benzene as the liquid and carried out in exactly the manner described above. ln the following table the results for the ten liquid mixtures are given. It will be noted that the empty condenser capacity varied over a range of about 1% during the measure-This was due to changes in the experimental condenser ments. itself, as is shown by the constancy of the lead correction which was calculated from benzene measurements made several

times between liquid mixture measurements.

Liquid Number	Empty Condenser (d ₁)	Filled Condenser (d ₂)	Lead & End Correction (d ₃)	Dielectric Constant
l	41.33	118.09	17.63	4-239
2	41.35	123.53	17.63	4.465
3	41.32	131.09	17.63	4,789
4	41.33	133.83	17.63	4,904
5	41.33	137.54	17.63	5,059
6	41.23	145.54	17.63	5.420
7	41.21	155.60	17.63	5,851
8	41.11	159.89	17.63	6,053
9	41,13	167.92	17.63	6.393
10	41.17	172.97	17.63	6,570

The above measurements were made before any of the liquid mixtures had been used for cellulose measurements. Some of the mixtures, especially numbers 6 and 9, were used for a large number of cellulose measurements. It would be expected that the more highly polar ethylene dichloride would be preferentially adsorbed on cellulose. However this did not affect the concentrations in the liquid mixtures since all liquid was recovered. The part removed to the "dry ice" trap was also returned to the liquid container. However during the period in which these liquids were used the empty condenser capacity and especially the lead and end correction changed frequently. The dielectric constants of the most used liquids were checked periodically throughout the work and they were found to remain practically Sample checks appear in the table below. constant.

5

Liquid Number	Empty Condenser (d _l)	Filled Condenser (d ₂)	Lead & End Correction (d ₃)	Dielectric Constant
6	41.05	145 37	77 /5	5 497
6	41.05	146.10	17.30	5,425
9	41.04	168.18	17.45	5.389
9	41.05	169.22	17.30	5.397
7	41.05	155.59	17.45	5,853
9	40.98	171.98	16,68	5,390

These results indicate the precision of the method. They also show that the cellulose samples lead no appreciable effect on the liquid mixtures.

In Graph No. 1 the dielectric constants of the liquid mixtures are plotted against their compositions. The resulting curve is of exactly the same shape as that obtained by De Luca. The positions of the points are not quite the same due to the fact that the liquids used in the present work had been specially purified. Reference is made to this curve in all the succeeding measurements on cellulose.

(b) <u>Cellulose Samples</u>

The cellulose sample was packed into the experimental condenser and the condenser replaced in the dielectric cell. The method of packing was important and is described for each sample in the experimental results. The leads were connected, the stopper replaced

56.

at the top of the cell and the mercury seal raised around

it.


It was necessary to remove the moisture ordinarily contained by cellulose at atmospheric humidity. Most of this moisture was removed at room temperature by evacuation through S_2 and was caught in a phosphorous 4 pentoxide trap in the vacuum system. It was, preferable to remove the first moisture at low temperatures, since fast removal of large amounts of water might affect the structure of the cellulose itself. After three hours under vacuum at room temperature, the temperature was raised to 98°C by bubbling steam into the water bath. Four hours at this higher temperature were always found to be sufficient to give a constant capacity reading. An extra hour was then given to make absolutely sure of constant conditions. Actually, after the first two hours a capacity measurement was made at 25°C. A constant reading at 25°C was obtained after two more hours at the higher temperature and this was verified after one more hour at 98°C. Cellulose thus treated was designated as "dry" cellulose, in accordance with common practice in cellulose studies (65).

After once obtaining this dry cellulose it was very important to observe special precautions in keeping it dry. Air which had been dried by passing through the sulphuric acid tower B and the phosphorus

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pentoxide tubes. D was let into the evacuated system slowly through S₁ to atmospheric pressure.

Å.

It was now necessary to introduce a liquid into the dielectric cell under vacuum conditions in order to eliminate the trapping of air bubbles in the fibre mat. The procedure of frozen seals used here was developed by De Luca, Campbell and Maass (43). However, major changes in the details of their procedure have been made and the entire method is described below as used in this work.

A liquid having a dielectric constant in the range of the expected constant for the cellulose sample was selected from the ten previously described. Dry air was passed slowly through the system from S1 to S2. This was necessary to prevent introduction of moisture when the system was opened on the right side of the dielectric The tip T_2 was then broken and some of the liquid cell. contained in a beaker placed around it. The air stream was turned off and enough liquid to fill the tip T and 3 cm. on each side of the U - tube was introduced through T_2 by application of slight suction through S2. The level on the cell side of the U - tube was adjusted to about 2 cm. by slightly raising the mercury in manometer M₁. This liquid was then frozen by placing a small Dewar flask

containing a dry-ice acetone mixture around the U - tube.

When this frozen seal had been made, enough liquid to

fill the dielectric cell was introduced by means of suction through T_2 into the vessel A above the frozen seal. An air stream introduced through S_2 served today T_2 which was then sealed.

The system on the cell side of the frozen seal was then evacuated through S_1 to a pressure of less than 10^{-2} mm. of mercury. The vacuum system used in reducing pressure to this value consisted of a Langmuir diffusion pump in conjunction with a Hy-Vac pump. Pressure was measured by means of a LcLeod gauge. This evacuation usually required about one hour if care was taken not to allow any melting at the frozen seal. When the pressure had been sufficiently reduced the mercury in manometer M_1 was raised to form a cut-off and S_1 was closed. The air in the system above the liquid in A was removed by evacuation through S_2 . The pressure was reduced to the vapour pressure of the liquid and a little of the liquid was allowed to boil off into the "dry-ice" trap R_2 .

The difference in pressure on the two sides of the frozen seal was now just the vapour pressure of the liquid. The frozen seal was melted and this difference in pressures pushed the liquid about half way up into the dielectric cell. Time was now allowed for boiling in the

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liquid to cease. Previous work had shown that the liquid must be run into the condenser at least six times in order to insure complete wetting. In this work the liquid was introduced eight times by alternately turning S₂ slowly to the air line and then to the vacuum line. Care was very necessary here since a small change in pressure had*a large effect on the liquid level. This level was never permitted to go up to the side tubes of the dielectric cell or below the level of the bottom of the water bath. The liquid was finally raised to a point 2 to 5 mm. above the usual mark on the condenser binding post, depending on the type of sample, and the frozen seal remade. It was not necessary to allow pressure equilibrium conditions to be established before making this seal.

The mercury in cut-off M_1 was lowered and dry air was allowed to enter very slowly through S_1 and S_2 to atmospheric pressure on both sides. At this point the oscillator filaments were turned on and the bath temperature was brought to 25° C and maintained at that temperature. When atmospheric pressure had been reached on both sides, S_1 and S_2 were closed and the mercury in manometers M_1 and M_2 was raised to cut-off. As was previously mentioned, it was necessary that the liquid level be accurately adjusted to the binding post mark. During the introduction

of the air the liquid level had fallen to a point very close

to this mark due to collapse of vapour bubbles trapped in

the cellulose mat. In fact, sometimes the level was accurately at the correct mark and no further adjustment was necessary. However, this was fortuitous and in the majority of cases it was now necessary to melt the frozen seal and to adjust the level accurately by slight changes in the mercury levels in M_1 and M_2 . When the seal was melted the liquid level always dropped, but never as far as the top of the condenser. The seal was again frozen to keep the liquid level constant during measurement. By this time temperature equilibrium with the bath had been established. The capacity of the condenser filled with cellulose and liquid mixture was then measured according to the procedure already described.

The above procedure accomplished the introduction of liquid into the condenser under vacuum and eliminated the possibility of trapped air being present in the cellulose sample. Any air bubbles present at a pressure of 10^{-2} mm. of mercury had a negligible volume under atmospheric pressure. If at any time after introduction of the liquid, air was allowed to come into contact with the cellulose it was necessary to start

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the run over again.

After completion of the capacity measurement

the frozen seal was melted and the tip T_1 broken to allow

the liquid to drain into a beaker. The mercury cut-offs M_1 and M_2 were lowered and stopcocks S_1 and S_2 opened to the air line for this purpose. When nearly all the liquid had run out of the system, a dry air stream was passed in through S1 This was allowed to continue for at least fifteen minutes in order to remove as much free liquid as possible. With the air stream still passing through, the U - tube and tip were dried by application of heat. The tip was then sealed in such a way as to prevent entrance of moisture from the glass-blowing flame. The air stream was continued but had two exits, at the tip and through S2. The end of a small piece of glass tubing was melted and closed the tip T₁. The tip was then drawn off and a proper seal made in the usual way. When the sample was particularly absorbent it was not always possible to seal the tip in this way because of the charring of liquid which could not be removed by the air stream and yet continued to drop down into the tip. In this case a "dry ice" jacket was placed around the tube between the cell and the This effectively prevented the vapours or liquid from U. reaching the point of sealing. On completing the seal, the air stream was turned off and the liquid retained by

the cellulose was removed to the trap R₂ by evacuation

through S2. After between one and two hours evacuation

all the liquid had been removed, as was shown by the return

of the capacity reading for the condenser plus dry cellulose. It was then necessary to introduce dry air through S1 and S₂ to atmospheric pressure. The liquid which had been caught in the trap R_2 was melted, the tip T_3 broken and the liquid forced out into a beaker by dry air passed in through S1. The tip was then sealed in the same manner as used for T₁. The system was again evacuated until the 25°C capacity reading for the condenser plus dry cellulose remained constant at the original value obtained before the run was started. In all cases the same procedure was repeated at least once using the same liquid.

