INVESTIGATIONS OF SOME DIELECTRIC
PROPERTIES OF NATURAL RUBBER

by

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This paper deals with the problem of measuring the dielectric properties of rubber under various conditions of stress and temperature over a broad range of frequencies. A discussion of the more modern theory of dielectrics is given and a survey made on the mechanical and electrical properties of natural and synthetic rubbers.

Values of dielectric constant and dissipation factor are presented for natural rubber gum stock (2% sulphur) unstretched and stretched 300% at 25°C and unstretched and stretched 300% at 68°C over the range of frequencies $10^2$ to $10^7$ c.p.s. The dielectric constant decreases and the loss peak shifts to higher frequencies when the temperature is raised. Stretching the rubber at 25°C lowers the dielectric constant and increases the losses. The changes upon stretching may be due to orientation and crystallization of the molecular dipole components of the rubber. Heating the stretched rubber to 68°C seems to increase the dielectric constant and to lower the loss peak. This may be explained by the assumption that the higher temperature lowers the degree of orientation and melts the crystallites.
ACKNOWLEDGEMENT

The research was started under the direction of Dr. H. D. Smith, now President of the Nova Scotia Research Foundation, to whom I am indebted for his guidance and support. I also wish to express my thanks to Dr. O. Blüh, under whose supervision the work was finished, for his help in discussing and formulating the results; and to Dr. Guth of the University of Notre Dame for his hospitality in his laboratory during the summer of 1946. I acknowledge gratefully the assistance of my colleagues Messrs. Paulin, Codrington and Ozeroff, and Messrs. Price and Fraser of the workshop, in building the apparatus.
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INVESTIGATIONS OF SOME DIELECTRIC PROPERTIES OF NATURAL RUBBER

I. INTRODUCTION

The problem of measuring the dielectric constant and dissipation factor of natural and synthetic rubbers as a function of frequency, temperature, stretch and time has not as yet been systematically undertaken. Some results on natural rubber are given in this thesis. The interdependence of the above-mentioned variables should throw light on the molecular structure of rubber and related polymers. Rubber is assumed to be a chain polymer and many of its properties can be explained by the nature of these chains. Natural rubber, for example, contains chains of from 20,000 to 30,000 carbon atoms. The chains straighten out upon stretching and the molecules are prevented from slipping over one another by internal friction; this friction is due to secondary bonds or crosslinkages between the molecules. The extension of most rubber and rubber-like substances is not completely reversible; a certain degree of deformation persists after the tension is removed. Under constant deformation the tension diminishes,
i.e. relaxation occurs. This relaxation may take place over a long period of time and in general the length of time for a given substance is in some way dependent on the deformation and the temperature.

Rubber is a peculiar substance in that some types of rubber, upon stretching, become crystalline. X-ray spectra show that crystals are found at room temperature, on stretching to 80% or more. The intensity of the reflections increase approximately in proportion to the degree of stretching while their positions are not changed. The heat developed in the Joule effect on stretching is also proportional to the increase in intensity of the spectra and is thus dependent on the amount of crystallization. Upon raising the temperature there will be a definite point at which this diffraction pattern will disappear. For 600% stretch, this temperature is about 80 - 90°C.

If rubber is stretched and then cooled in liquid air, the rubber will become brittle and when pulverized, break up into fibers (Hock's pulverizing experiment). This proves that rubber when stretched, becomes somewhat crystalline in nature, with a preferential arrangement along the direction of stretching. Rubber if maintained at temperatures slightly above zero or lower will become crystalline. It will remain supercooled for months and the process of crystallization will sometimes take place over a period of years. The crystallites formed are often called fringed micells, and consist of ordered regions from which chains
A theory of rubber which will explain quantitatively all its properties would be difficult if not impossible to derive. It is possible, however, to develop a theory which satisfies the above requirements within limits, by making certain simplifying assumptions about the structure of rubber. The theory of elasticity by James and Guth\(^1\) is an example of such a development. To quote from their article; "This new theory introduces a clear cut three dimensional model for bulk rubber, and it also resolves the dilemma between flexibility (free rotation) of the chain molecules and the steric forces binding them to a network. It yields a single analytical expression for the stress-strain curve which exhibits the characteristic S-shape of the typical rubber stress-strain curves. It also predicts the occurrence of a "a thermoelastic inversion point" or critical extension below which rubber shows normal thermoelastic behaviour, and above which it is rubberlike".