It was now possible to make an approximate calculation which would show whether the resultant dielectric constant of the liquid plus the cellulose was above or below that for the liquid alone. If it was above, the next liquid selected should have a still higher dielectric constant and if below, the next liquid should have a still lower dielectric constant. The above calculation was only approximate because at that stage the exact capacities of the empty condenser and of the lead and end correction under the conditions of the measurement were not known. However by using one of the sets of values for d_1 and d_3 obtained when the liquid mixtures were measured it was possible to calculate the

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dielectric constant with enough precision for the purpose.

The capacity of the condenser filled with the selected liquid and the cellulose sample was then measured at least twice in exactly the same way as described above.

It was then necessary to determine accurately the capacity of the empty condenser and the lead and end correction under the conditions of the above measurements. The positions of the condenser and the leads in the cell were measured and recorded. With the system at atmospheric pressure the ground glass stopper at the top of the dielectric cell was removed. It was usually necessary to surround this seal with hot water in order to loosen it. A long screw driver inserted at the top of the cell served to disconnect the leads from the binding posts and the condenser was removed from the cell by means of two long pieces of stiff wire which were attached to the binding posts in place of the leads. The positions of the glass rings and the cylinders were accurately marked and then the condenser was taken apart and the cellulose sample removed. The empty condenser was reassembled and replaced in the dielectric cell in as nearly as possible the same position as that which it occupied when measurements on the cellulose sample were made. The empty condenser capacity was then measured and the capacity of the condenser filled with

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benzene was measured as described under part (a) of this section for the calculation of the lead and end correction.

This calibration measurement is the largest single source of error in this work, for it involves the assumption that the condenser and leads are in exactly the same position before and after the removal of the cellulose sample. That this assumption is justified is shown by the reproducibility of the dielectric constants measured. However, unless great care is taken erroneous results will be obtained.

IV Calculation for the Dielectric Constant.

It has been shown previously that the dielectric constant of a material is the ratio of the capacity of a condenser filled with that material and the capacity of that condenser with only air or vacuum between its plates. This method can be used if the lead capacity can be measured. The value of the latter could not be directly measured in this work. This was due to the fact that the constant capacity at the ends of the condenser, where neither cellulose nor liquid penetrated due to the glass rings, could not be measured. However a value for d_3 , which is the lead capacity and the above end correction, can be arrived at indirectly.

It has been previously shown that the dielectric constant E is given in terms of scale deflections by the

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relation



where d_1 is the measured deflection for the empty condenser. d_2 is the measured deflection for the filled condenser. d_3 is the part of d_1 and d_2 due to the capacity of the leads and end correction.

This equation can be rewritten in the form

$$d_3 = \frac{d_1 E - d_2}{E - 1}$$

It is possible to calculate a value for d_3 if d_1 , d_2 and E are known. De Luca selected benzene as the liquid for performing this calibration, and, as has been previously indicated, benzene was used in this work. It was necessary to measure the deflection produced by the condenser filled with benzene and empty. The dielectric constant of benzene at 25° C and the frequency of these measurements was taken as 2.27. This is the value reported by Colley (66), Tangl (67), Turner (68), Graffunder (69), Isnardi (70), Hartsborn (71), Ball (72), and Linton and Maass (73).

In the case of the measurements made on the liquid mixtures, this lead and end correction was measured whenever a change was indicated by a change in the empty condenser deflection. The calibration for the cellulose samples was always carried out immediately on the completion of the liquid plus cellulose measurements for that sample.

After having determined the value of the lead and

end correction d₃ for the liquids alone, their dielectric constants were easily calculated by using the above equation.

The same was true for the dielectric constants of the compound dielectrics consisting of cellulose plus one of the liquid mixtures. The method of plotting these latter values in order to determine the percentage composition of the liquid mixture having the same dielectric constant as the cellulose sample has already been described. The dielectric constant of this liquid was then obtained by reference to Graph No. 1. That this was the dielectric constant of the cellulose sample was proven conclusively by De Luca (56), who made up the liquid mixture indicated by his graph and found the condenser had exactly the same capacity whether filled entirely with this liquid or partly with cellulose and partly with liquid. Abundant proof of this fact was also given by Starke (63).

D Preliminary Measurements

The early measurements in this work were made with the apparatus described by De Luca (56) and using his procedure. The liquids used were not purified since at that time this was not considered to be necessary. The chief objects of these measurements were to check De Luca's results for standard cellulose and to increase the precision of the determination. The exact values

67_m

obtained have little importance in the light of the

measurements which followed them, but they did provide

the clue which led to the more important results obtained

in this work.

The standard cotton cellulose was prepared according to the method detailed by Argue (55), except that the reflux periods with sodium hydroxide were extended to twenty-four hours each and the number of them to about twenty. The density of this standard cellulose was measured by Soley (74) and its heat of wetting by Skey (75). Both of these values checked with previous measurements on other standard cellulose samples.

De Luca used standard cellulose in its long fibrous form. In these preliminary measurements the standard cellulose was used in the form of paper, which could be packed into the condenser much more compactly thus increasing the effect on the capacity due to the cellulose. The sample was cut by hand until the average fibre length was approximately 1 mm. The fibres were suspended in two litres of distilled water contained in a clean Monel metal pail. This suspension was disintegrated for ten minutes in a standard laboratory disintegrator. Sheets of approximately 5 grams oven-dry weight were made on a British sheet machine using a low deckle. The sheets were pressed under a wet pressure of 100 lbs. per in.² for three minutes and then dried in a sulphuric acid desiccator while still attached to their polished steel plates. Strips cut

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from these sheets were wrapped around the inner cylinder

of the experimental condenser and the assembled condenser

placed in the vacuum system. Thus the measurements were made with the dielectric field approximately perpendicular to the fibre axes.

A value of about 5.2 was obtained for the dielectric constant of this sample. This value was about 15% lower than that obtained by De Luca for the longfibred form of standard cellulose. The only apparent difference between this and former work was in the fact that the sample in the present work was in sheet form. It was therefore probable that the low value was connected with this sample form. At that time two explanations were suggested:

(1) The liquids used in the measurements may have been prevented from completely filling the condenser by the paper formation.

(2) If the strength in paper were due to the formation of fibre-to-fibre secondary valence bonds, the fixing of these neighbouring hydroxyl groups would be expected to lower the dielectric constant due to the resultant decreases in atomic polarization P_A .

A third and much more probable reason was discovered and will be discussed later in the section on Linen Papers. An attempt was made to investigate the two

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reasons cited above by breaking down the paper structure.

This was partially accomplished in situ by successive

introductions and removals of water vapour. The cellulose sample was saturated with water vapour and then completely dried four times. At the end of this treatment the dielectric constant was again measured. A rise of almost 4% with respect to the old value was found, thus indicating that the hypotheses with respect to the low value for the dielectric constant of standard cellulose were worthy of further investigation.

The above results led to the discovery of a relationship between dielectric constant and strength in paper and later to the measurement of the anisotropy of cellulose as a dielectric. Discussion of them is more appropriately carried out in connection with these latter measurements.

Preliminary measurements with the rebuilt apparatus were made on standard cotton cellulose in its long-fibred form and using the liquid mixtures previously described. The fibres were brushed out and wrapped around the inner cylinder of the experimental condenser. Again the electric field was approximately perpendicular to the fibre axes, although this approximation was not nearly as close as in the case of standard cellulose paper.

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The dielectric constant of this sample, which

weighed about 8 grams, was measured twice. Between the

measurements the sample was removed from the condenser so that the lead and end correction could be measured. The results obtained are contained in the table below.

Empty Condenser	Lead Correction	Condenser + Dry Cellulose	Liquid Used	Liq uid + Cellulose	Dielectric Constant
41.10	17.30	47.86	#7	156.00	5 . 829
41.05	17.30	47.84	#9 #6 #7	167.11 146.80 155.87	6,295 5,454 5,822

In Graph number 2 the changes in the dielectric constants of these liquids caused by the cellulose sample are plotted against the liquid compositions. The lines thus obtained cross the composition axis at 64.3% and 63.6% ethylene dichloride. The dielectric constants of liquid mixtures of these compositions as obtained from Graph number 1 are 5.70 and 5.65 respectively.

These results have been given chiefly to illustrate the method of plotting used in this work. Later results showed that measurements of the dielectric constant of cellulose in this approximate fibre arrangement can have little significance due to the anisotropy of the cellulose. However, they are a measure of this fibre arrangement as will be shown later.

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DIELECTRIC CONSTANTS OF SULPHITE PAPERS (THE RELATIONSHIP BETWEEN DIELECTRIC CONSTANT AND STRENGTH IN PAPER.)

E <u>Dielectric Constants of Sulphite Papers</u>. (<u>The Relationship Between Dielectric Constant and</u> Strength in Paper.)

1. Purpose of Measurements.

These measurements were suggested by the preliminary results obtained with standard cotton cellulose sheets. The two possible reasons suggested for the low results obtained with these sheets were: (1) the paper formation contained volumes impenetrable to the liquids used in the measurements, and (2) the formation of fibre-to-fibre bonds in the paper.

The former of these reasons was shown to be very unlikely by reference to specific volume measurements in the literature. Richter obtained exactly the same specific volume for standard cellulose and for filter paper, using benzene as the measuring medium (76). Stamm and Hansen measured the specific volume of unbeaten and beaten white spruce sulphite pulp in benzene (77). They obtained a smaller specific volume for the beaten sample, but this sample had received 20 hours of beating treatment and was therefore far more changed than any in this work. Even then the change in volume they obtained, equivalent to

0.023 cc. per gram, would not be nearly enough to account

for the difference in dielectric constant obtained for

standard cellulose sheets.

The following measurements were carried out in an effort to prove or disprove the second reason reported above. If the drop in dielectric constant on formation of sheets was in fact due to the formation of numerous fibre-to-fibre bands, a further drop would be expected the stronger the sheet was made. Accordingly dielectric constant measurements on papers of various strengths were carried out.

2. Preparation and Properties of Samples.

The pulp used for these samples was a special bleached sulphite, rayon pulp provided by the Canadian International Paper Company, Hawkesbury, Ontario. The properties of this pulp in its unbeaten state were:

alpha cellulose	90.91%
viscosity (cuprammonium)	18.76 cps.
resins soluble in benzene-	
ethylene dichloride	
mixture	0.136%
water content	4.5%
freeness	630.~

The soluble resins were removed by refluxing with benzene-ethylene dichloride mixture for six hours and then with fresh liquid for six more hours.

Six paper samples were made from this pulp on a standard British sheet machine and using a high deckle. The beating was carried out in a small laboratory scale

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Valley Beater. Most of the sheets made weighed about

All were pressed for a period of 7 minutes. 2.4 grams.

The properties of these samples, numbered 0 to 5, are listed in the table below.

Sample No.	Beat- ing Time (Min)	Free- ness	let Pres- sure lbs/ in2.	Mullen Burst Factor	Bulk c c/gm	Air Porosity sec/ 100 cc.	Oil Flota- tion sec. 21.1°C	•
0	-	630	50	6.1	2,64	0.53	3.34	
1	23	339	25	20.8	1.80	8 .61	18.7	
2	23	339	200	25.2	1.34	62.3	90 . 5	
3	38	107	50	20,9	1.46	55 . 6	152	
4	6	540	50	12.1	1,90			
5	11	490	50	19.4	1.72			

These samples were dried on polished steel plates in a room maintained at a relative humidity of 65%and a temperature of 70° F. The Mullen burst tests were carried out in this room.

3. <u>Results</u>

:

In all cases the paper samples were wrapped around the inner cylinder of the experimental condenser, so that the electric field was perpendicular to the fibre axes. The data for these samples are contained in the table below.

No.	Wt. of Sample	Empty Con- denser cm.	Lead Corr. cm.	Con- denser + Dry Cel- lulose 	Liquid Used	Liquid + Cel- lulose cm.	Dielec. Constant	Dielec. Constant of Cellulose
0	15.6	41.01	17.30	50,76	#6	148.28	5,525	5,82
0	16.5	41.01	17.22	51.26	#9 #6	165,96 148,52	6,258 5,520	5.84
1	18.2	41.04	17.30	52 . 39	#9 #6 "0	166.50 147.93	6.274 5.503	5.685
2	25.2	41.04	17.30	56.04	#9 #6	165.96 148.17	6,193 5,513	5.65
2	24.0	41.01	17.06	54.51	#9 #6	162.69	6.127 5.496	5.63
3	22.8	41.01	17.30	54.45	#9 #6	163,91	6.133 5.520	5.69
4	17.9	40. 65	16.87	52,46	#9 #6	163.24 148.07	6.156 5.518	5,73
4	17.7	41.22	17.39	52.19	#9 #6	164.66 148.64	6,212 5,508	5,74
5	19.4	41.25	17.35	52, 29	#9 #6	165.92 148.65	6,233 5,494	5,68
					#9	T02*00	6.205	

The above data are plotted in the usual way on Graph number 3, and the dielectric constants were obtained by reference to Graph number 1.

4. Discussion of Results.

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In the table below, the dielectric constants of the sulphite samples are listed beside their corresponding Mullen Burst Factors. These results are plotted in Graph number 4.

Sample No. Mullen Burst Factor Dielectric Constant

6 . 1	5 ,83
12.1	5,74
19.4	5,68
20.8	5,69
20.9	5,69
25.2	5,64





Examination of Graph number 4 shows an almost straight-line relationship between dielectric constant and strength in paper. The differences are comparatively small, amounting to about 3.4% between the extreme cases of unbeaten (#0) and highly pressed (#2). At the time these measurements were made it was not entirely certain that such small differences were outside the limits of possible experimental error. On completion of the measurements for samples numbers 0, 1, 2 and 3, samples numbers 4 and 5 were made to a pre-determined strength and their dielectric constants were measured. The fact that the values obtained fell on the previous dielectric constant versus strength curve provided a very good check of the method. In order to make doubly certain, the dielectric constants of samples numbers 0, 2 and 4 were remeasured. The results of these latter measurements showed a maximum deviation from the mean of \pm 0.01 dielectric units. This was the first time that the accuracy obtainable by the method had been measured.

These results tended to confirm the hypothesis proposed as an explanation of the preliminary results. Since the measured dielectric constant actually does fall as the strength goes up, it is logical to expect that the

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reason must be found in some change in the polarizability

of the cellulose molecules. That such a change is not due to beater treatment but is independent of how the strength is produced is shown by comparison of the results for samples numbers 1 and 2. Both of these samples were removed from the beater at the same time. The only difference in their treatment was in the wet pressure applied to the sheets. As would be expected, this treatment led to a considerable difference in their Mullen Burst Factors, but it also gave a corresponding change in dielectric constant which was independent of beater treatment.

It is interesting to note in this connection the Heats of Wetting obtained by Skey in measurements on these samples (86). These are contained in the table below.

Sample No.	Free- Ness	Wet Pressure <u>lbs/in²</u>	Mullen Burst	Heat of Wetting <u>cals/gm</u> .	
Ø	640	50	6.1	13.52	
1	339	25	20.8	14.04	
2	339	200	25.2	13.94	
3	107	50	20 . 9	14.33	

These results show no relation to strength but rather are dependent on the freeness of the pulp used. The heat of wetting is a measure of the surface available for wetting and apparently bonding has no measurable effect.

The effect of beating in increasing the strength

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of paper is generally recognized to be an increase in the

cellulose surface due to cutting and fibrillation. The

effect of pressure is to bring the surfaces thus formed into close proximity. The greater the pressure, the greater will be the amounts of cellulose surface brought into con-Thus since the effects of beating and of pressure on tact. strength in paper are the same it has been concluded that the close approach of cellulose surfaces while wet is the important factor in the development of strength in paper. The nature of the adhesive forces which come into play under such conditions is still a controversial matter. Some investigators believe a cementing material is formed or liberated by the beater treatment (37, 38, 39, 84). Strachan has stated that strength in paper is mainly due to entanglement of the fibrils (83) Campbell (27) and many others believe the adhesion is due to secondary valence forces arising from the polarity of the hydroxyl groups attached to the cellulose chains.

The results obtained in this work, if interpreted as arising directly from the development of strength, support the explanation based on secondary valence forces. The larger the number of such bonds the smaller will be the dielectric constant, since the bonds restrict the movements of the hydroxyl groups in the electric field thus lowering the value of the atomic polarization P_{A} .

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However, another explanation based on the anisotropy of cellulose as a dielectric was suggested by the known anisotropy of cellulose to light. The close relationship between the transmission of light waves and of electric waves in a dielectric has been discussed in the Introduction. In view of this relationship, cellulose fibrils would be expected to have two dielectric constants, one larger value parallel to and one smaller value perpendicular to the fibril axis. The value of the dielectric constant obtained in any one measurement would then be dependent on the orientation of the fibril in the fibre and the orientation of the fibre in the electric field. If, then, increased strength in paper is accompanied by increased flatness of the fibres in the paper, it should also be accompanied by a decrease in the dielectric constant. This explanation is discussed in more detail in the following two sections.

F The Anisotropy of Cellulose as a Dielectric.

1. Purpose of Measurements.

The object of the measurements described in this section was to establish the anisotropy of cellulose as a dielectric and to obtain the true values for the dielectric constants of cellulose crystallites. Such values have never

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been measured previously nor have any investigators

suggested in their papers that cellulose should have more

than one dielectric constant.

The double refraction of cellulose for light waves has been discussed in the Introduction. Such measurements have been very useful in following structural changes in the fibres. The double refraction of cellulose for electric waves should be similar. The anisotropy is associated with the crystalline structure in the fibre. Since the crystallites are oriented with their long axes parallel to the fibril axis the true value of the axial dielectric constant will be associated with the fibril axis as in the case of the axial refractive Similarly the transverse dielectric constant index. will be associated with the direction perpendicular to the fibril axis as in the case of the transverse refractive index.