The treatment is essentially a thermodynamical one. The most probable configuration of an unstretched molecule is the coiled rather than the straight form. This contracting tendency is hindered by steric forces acting in the opposite direction in the chain molecule. For the unstretched state there is equilibrium between the contracting forces and the outward push of a "liquid" representing the steric forces.

\(^{1}\)H. James and E. Guth, Ind. and Eng. Chem., Vol. 34, November, 1942.
In the thermodynamic formulae we replace pressure (p) by tension (-F) and volume (V) by length (L). Then the probability of finding a given length of the chain will depend on the extended length of the chain and the number and lengths of the segments. Thus if L is the relative length, on the number of segments per chain, and l the length of the segment, P is found to be gaussian and of the form

\[ P = Ae^{-BL^2} \]

where B = B(n,l) and A a constant.

Then if entropy

\[ S = k \ln P \]

and if pressure

\[ p = T \left( \frac{\partial S}{\partial V} \right)_T \]

goes over into

\[ -F_l = T \left( \frac{\partial S}{\partial L} \right)_T \]

then

\[ F_l = KTL \]

where K is a constant of the rubber network and T is the absolute temperature. If an external force is applied, this external force should be added algebraically to the contracting force, and in equilibrium, using the condition of incompressibility we get for the total stress F

\[ F = KT \left( L - \frac{1+a(T-T_0)}{L^2} \right) \]
where

\[ K = \text{a constant} \]
\[ L = \text{relative length} \]
\[ a = \text{coefficient of expansion} \]
\[ T_0 = \text{room temperature} \]
\[ T = \text{temperature at which } F \text{ is measured.} \]

It is possible with the aid of such a theory to explain and predict results in rubber phenomena as is done for example, in an article by Dart and Guth on "The rise of temperature on fast stretching of Butyl rubber"\(^1\).

Few of the physical properties of rubber have remained uninvestigated, but the great number of rubbers leaves any one field of investigation inexhaustible. As research goes on, however, a better knowledge of the interrelations between the various properties of rubber gradually becomes realized. The mechanical properties of rubber have, up till now, been the main interest of research workers. Electrical research was limited to a study of its insulation and power frequency characteristics, and it is only recently that systematic investigations on the dielectric properties has been performed. The recently developed field of supersonics is bridging the gap between mechanical and electrical properties,\(^2\) since the mechanism for mechanical losses in rubber is postulated to be similar to that for electrical losses.

The electrical investigations lead logically to optical re-

search and this latter field has made large contributions, not only to the understanding of the fundamental structure of rubber, but also in industrial control and standardization of rubber products. A more detailed discussion of the dielectric characteristics of rubber will follow, after a survey of the theory of dielectrics in general.

II. PROPERTIES OF DIELECTRIC MATERIALS

A. General Theory of Dielectrics

(a) Definition of Terms.

If a dielectric material placed in the homogeneous field of a condenser is subject to an alternating field strength $E$, it can be affected in two ways; first, the charging current can increase because of the polarization of the medium and secondly, a loss current may flow heating up the material. The term polarization refers here to the effect of the field on electrically unsymmetrical molecules commonly called dipoles\(^1\). The total effect can be represented by a dielectric displacement current with the current density

$$j = \frac{\partial (\varepsilon E)}{\partial t}$$

The dielectric constant $\varepsilon$ is generally defined as

\(^1\)P. Debye Polar Molecules
the ratio of the capacity of a condenser filled with a dielectric to the capacity of the same condenser filled with air. If $\varepsilon$ is independent of time, only a charging current results, otherwise

$$\frac{d}{dt}(\varepsilon E) = \varepsilon \frac{dE}{dt} + E \frac{d\varepsilon}{dt},$$

the second term representing an energy transfer into the material.

For a field of angular frequency $\omega$

$$E = E_0 e^{i\omega t}$$

$$\frac{d}{dt}(\varepsilon E) = \frac{dE}{dt}(\varepsilon - \frac{i}{\omega} \cdot \frac{d\varepsilon}{dt}) = \frac{dE}{dt}(\varepsilon' - i \varepsilon'')$$

using a complex dielectric constant

$$\varepsilon^* = \varepsilon' - i \varepsilon''$$

If the angle between the current and the $E$ vector be $\frac{\pi}{2} - \delta$

$$\tan \delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'}$$

whence

$$\varepsilon'' = \varepsilon' \tan \delta$$

Tan $\delta$ is called the dissipation factor.