2. Method employed for Two Dielectric Constants.

It was necessary to choose a fibre for these measurements which had a fibril arrangement parallel to the fibre axis. In such fibres the crystallites are all arranged nearly parallel to the fibre axis and the actual transverse and axial dielectric constants could then be measured perpendicular to and parallel to the fibre axis. Two types of cellulose fibres have these specifications,

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linen and ramie. Linen was used in this work.
 It was then necessary to devise a method for
orienting these fibres in the two directions in the
electric field. If the sample was in the form of paper

and wrapped around the inner cylinder of the experimental condenser, then the arrangement of the fibres was approximately parallel to the condenser plates and the dielectric constant measured was the transverse dielectric constant. There are two assumptions in the above statement; (1) All the fibres must be perfectly flat in the sheet and the sheets perfectly flat around the condenser cylinder. (2) It ignores the result obtained in the previous section and assumes the lowering of dielectric constant due to increase in strength is not due to bonding between the fibres.

In order to make the first assumption as true as possible the sheets used in these measurements were made with an average thickness of 0.0032 inches. The sheets were of high density and strength. This eliminated practically all chance of a non-parallel arrangement of fibres between the condenser plates.

It was not actually justifiable to make the second assumption. However, later work showed that fibre-to-fibre bonds actually contribute very little to the dielectric constant change observed with sulphite papers. There is some lowering due to this cause, but its amount must be very close to the experimental error in the measurements. Since it was not possible to obtain fibre orientation as

81.

well as high density other than by using paper, it was

necessary to use that method and the results may accordingly

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be slightly low.

In order to measure the value of the dielectric constant parallel to the fibre axis it was necessary to pack the experimental condenser with rings of linen paper to fill the annular space between the condenser cylinders. This method was arrived at as a result of the following

considerations.

Schmidt in 1903 measured the dielectric constants of crystalline substances in powder form (86). He showed that the values he obtained were actually the means of the dielectric constants in the three major directions in the crystal. The value he obtained, E_m , for a powdered, uniaxial, crystal line substance was,

$$3E_m = E_p + 2E_n$$

- where E_{m} was the measured dielectric constant of the powder. E_{p} was the dielectric constant parallel to the optic axis.
 - E_n was the dielectric constant normal to the optic axis.

This was easily understood on the basis of the random crystal orientation present in the powder between the condenser plates. Since the orientation was random, there was an equal chance for each of the three crystal dimensions to be perpendicular to the condenser plates.

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The mean value E_m was therefore made up of equivalent
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contributions from each of the three directions, two of which have the same value in uniaxial crystals. Similarly, for orthorhombic crystal powders, he obtained

$$3 E_m = E_a + E_b + E_c$$

where E_a, E_b, E_c were the dielectric constants measured with the electric field parallel to the bracky (a), macro (b) and crystallographic (c) axes respectively. For monoclinic crystals the equation was

$$3 E_m = E_1 + E_b + E_2$$

where E_1 and E_2 were the values of the dielectric constant along the principal axes of the electric indacatrix and perpendicular to the ortho axis (b).

E was the dielectric constant in the direction of the ortho axis.

As has been previously stated: X-ray studies have shown that cellulose has a monoclinic crystalline structure. However, since orientation occurs only in the structural chain direction, only two refractive indices and therefore also only two dielectric constants may be distinguished. That is to say, in the above equation for monoclinic crystals, E_1 and E_2 would have the same value. The equation thus becomes similar to that for uniaxial



 $3 E_m = E_b + 2E_n$

where E_n is the dielectric constant in a direction perpendicular to the ortho (b) axis.

It would be difficult to obtain cellulose in powder form. However, it is possible to obtain a random arrangement of fibres in one plane. Test sheets made on a British sheet machine have a random fibre arrangement in the plane of the sheet. If, then, the dielectric constant is measured with the electric field parallel to the plane of such a sheet, a mean value will be obtained. Since the orientation is in one plane, there will no longer be an equal chance for each of the three crystal directions to be perpendicular to the condenser plates. The two directions normal to the long axis, which are actually equivalent, will each have half the chance they had in the three-dimensional case. The equation for the measured mean dielectric constant Ξ_m in this special case of a random arrangement of cellulose crystallites in a plane perpendicular to the condenser plates then becomes

$$2 E_{m} = E_{b} + E_{n}$$

The method for the measurement of E_n or the transverse dielectric constant has already been described. It is therefore a simple matter to calculate the value of the

84.

axial dielectric constant E_{h} , after measuring E_{n} and the

mean value Em

The paper rings used in the measurement of E_m were cut with a special tool having two circular cutting edges of the proper dimensions to give rings that would fit loosely yet lie flat in the annular space between the condenser cylinders. After a considerable amount of trial the best method for using this cutter was found to be as a press. It was placed as a bit in a large drill and pressed into the paper sample by mechanically applied pressure. It was possible to cut from four to six rings at a time by this method.

3. Preparation and Properties of Sample.

The linen stock for this sample was supplied through the courtesy of Howard Smith Paper Mills, Limited. As received, this stock was described as short, extra strong, linen fibre. It had been put through the machine, boiled and washed in the washers, put down in the drainers and was just ready for the beating operation.

The pulp was beaten for five minutes in the laboratory type Valley Beater under conditions to give a maximum of cutting effect and a minimum of beating. That is, the consistency was low (0.82%) and the weight on the beater roll was high. The sheets were made on a

85.

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British sheet machine using a high deckle. They were
pressed while still wet at 50 lbs/in^2. for seven minutes
and dried at a constant humidity of 65% and temperature
of 70°F. The following properties were measured.
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average weight per sheet	= 1.13 grams (oven-dry)
average thickness of one sheet	= 0.0034 inches
Bulk	= 1.55 cc/gm.
Mullen Burst Factor	=50,7

4. <u>Results</u>

All three samples were cut from the linen sheets described above. Number δ was the wrap-around sample for measuring the value of the transverse dielectric constant E_n . Samples numbers 7 and 7A were rings packed into the annular space in the condenser for measuring the mean dielectric constant $E_{m^{\bullet}}$ The data for these samples are contained in the table immediately below.

No.	Wt. of Sample gm.	Empty Con- denser cm.	Lead Corr. cm.	Con- denser + Dry Cel- lulose	Liquid Used	Liquid + Cel- lulose cm.	Dielec. Constant	Dielec. Constant of Cellulose
	ومشيق مرمواني			<u> </u>				
6	21	41.12 ⁰	17.32	52.31	#5 #6	139 .3 6 145.26	5.128 5.375	5,27
7	7	40 •96	16.79	51.10	#9 #10	170,59 174,13	6,363 6,510	6,22
7 <u>A</u>	4	40 • 59	16.36	49.16	"#9 #10	171.19 175.35	6 . 390 6.563	6,24

The results in the above data are plotted in Graph number 5 and the dielectric constants of the samples are obtained by reference to Graph number 1. The results



2.434 2. . .



En	-	5.27
Em	=	6.23
E _b	=	2E _m - E _n
	=	12.46 - 5.27
	=	7.19

87.

Therefore, accepting the assumptions already mentioned, the transverse dielectric constant of the cellulose crystallite, E_n , is 5.27. The axial dielectric constant of the cellulose crystallite, E_h , is 7.19.

(5) Discussion of Results

The measurements described above definitely establish the anisotropy of cellulose as a dielectric. It is interesting to examine previous results in the light of these values. The dielectric constant obtained in any one measurement should lie between the limits of 5.27 and 7.19 for the cellulose crystallites. Its exact value will be dependent on the orientation of the cellulose crystallites in the electric field of the measuring condenser. Thus, for linen or ramie, it should be possible to obtain any value between these limits solely by varying the fibre orientation. For cotton the case is different due to the spiralling of the fibrils about the fibre axis. The same is true for all other fibres in which the crystallite orientation is not

the same as the fibre orientation. In all of them the

limits will be narrower, how much being dependent on the
amount the orientation of the fibrils differs from parallel to the fibre axis. The limits of 5.27 and 7.19 are only applicable for measurements at 25°C and made at frequencies in the neighbourhood of 300,000 cycles.

Campbell's value of 6.7 was for the dielectric constant of regenerated viscose cellulose and was measured at 800 cycles and 20°C. His samples were dried for several days in an oven at 80-110°C. Stoops measured the dielectric constant of glycerol-free cellophane sheets and followed the change in the value with temperature and frequency (59). His results checked those of Campbell. At 25°C and a frequency of 300,000 cycles his value was 7.1. This dielectric constant is not an absolute value since Stoops did not apply any correction for the air content of the sheets. The true dielectric constant of the cellulose in cellophane as measured by Stoops should then be somewhat higher. It is difficult to explain this high value, especially since the measurement was made with the electric field transverse to the sheets. Cellophane is pure regenerated cellulose and in the extrusion process the molecules take up an orientation which is in the plane of the sheet and more or less parallel to the direction of the The dielectric constant measured was then extrusion.

transverse to the molecules. The fact that the value obtained

was 7.1 and not 5.27 and that Campbell with similar material obained similar results would therefore indicate that the polar groups in cellophane have more freedom than in natural cellulose fibres. Examination of Stoops' experimental method shows that he dried his samples at 105° C until no change in electric properties resulted. There is no mention of the use of vacuum and therefore his samples were not "dry" as defined in this work. However, it is doubtful if this could account for the large difference reported above.

De Luca, Campbell and Maass obtained a value of 6.1 for the dielectric constant of standard cotton cellulose at 25° C and a frequency of 10^{6} cycles (43). At the frequency used in the present work this value would be slightly higher. In their work the arrangement of the sample was very nearly completely random, since they used a long-fibred form of cotton which was stuffed as compactly as possible between the condenser plates. The value obtained indicates this random arrangement since it is very $\frac{1}{2}$

In preliminary measurements in this work standard cotton cellulose in its long-fibred form was measured at 25°C and 300,000 cycles. The dielectric constant obtained was 5.65 to 5.70. In this case the fibres were brushed out

89.

and wrapped around the inner cylinder of the condenser. The arrangement approximated perpendicular to the electric field and the value obtained indicates this fact. The transverse dielectric constant for cotton cellulose, due to the spiral arrangement of the fibrils, would be expected to be higher than that for linen and probably is not much below the value measured above for standard cotton cellulose.

The dielectric constant obtained for standard cotton cellulose in paper form also showed the large effect due to fibre orientation. This value was almost 15% lower than De Luca's value for the long-fibred form of standard cotton and this difference was undoubtedly due almost entirely to the difference in fibre orientation in the two measurements. By breaking down the sheet structure with water vapour it was possible to raise the dielectric constant of the standard cotton sheets about 4%. This may have been due directly to the release of hydroxyl groups in the break-up of fibre-to-fibre bonds. It may also be due to a change in the orientation of the fibres so that on the average they were less nearly parallel to the condenser plates.

Exactly the same considerations enter as explanations for the dependence of dielectric constant on strength

90.

in paper. If the change in dielectric constant was due

entirely to orientation changes, it is possible to make an

approximate calculation of the average orientation change necessary to account for the dielectric constant change. Thus, in the sulphite papers, the orientation change is calculated as follows. Since the lowest transverse dielectric constant measured for these wood fibres was 5.64 this value may be taken as the true transverse dielectric constant. This is 0.37 higher than the transverse value measured for the cellulose crystallite. If it is assumed that an equal change applies to the axial dielectric constant, which is legitimate if the change is due only to the spiral orientation of the fibrils in wood fibres, the axial value for these fibres must be 7.19 - 0.37 = 6.82. The maximum change in dielectric constant with strength noted in the measurements on sulphite papers was 5.83 - 5.64 = 0.19. The maximum change possible if all the fibres had changed from parallel to the condenser plates to perpendicular would be 6.82 - 5.64 = 1.18 dielectric constant units. This change is equivalent to a 90° orientation change. Therefore the change with strength of 0.19 units is equivalent to an orientation change of

$$\frac{0.19}{1.18} \times 90 = 14.5^{\circ}.$$

91.

This calculation makes the further assumption that the

measured dielectric constant is directly dependent on the

angle between the fibre and the electric field whereas it is actually dependent on the angle between the wave normal in the fibre and the electric field. However, the result of 14.5° is of the correct order.

This result does not necessarily signify an actual difference of that amount in the orientation of the Besides the possible effect of fibrefibres themselves. to-fibre bonds the angle calculated might be explained equally as well by the fibrillation present in a beaten pulp. If the spiral arrangement of the fibrils in the wood fibres is partially removed by the fibrillation the dielectric constant will be lowered. However, this is certainly a minor effect since a lowering of the correct magnitude was measured for sample number 2 as compared with sample number 1. These samples were identical except in the wet pressure used in forming the sheets. The entire difference in strength and in dielectric constant was due only to the difference in wet pressure since no change in fibrillation had taken plaċe,

It would seem to be impossible to separate the effects of fibre-to-fibre bonds and fibre orientation on the basis of the present work. Fibre orientation must account for at least part of the change in dielectric

92.

constant with strength since it is difficult to explain

the change in bulk or in caliper of paper with strength

except as due to a change in flatness of the fibres in the sheet. In a later section of this work an attempt to determine how much of the change is due to orientation will be described.

The examination of previous results discussed above serves to show the importance of fibre and fibril orientation in all dielectric constant measurements on cellulose. The values given in the literature mean little unless they are associated with a specific orientation as well as a definite temperature and frequency.

The measurement of the axial and transverse values for the dielectric constant of cellulose fibrils permits calculation of the relative freedom of groups in the cellulose molecule. In the general introduction the molecular theory of dielectrics as developed by Debye (2) was discussed This theory shows the proportionality between the briefly. dielectric constant and the molar polarization P.

This molar polarization is made up of three factors such that

$$P = P_E + P_A + P_M$$

where P_E is the electronic polarization and expresses the distortion in the electron orbits.

is the atomic polarization arising from displacement

of atoms and groups.

$\boldsymbol{P}_{\boldsymbol{M}}$ is the molecular polarization and is due to

orientation of the entire molecule.

The molecular polarization does not enter into considerations on cellulose in the solid state since the cellulose chain is obviously too long to rotate in an electric field. The electronic polarization is proportional to the square of the refractive index which is equal to the dielectric constant measured at the frequency of the light wave. At radio and audio frequencies there is sufficient time in each alternation for some displacement of polar groups on the molecule, the amount of the displacement being the greater the smaller the frequency. The dielectric constant at the frequency of this work is therefore a measure of the electronic polarization plus the atomic polarization.

The refractive indices of linen fibres have been reported by Frey (32) and by Preston (33). The mean value for the transverse refractive index is 1.530 and for the axial refractive index 1.595. The transverse electronic polarization may therefore be represented by $(1.530)^2 = 2.34$. The axial electronic polarization may be represented by $(1.595)^2 = 2.55$. The total molar polarization at 300,000 cycles may be represented by the transverse dielectric constant of 5.27 and by the axial dielectric constant of

94.

It is therefore possible to obtain values to represent 7.19.

the atomic polarization in the two directions by subtraction. Thus the two values for the atomic polarization at the above frequency and in dielectric constant units are:

transverse	5.27 -	- 2.34	=	2,93
ax ial	7.19 -	- 2.55	Ħ	4.64.

These figures indicate a much larger displacement effect along the structural chain direction than perpendicular to this direction.

Stoops found considerable absorption and dispersion at higher frequencies (above 10,000 cycles) for the dielectric constant of cellophane (59). The measurements were made with the electric field perpendicular to the cellulose chains. He did not believe it reasonable to assume that this dispersion and adsorption were due to inability of the hydroxyl groups to respond to the applied field since their resonant frequency in the molecule should be in the Raman spectral region. As additional evidence for this he reported a similar but less marked dispersion in cellulose triacetate. It was therefore concluded that the dispersion and absorption in the temperature and frequency range used was probably due to rotation of the glucose anhydride rings of the cellulose chain.

Measurements in the present work were made at a

constant frequency and temperature and therefore indicate nothing as to the amounts of dispersion and absorption.

However, as shown above, they do indicate a relatively much greater displacement along the structural chain than perpendicular to it. Now rotation of the glucose anhydride rings is practically impossible in the chain direction. Therefore this factor cannot enter into the axial atomic polarization. The fact that this polarization is so much greater in the axial than in the transverse direction would suggest that rotation of the glucose anhydride ring is only a minor effect in Stoops' transverse measurements. This point could be decided by measurement of absorption and dispersion in the axial direction.

It is suggested that the absorption and dispersion of cellulose in the transverse direction indicate instead that the hydroxyl groups are restrained. This would be true if these groups entered into secondary valence bonds, and the restraint would be even greater if the hydroxyls were coordinated to neighbouring chains through hydrogen bonds. The displacement of the polar hydroxyl groups in the direction of the cellulose chain would then require a change in valence angle of the primary hydroxyl bond and also a lengthening of the secondary or hydrogen bond. A displacement perpendicular to the chain direction requires the above type of change and also another type in which the

96.

primary bond as well as the secondary must be either

lengthened or shortened. The fact that the displacement has been shown to be smaller in this transverse direction by the present work therefore indicates that a smaller force is needed to bend a primary valence bond than to lengthen or contract it by a corresponding amount.

This discussion of the anisotropy of cellulose as a dielectric has served to point out a few of the many cellulose problems to which dielectric constant measurements may now be applied. It is possible to follow fibre orientation in a sheet and fibril orientation in a fibre. It is also possible to interpret dielectric constant measurements in terms of different structural changes.

G. Orientation Studies.

1. Purpose.

An attempt was made in the following section to determine the change in fibre orientation in the crosssection of a sheet as the strength was varied. The necessity for such a determination was pointed out in the last section. In explaining the variation of dielectric constant with strength in paper it was found to be impossible to separate the effects of fibre orientation and fibre-to-fibre bonds.

97.

Since it is possible to see fibre orientation with the aid of a microscope, this study of fibre orientation was made

with the object of separating the effects of the above two causes.