In the practical applications of dielectric material, the "Q" of a capacitor is important and is defined as the ratio of stored energy to dissipated energy per cycle.

$$\text{thus } Q = \frac{1}{\tan \delta};$$

for small angles, the power factor $\cos \theta (\theta = \frac{\pi}{2} - \delta)$ is identical with the dissipation factor $\tan \delta$.

(b) Electron Theory of Dielectrics

A dielectric may be thought of as an assemblage of
bound charges; these charges include the electrons and positive nuclei in atoms and molecules, the ions held at lattice points in ionic crystals, and in general any bound charged particles which are not able to drift from one electrode to another. In actual dielectric insulators some free conduction electrons or ions exist, producing a direct current conductivity, although this effect is small at ordinary temperatures. The sum of the products of charge and amplitude extended over all the bound charges in a unit volume for an applied electric field of unit intensity determine the dielectric constant. The energy dissipated as heat by the motions of the bound charges in the applied electric field represents the dielectric loss per second, a quantity which is proportional to the a.c. conductivity after the d.c. conductivity has been subtracted from it.

The polarization of an assemblage of charges is defined as the vector sum

\[ \overrightarrow{P} = \sum_{i=1}^{n} e_i \overrightarrow{s_i} \]

where \( \overrightarrow{s_i} \) is the distance of the \( i \)th charge \( e_i \) from a point chosen as origin. If we consider an electron (\( e = 4.77 \times 10^{-10} \) e.s.u.) and a proton separated by a distance equivalent to atomic distances (10^{-8} cm.) \( \overrightarrow{P} \) has a value \( 4.77 \times 10^{-18} \) e.s.u. or 4.77 Debye units. For an isotropic medium the polarization per unit volume \( \overrightarrow{P} = \sum e_i \overrightarrow{s_i} \) per unit volume. For many materials \( \overrightarrow{P} \) is zero when no electric field is applied, though some crystalline materials have a finite
value of \( \mathbf{F} \) even in the absence of an applied electric field. The value of \( \mathbf{F} \) with no field is \( \mathbf{F}_0 \) and with the field \( \mathbf{F}_E \), thus \( \mathbf{F} = \mathbf{F}_E - \mathbf{F}_0 \).

For isotropic materials \( P \) is proportional to the electric field \( \mathbf{E} \),

\[
\mathbf{P} = \frac{\varepsilon - 1}{4\pi} \mathbf{E}
\]  

where \( \frac{\varepsilon - 1}{4\pi} \) is the susceptibility of the dielectric in e.s.u.

In non-isotropic bodies, \( \mathbf{P} \) is not always in the same direction as \( \mathbf{E} \) but is assumed to be a linear vector function of \( \mathbf{E} \).

The contribution which the polarization of the dielectric makes to the force upon a charged particle in it, has been calculated by Lorentz to be \( \frac{4\pi}{3} \mathbf{P} \). Therefore, the internal or local field \( \mathbf{F} \) is given by

\[
\mathbf{F} = \mathbf{E} + \frac{4\pi}{3} \mathbf{P} 
\]  

If we assume for isotropic dielectrics that \( \mathbf{P} \) is a linear function of \( \mathbf{F} \) then

\[
\mathbf{P} = k \mathbf{F}
\]

where \( k \) is the polarizability per unit volume. For gases the term \( \frac{4\pi}{3} \mathbf{P} \) becomes negligible and the polarizability equals the susceptibility. Solving for \( k \) from (1), (2), and (3) we obtain

\[
k = \frac{3}{4\pi} \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right)
\]

On multiplying (4) by the molecular weight of the material and dividing by the density we get

\[
\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{M}{\rho} k = \frac{4\pi}{3} N \gamma
\]
Expression (5) is the Clausius-Mosotti relation, and if \( \gamma \) is considered a constant, it is independent of density for a given molecule.

The Clausius-Mosotti formula gives good results when applied to atomic and electronic polarization, but is not satisfactory when applied to highly polar liquids such as water. The difficulty lies in the calculation of the internal field \( F \). The factor \( \frac{4}{3} \gamma F \) calculated by Lorentz must be modified due to the strong interaction between adjacent polar molecules. Kirkwood has extended the theory by introducing in a hypothetical cavity surrounding the dipole, a first shell of near neighbours. This extension leads to a better value of the dielectric constant of water than the unmodified theory.