2. Preparation and Properties of Samples.

Three samples were made from the same sulphite pulp used in samples numbers 0 to 5. These were number 8, unbeaten; number 9, medium strength; number 10, high strength. In order to eliminate difficulties due to the large number of fibres that would ordinarily have to be examined, 5% of the fibres in each sample were dyed with Congo Red. In the finished sheets these dyed fibres were prominent in the field of the microscope. The procedure for dyeing these fibres was the same for each sample and follows.

After the beater treatment approximately 5% of the stock was removed and the pulp was separated from the water by filtration through a fine cotton cloth. A 0.07% solution of Congo Red in distilled water was then added to the pulp contained in a beaker. The fibre suspension was well mixed and allowed to stand for one hour. At the end of this time the suspension was diluted and filtered through the same cloth. The pulp was washed three times with water to remove excess dye and the fibre mat was then disintegrated

98.

in water and well mixed with the undyed stock. The sheets were made in the usual way on the British sheet machine. The

data for these samples are contained in the table below.

Sample No.	Sheets made	Beating time min.	Wet Pressure lbs/in.	Bulk cc/gm	Mullen Burst
8	10	-	50	2.16	7.7
9	10	10	50	1.73	17.8
10	10	22	200	1.47	21.4

3. <u>Results</u> and Discussion.

Several methods of examination were tried, none of which gave convincing results. In the first attempt crosssections were made of each of the samples and these were examined under the microscope by reflected light. No red fibres were observed to vary very much from a planar orientation parallel to the sheet surface. However, this could not be taken as an indication because only one or two red fibres per section could be observed. In another trial the sheets were examined by transmitted light and individual fibre orientation followed by the focus of the microscope. Difficulty was encountered due to diffracted light from the red fibres, which caused all the fibres to appear reddish. This was partially overcome by using blue light for illumination thus causing the red fibres to stand out as black. A further improvement was effected by wetting the paper to be examined with ethylene bromide. This liquid has a refractive index at 20°C and using daylight of 1.541

which was very close to the value for the transverse refractive index of the sulphite fibres. As a result the

undyed fibres became practically invisible and the orientation of the red fibres could be followed. This method gave the best results.

A magnification of 440 diameters was used. With this magnification any fibre leaving the focal plane by more than ± 0.005 mm. was clearly out of focus. A wernier scale on the microscope allowed the measurement of any variations from the focal plane. The thickness of the sheets of all three samples was approximately 0.2 mm. and the average fibre length even in sample number 10 was greater than 1 mm. Thus if any deviation from planar orientation large enough to account for the dielectric constant changes was present it should have been easily detected.

Actually, although hundreds of fibres were followed in this way, no marked deviation from the focal plane was noted even in the unbeaten sheets. In an occasional case the fibre left the focal plane slightly but never by more than 0.03 mm. Such fibres were so rare that their effect would not be detected in dielectric constant measurements. This result was not taken to indicate that fibre orientation played no part in the change of dielectric constant with strength since it could not decide

100.

The fibres undoubtedly lie in an undulatory plane the point.

in the paper. In this work such undulations could be seen but they were never large enough to put the fibre out of focus, nor were they large enough to detect any differences in the three samples. However, if these undulations are frequent enough, they can be just as effective as tipping of the fibre as a whole in changing the dielectric constant.

The problem of the change of fibre orientation with strength of paper cannot be settled on the basis of the present results. It is probable that both fibre-tofibre bonds and fibre orientation enter into the relationship between dielectric constant and strength in paper. It is not possible at present to distinguish between the two effects.

101.

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THE DIELECTRIC CONSTANT OF WATER ADSORBED ON CELLULOSE.

102.

THE DIELECTRIC CONSTANT OF WATER ADSORBED IN CELLULOSE

A. Introduction

The importance of the relationship between cellulose and water has already been indicated. The nature of the adsorbed layer of water has been the subject of a large number of investigations. It was to increase our knowledge of the condition of this layer that Argue and Maass (60) and later De Luca (56) attempted to measure the dielectric constant of water adsorbed on cellulose. The work to be described here was a continuation of their measurements.

That the first water added to dry cellulose is very strongly held on the cellulose is shown by the difficulty encountered in removing this water. This is easily understood when one considers the highly polar nature of both water and cellulose. The condition of this water layer is the subject of many theories and cannot yet be said to be known.

Katz (78) has shown by X-ray diffraction measurements that water does not enter the crystalline structure of cellulose. However, it can enter the considerable amorphous part of the cellulose structure and Katz (65) has

suggested that the adsorption-compression effects noted by

many investigators (87, 88, 89, 90) are due to a kind of solution of the parts of the cellulose chains lying between crystallites. Similar effects are noted in the solution of other desiccating agents such as sulphuric and phosphoric acids and in those cases are thought to be due to association in the liquid.

There has been some discussion as to whether some of this water is actually chemically combined. Thus Tankard has stated that, although results do not indicate that cellulose and its compounds form a limited number of definite hydrates, for each substance there is a definite amount which may be regarded as entering into chemical combination (91). This amount he states as 0.5 molecules of water per glucose anhydride unit in bleached cotton and linen. Such a result might be thought to ignore the smooth sigmoid shape of the absorption curves for water on cellulose as obtained by many investigators (92, 93, 94), but Tankard supports an explanation given by Pierce (95) in which the curve is an - average curve made up of one for chemically combined water and one for adsorbed water.

Most properties of cellulose when measured as a function of water content show a fairly marked change in the region of 2.5 to 3.0% water. Thus the adsorption curve

103.

shows a bend in that region (90). The heat of wetting and

density of adsorbed water curves also show such a bend (86, 96). Such facts indicate that this first water is bound differently from succeeding increments. It may have a structure similar to that in ice and this has been suggested. Kolkmeijer and Favejee have even suggested that in powder X-ray diagrams of cellulose containing adsorbed water the greater part of the lines originates from the structure of the adsorbed water (97).

The chief feature in water sorption by cellulose is again the free hydroxyl groups on the cellulose chain. Meyer and Mark, assuming micellar dimensions of forty to sixty chains, have calculated that about half the available hydroxyls would be on the surface, the others ensuring cohesion in the crystallite (98). They state that only part of these hydroxyls could be free to adsorb water molecules since peptization would take place if all were The importance of these hydroxyls was shown by free. Sheppard in experiments on adsorption of water by different acetylated celluloses (99). He found that the integral heat of adsorption of water vapour approaches the heat of condensation as acetyl groups are added. This indicated that with elimination of the hydroxyl groups more and more of the water was just capillary absorbed.

104.

Evidence against actual chemical combination of

water with cellulose was presented by Shipley who measured

the specific heat of water (100). The high specific heat of the sorbed water was explained by assuming that some of the heat supplied went to decrease the amount of bound water. This would then be a true adsorption equilibrium.

It is clear from the foregoing that part of the water sorbed by cellulose is bound closely and has distinctly different properties than ordinary water. For this reason it was thought that dielectric constant measurements might give some new evidence on the condition of this bound water. The large difference between the dielectric constants of water and ice would be expected to give such measurements an advantage in determining the freedom of the bound water.

Several investigators have previously resorted to dielectric constant measurements in sorption studies on different materials. So far as is known, with two exceptions, none have reported results in terms of the actual dielectric constant of the sorbed water but rather as the dielectric constant of the compound dielectric consisting in most cases of air, water vapour, solid material and sorbed water. Interpretation of such values in terms of the sorbed water alone requires the assumption that the other factors have remained constant, which ordinarily is justifiable. In any case, such a method has little utility when applied to cellulose because such a small proportion of cellulose, and therefore of sorbed water, can be put into a condenser.

105.

For this reason attempts have been made to calculate the dielectric constant of the adsorbed water by using equations relating distribution to resultant dielectric constant. These equations are extensions of equations 1, 2 and 3 contained in the section on a method for fibrous materials and were proposed by Argue and Maass (60). They make the assumption that the sorbed water has exactly the same orientation as the solid material. This assumption is probably justifiable for small proportions of water However, as will be shown later, the use of the equations is not supported by experimental evidence. No method is known at the present time by which the dielectric constant of water sorbed on fibrous materials can be calculated from measurements on the compound dielectric.

Tausz and Rumm distinguish between the dielectric constant of the sorbed water and the dielectric constant of the compound dielectric of vapour, solid and sorbed water by calling the latter the "dielectric value" (62). This terminology will be continued in the present discussion. These authors made measurements on sugar, various starches, borax, fine-cut tobacco, and other substances. They reported most of their results in terms of dielectric values and found that under similar experimental conditions good

106.

comparable values were obtained. From their results they

concluded that the sorbed water existed in two states on the solid material, part in a state similar to ice and having a low dielectric constant. The first they designated as "solid" water. It had little effect on the dielectric value and was practically independent of frequency and temperature changes. The second was called "movable" water. With samples containing movable water the dielectric value was strongly dependent on temperature and frequency. The ratio of the amounts of the two, which could be estimated from the variation of the dielectric value with temperature and frequency was found to be a function of the structure of the solid material. Thus it was found for the different starches that at constant relative humidity that one which had the smaller dielectric value and therefore the largest content of solid water also had the largest total water content.

Alexander and Shaw obtained rather similar results in dielectric constant measurements on soils, potatoes and peas (101). They were using the dielectric constant to follow "freezing" of adsorbed water and obtained breaks in the dielectric constant-temperature curves which were not indicated by a thermometric method. Zhilenkov measured the dielectric constant of quartz powder containing

107.

various amounts of water and showed that the water had a dielectric constant less than that for normal water (102).

108.

Argue and Maass (60) and De Luca (56) obtained similar results in their measurements of the dielectric value of standard cotton cellulose containing various amounts of sorbed water. Their curves of dielectric value versus water content show an increasing slope with increasing water content and this may be interpreted as indicating an increasing dielectric constant for the water. These investigators also attempted to calculate the dielectric constant of the sorbed water using one of the previously mentioned equations. Their calculations and results are discussed later in connection with the results obtained in the present work.

B. Apparatus and Experimental Procedure.

The electrical measuring apparatus was not changed for this work and only two changes were necessary in the glass apparatus. The trap R_{\downarrow} (diagram 2) was removed and in its place was sealed a glass tube graduated in divisions of 0.05 ml. This was connected to the system through a stopcock having a large bore (4 mm.) in order to facilitate evaporation from the tube. The U - tube was disconnected on the dielectric cell side and the tube from the dielectric cell sealed at this point. None of the

vacuum system to the right of this point was used in these

measurements.

The cellulose sample used was made from some of the previously described linen stock. It was in sheet form and had the following properties: bulk = 1.64 cc/gm. and Mullen burst factor = 51.8. Immediately before packing the condenser the moisture content of the sample was determined as 4.627%. This gave for the dry weight of the cellulose in the condenser 17.824 gm. The sample was inserted in the condenser in wrap-around form. This orientation was preferred because the effect of the cellulose itself was then at a minimum and the effect of the water would be in greater proportion.

The experimental condenser was put in place in the dielectric cell and the graduated tube was filled with distilled water. This water was degassed in the usual way. It was frozen by slowly raising a dry-ice acetone mixture around it. Then the air, in the system was removed to a pressure of 10^{-3} mm. of mercury. With the stopcock closed the ice was allowed to melt thus permitting the escape of the air which had been frozen This procedure was repeated three times at the end out. of which the water was noted to freeze without the inclusion of air bubbles. The cellulose sample was then carefully dried using the previously described five-hour

109.

heat treatment to constant capacity. The degassed water was of course kept intact by the closed stopcock during

this drying. On conclusion of the drying the system was brought to a pressure of 10^{-3} mm. of mercury and the manometer M, raised. It was very important that the dielectric cell-water system be very air-tight since this pressure of 10^{-3} mm. of mercury had to be maintained for a period of over two weeks. For this reason all seals had been carefully checked beforehand.

Water vapour was introduced into the system by merely opening the graduated tube to the evacuated system. At low humidities evaporation from the water surface was sufficiently rapid but at high humidities the evaporation was speeded by placing warm water around the graduated tube. The water was introduced in stages of about 0.5%, that is 0.005 ml. of water per gram of dry cellulose, up to about 10% water content. The readings on the graduated tube were estimated to the nearest 0.005 ml. After each water increment had been added the graduated tube was closed off and time allowed for the cellulose sample to come to equilibrium with the water The attainment of this equilibrium was followed vapour. by capacity measurement. Identical readings made one hour apart were taken as indicating the final value. The time necessary varied with the water content and

ranged from less than half an hour below 1% water to

twelve hours at 10%.

The bath was not thermostated for this work and temperature was controlled in the usual way by hand. During the attainment of equilibrium the room temperature was kept at $25 \pm 2^{\circ}$ C. Thus the position of the equilibrium was, within experimental error, not changed when the bath was adjusted to $25 \pm 0.1^{\circ}$ for the capacity measurements.

C. <u>Results</u>

The results obtained in this phase of the work are contained in the table below. In this table the weight of sorbed water was taken directly as the weight of water which had evaporated into the system from the graduated The weight of water vapour which was not sorbed tube. could be neglected because even at the highest vapour pressure used the correction amounted to only a small The percentage of sorbed water was number of milligrams. calculated on the basis of the dry weight of the cellulose sample, 17.824 grams. The significance of the term dielectric value has already been defined. For its calculation it was necessary to use values for the empty condenser capacity and the lead and end correction. These were measured at the end of the water run by means The empty condenser capacity of a benzene calibration. d was 40.43 cm. The lead and end correction d was The results contained in this table have been 16.14 cm. plotted in Graph number 6. In this graph also have been



plotted the curves obtained by Argue and Maass (60) and by De Luca in his first adsorption run (56).

Weight of Sorbed Water gm.	% Sorbed Water	Mean Capacity	Dielectric Value.
0.000 0.090 0.185 0.270 0.365 0.490 0.575 0.670 0.770 0.875 1.180 1.550	0.51 1.04 1.52 2.05 2.75 3.23 3.76 4.32 4.91 6.62 8.69	<u>49.26</u> 49.45 49.94 49.95 50.13 50.43 50.43 51.04 51.39 51.79 53.20 55.55	1.363 1.371 1.392 1.392 1.400 1.411 1.424 1.424 1.436 1.451 1.468 1.526 1.693
1.860	10.43	59.16	1.771

D. Discussion of Results

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Argue and Maass (60) and De Luca (56) did not attempt interpretation of their curves in Graph number 6 but rather calculated values for the dielectric constant of the adsorbed water from the dielectric values contained in these curves. However, it is possible to gain some indication of the condition of the sorbed water from examination of the dielectric value curves.

Tansz and Rumm (62) obtained similar curves in their measurements on starches and cut tobacco. In most cases they obtained much larger differences at different

water contents but that can be traced to two differences

in the conditions under which their measurements were made.

The type of sample which they used allowed close packing in the condenser The dielectric value was therefore much higher since it is dependent on the fractional volume occupied by the sample. The total water present in the condenser was also much higher at a given water content. The second difference was in the frequency of measurement which was very low (500 to 2000 cycles). They found that the dielectric values for water-containing substances were very dependent on frequency of measurement, being higher the lower the frequency. This was true except at low water contents and they interpreted this fact as indicating that at low water contents the sorbed water was very firmly bound and thus not greatly affected by frequency changes. At higher water contents the water was in the liquid state and thus more free to orient in the electric field, the amount of such orientation being dependent on the frequency. The relative proportions of these two kinds of water were found to be dependent on a "material" constant relating to the structure of the solid and on the temperature.

Taylor and Kemp measured the dielectric values of rubber at different water contents (103). Unfortunately their results are uncertain at low water contents. However,

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it is certain that the dielectric values in this case

increase very rapidly at first and then at an even slow

rate. Although these authors do not report their frequency or temperature it may be said that their results indicate that the first water is strongly adsorbed.

Similar interpretations may be made from the curves in Graph number 6. If the sorbed water were in the form of ordinary liquid water the dielectric value curve should have a constant and much greater slope due to the high value for the dielectric constant of liquid water. The very small slope at low water content shows that this water has a very low dielectric constant. It is the "solid" water described by Tausz and Rumm. As the water content increases the curvature also increases and at 10% water the slope of the dielectric value curve indicates the water is going on in liquid form. Between these two extremes the change is gradual, indicating a gradation from strongly adsorbed water through less strongly adsorbed water to absorbed water at higher water contents.

A contribution to the above effect may be due to viscous hindrance in very small capillaries. O'Sullivan has suggested such an explanation for the high electrical resistance of fibres at low water content

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(104). Viscous hindrance is inversely proportional to

the fourth power of the capillary radius. Thus in very small capillaries, which would be filled first, the hindrance may be enough to prevent rotation of water molecules in the rapidly alternating electric field. This would be indicated by a low dielectric constant for the first water to be sorbed.

The three equations given previously have been used in attempts to calculate the dielectric constant of These equations follow. If the solid the sorbed water. dielectric is in regular arrangement in layers parallel to the condenser plates with air layers between

$$\mathbf{E}_{\mathrm{m}} = \frac{1}{\frac{V_{1} + V_{2}}{\sqrt{1} + \frac{V_{2}}{\sqrt{E}}}} \qquad (1)$$

where E_m is the dielectric value $\frac{V_1}{V}$ is the volume ratio of air

 $\frac{V_2}{V}$ is the volume ratio of solid

is the dielectric constant of the solid. E If the solid is in regular arrangement in layers perpendicular to the plates with air layers between

$$E_{m} = \frac{V_{1}}{V} + \frac{V_{2}}{V} E \dots (2)$$

If the solid consists of a random distribution of small

particles in air

$$\log E_m = \frac{V_2}{V} \log E$$
(3)

Tausz and Rumm tested equation 3 with starch containing varying amounts of sorbed water. They calculated the dielectric constant of the compound dielectric consisting of starch and sorbed water with different volume ratios of starch to air. They found some variation with volume ratio but concluded that the equation gave results of the correct order except at higher water contents.

This equation was obviously not applicable to fibrous materials such as cellulose. Argue and Maass (60) and De Luca (56) chose equation 2 as most closely representing their random arrangement of cellulose in the condenser. They based their choice on the fact that this equation gave a dielectric constant for dry cellulose more nearly approaching the true value. Equation 1 gave a negative value in their work and in the present work and equation 3 gave a value of more than 11. Then by assuming that sorbed water had the same arrangement as the fibres themselves they extended this equation 2 to include a third term for the water. This new equation is:

$$E_{m} = \frac{V_{1}}{V} + \frac{V_{2}}{V} E_{2} + \frac{V_{3}}{V} E_{3}$$
 (4)

where E_2 is the dielectric constant of the cellulose

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sample.

 E_3 is the dielectric constant of the sorbed water. $\frac{V_3}{V_3}$ is the volume ratio of water. Using this equation these investigators obtained similar curves for the dielectric constant of the sorbed water versus water content of the cellulose. These curves showed a slight inflection in the neighbourhood of 3% water and the dielectric constants of the increments of water increased from less than 10 at low water content to over 70 at 10% water content.

The validity of these calculations is dependent on the assumption with regard to orientation of the sorbed If, for instance, the water were adsorbed on water. isolated active spots on the fibres a logarithmic term such as in equation 3 would be more applicable. The best evidence for the use of this assumption lies in the fact that the values for the dielectric constant of the water increments approach the value for liquid water. However, the value used for the dielectric constant of cellulose E_2 was not the true value but that one calculated by use of equation 2, which was about 30% too low. Another error was introduced by assuming the volume of the sorbed water was the same as the volume of an equal weight of liquid The adsorption-compression of water on swelling water. substances such as cellulose has been shown by many investigators (88, 89). How much of such compression is

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actually due to water in a high density form is not certain,
but it is probable that the adsorbed water does not have
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a density of 1.
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Attempts were made in the present work to correct for these factors. A constant was introduced into equation 2 so that it could give the correct value for E2. This constant was evaluated as the ratio of the true dielectric constant for the cellulose sample to the dielectric constant E_2 as given by equation 2. It may be described as a correction factor expressing the deviation from linearity of paths through the dielectric from one plate to the other in the condenser. This constant was then extended to the water factor in equation 4 since the water was assumed to have the same orientation as the cellulose sample. The new equation therefore became:

$$E_{m} = \frac{V_{1}}{V} + \frac{V_{2}E_{2}}{VK} + \frac{V_{3}E_{3}}{VK} \qquad \quad (5)$$

The constant K, being dependent on orientation, had to be calculated separately for each sample. Thus in De Luca's work, run number 1, K was calculated to be 1.54. For the linen sample used in the present work K = 2.16, if the dielectric constant is assumed to be 5.27. In these calculations the specific volume of the cellulose was taken as 0.640 and the measured volume of the condenser The term V_3 , the volume of the adsorbed was 45.10 cc.

water, was corrected by applying the density values obtained by Taylor using sulphite paper (96).

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In the table below the dielectric constant of the adsorbed water has been calculated for De Luca's results and for the results contained in the present work by using equation 5:

De Luca

% Adsorbed Water	Dielectric Constant	% Adsorbed Water	ed Dielectric <u>Constant</u>	
1 14	25.8	0, 51	15.6	
1.66	30.9	1.04	27.9	
2.28	35.3	1.52	19.2	
2,90	37.9	2,05	17.9	
3.62	39.9	2,75	16.5	
4.14	41,4	3.23	16.5	
4,66	43.2	3.76	16.2	
5,17	44.6	4.32	16.3	
5.80	43 . 6	4.91	16.7	
6,83	49.2	6.62	18+1	
8,28	53.8	8.69	20.7 26.0	
9.31	59.1	10.43	20.0	

Present

It will be noted particularly that the results for the two cases are entirely different. If the dielectric constants of the final increments of water in these results are calculated it is found that the values go above that for liquid water. The extraordinary sensitivity of the equation is shown in the calculations from the results in the present work. A very small error in the dielectric value measurement leads to a rise of almost 100% in the dielectric constant. These results indicate the inapplicability of the equation. The assumptions on which it is

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based are not justified.
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Equation 1 cannot be applied because it too is
very sensitive to slight changes in the dielectric values.
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This arises from the fact that a difference appears in the denominator which, with slight changes in the dielectric value, changes from positive to zero to negative. Dielectric constants varying from infinity to zero on both the plus and minus sides are thus obtained. This is shown when the equation is written in the form

$$\mathbf{E} = \frac{\mathbf{E}_{\mathrm{m}}\mathbf{V}_{2}}{\mathbf{V}-\mathbf{E}_{\mathrm{m}}\mathbf{V}_{1}}$$

It is suggested in view of the above considerations, that it is not possible at the present time to calculate actual values for the dielectric constant of water sorbed on cellulose. However, as already shown, interpretations may be made from the dielectric value curve itself. Also, calculations of the dielectric constants does indicate some important facts. The dielectric constant of the sorbed water is very low at low water contents in all methods of calculation. This fact has already been deduced from the shape of the dielectric value curve. In the curve for the density of sorbed water versus water content a marked inflection takes place between 2% and 3% water. When these density values are used in equation 5 a similar inflection is found in the dielectric constants of the adsorbed water curve (see table above). As discussed

previously such inflections in the region of 3% water

content are common in cellulose measurements. It is

probable that the equilibrium between adsorbed and

absorbed water begins to take effect in this region.

Actually it is not necessary to calculate dielectric constants in order-to learn a great deal from dielectric value measurements. Tansz and Rumm have shown that data on the variation of dielectric value with frequency and with temperature can be interpretated in terms of the freedom of the sorbed water. It is suggested that such a method should be used in any future work on this problem.

X
SUGGESTIONS FOR FUTURE WORK

SUGGESTIONS FOR FUTURE WORK

The importance of absorption and dispersion measurements has been mentioned several times in this work. In order to make such measurements the capacity measurement apparatus should be rebuilt. It should be variable over a wide frequency range, say 1000 to 1,000,000 cycles. This would, of course, require an accurate method for frequency measurement. Stoops has described an apparatus variable over such a frequency range (59).

Absorption and dispersion measurements in the transverse and axial directions of cellulose crystallites should lead to valuable information concerning the freedom of polar groups. Thus it should be possible to settle the postulate made by Stoops concerning rotation of the glucose anhydride rings (cf. p. 96). Measurements on mercerized and regenerated cellulose might well serve to elucidate their structures.

Absorption and dispersion measurements should also be made on the cellulose-water system. Tausz and Rumm have used this method with some success in discovering the condition of sorbed water (62). Such measurements

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would of course require prior knowledge of the absorption and dispersion of cellulose alone.
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It should be possible to measure the dielectric
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constant of the cellulose-water system at low water
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contents by means of the isodielectric liquid method. If this were done at two or three water contents below 3%, there would then be a good check for future attempts to calculate dielectric constants from dielectric value measurements.

It is possible that a slight error is introduced by using a liquid of very low dielectric constant (benzene) for the measurement of the lead and end correction. It is therefore suggested that a liquid having a dielectric constant in the neighbourhood of 6 be chosen for this purpose.

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CLAIMS TO ORIGINAL RESEARCH

CLAIMS TO ORIGINAL RESEARCH

The isodielectric liquid method for the measurement of the dielectric constants of fibrous and powdered materials as developed by Starke (63) and by De Luca, Campbell and Maass (43) has been improved in several ways. By using specially purified liquids the results obtained have become more reproducible. The most important improvement was in the method used for plotting the results. This has allowed the use of straight lines rather than very gradual curves with a resultant decrease in the number of points required and increase in the accuracy of the determination.

The designs of the dielectric condenser and of the dielectric cell were changed to permit the rapid change of samples. This greatly decreased the time required for the measurements. A further increase in precision was obtained by a method for taking capacity readings which eliminated the effects of frequency drift in the oscillators.

A relationship between dielectric constant and strength in paper was discovered. Increase in

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strength as measured by a Mullen Burst Tester is

accompanied by a decrease in dielectric constant. Two

explanations were made for this relationship, the increase of bonding with strength and the increased flatness of the fibres in paper with increased strength. It was found to be impossible to separate the effects of these two explanations.

The anisotropy of cellulose as a dielectric was established. A method was devised whereby the axial and transverse values of the dielectric constant of the cellulose crystallite could be measured. Those values were measured for the first time and were:

> Axial dielectric constant 7.2. Transverse dielectric

> > 5.3.

Previous values reported for the dielectric constant of cellulose have been shown to agree with the above if the fibril and fibre orientations are taken into account.

constant

Calculations of the atomic polarization in the two directions in cellulose have been made and these have been interpreted in terms of relative freedom of groups in the cellulose chain. It has been suggested that the absorption and dispersion explained by Stoops in terms of rotation of glucose anhydride rings (59) should probably be explained in terms of displacement of

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hydroxyl groups which are restrained by secondary or

coordinate bonds.

Dielectric values in the cellulose-water system have been measured for linen cellulose up to a water content of over 10%. The dielectric value versus water content curve has been interpreted as showing that the first water sorbed by cellulose is adsorbed while later water is absorbed. Several attempts have been made to calculate the dielectric constant of the sorbed water from the measured dielectric values. These attempts have served to show the impossibility of such calculations on the basis of present knowledge.

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