(e) Effect of Frequency and Temperature

The equation of motion for any charge \( e \) in a polarizable material

\[
ms + rs + fs = eF
\]

(6)

\( s = \) displacement
\( F = \) local field
\( m = \) mass of charged particle
\( r = \) frictional resistance coefficient
\( f = \) elastic restoring force coefficient

If we multiply through by \( e \), replace \( e \) by \( ne \) (\( n = \) the number of charged particles per unit volume), then (6) becomes

\[
m\ddot{P} + r\dot{P} + fP = ne^2F
\]

(7)
where \( P \) is polarization per unit volume.

\[
P = kF = kF_0 e^{i\omega t}
\]

is a solution of (7) if the polarizability per unit volume = 

\[
k = \frac{ne^2}{(i\kappa w - \omega w^2 + f)}
\]  \hspace{1cm} (8)

\[
(1 = \sqrt{-1})
\]

If \( f \) is much greater than either \( \kappa w \) or \( \omega w^2 \), then

\[
k_1 = \frac{n_1 e^2}{f_1}
\]  \hspace{1cm} (9)

This special type of polarization is independent of frequency and may be referred to as instantaneous or optical polarization. This contribution arises in the visible and infra-red, and since it is independent of frequency in the low frequency (power) range, may be computed from refractive index measurements.

A second case results when \( \omega w^2 \) is negligible by comparison with \( \kappa w \) and \( f \). Thus

\[
k_2 = \frac{n_2 e^2}{(i\kappa w_2 + f_2)}
\]  \hspace{1cm} (10)

This represents a variation with frequency to which the same anomalous dispersion is given. The term "anomalous" brings out that the variation of dielectric constant with frequency in the power and radio range resembles optical anomalous dispersion.

A third case arises if none of the terms in the denominator of (8) are negligible. This type of dispersion has been observed only in those dielectrics which are piezoelectric. It follows then, that the "inertia reaction term"
can be neglected in ordinary dielectrics at the lower electrical frequencies.

The total polarizability \( k \) is

\[
k = k_1 + k_2
\]

where \( k_1 \) = instantaneous polarizability

\( k_2 \) = absorptive polarizability

and using the values for \( k_1 \) and \( k_2 \) in (9) and (10) plus the Clausius-Mosotti relation (5) we obtain

\[
\frac{M}{\epsilon} \frac{(\epsilon - 1)}{\epsilon + 2} = \frac{4\pi N}{3} \left[ \frac{k_1}{L} + \frac{n_2 e^2}{f_2 L} \left( \frac{1}{1 + iw} \right) \right]
\]

(11)

where \( L \) = number of molecules per unit volume

\( t' = \) relaxation time = \( \frac{r_2}{f_2} \).

We may compare this with the result from the Debye theory\(^1\).

\[
\frac{M}{\epsilon} \frac{(\epsilon - 1)}{\epsilon + 2} = \frac{4\pi N}{3} \left[ \chi_0 + \frac{u^2}{3kT} \left( \frac{1}{1 + iw} \right) \right]
\]

(12)

where \( k = \) Boltzman's constant

\( T = \) absolute temperature

\( u = \) permanent electrical moment of the molecule.

\( \chi_0 \) corresponds to \( \frac{k_1}{L} \) in (11).

The essential difference in the derivation of (11) and (12) is that \( t \) in (11) is left in terms of \( r \) and \( f \), each of unspecified origin, while \( t \) in (12) was calculated by Debye to be \( \frac{3mv^2}{kT} \). He assumed that the orienting effect of the field on a molecule of dipole moment \( u \) is opposed by a viscous force proportional to angular velocity of rotation of the molecule. \( V \) is the volume of the spherical molecules immersed.

\(^1\) P. Debye Polar Molecules.
in a liquid of viscosity \( n \). This formula (12) introduces a specific temperature dependence of \( \varepsilon \).

If we consider the polarizabilities corresponding to \( w = 0 \) and \( w = \infty \), we obtain a value for the dielectric constant \( \varepsilon^\infty \)

\[
\varepsilon^\infty = \varepsilon_\infty \left( 1 + \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \right) \left( 1 + \frac{1}{1 + \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} w^2 t^2} \right) \tag{13}
\]

\( \varepsilon_0 \) = value of \( \varepsilon \) for \( w = 0 \) (static \( \varepsilon \))

\( \varepsilon_\infty \) = value of \( \varepsilon \) for \( w = \infty \) (optical \( \varepsilon \))

\[ t' = \frac{\varepsilon_\infty + \frac{2}{2} \varepsilon_0}{2} \]

The difference in the \( t' \)'s arises from the assumption in the derivation of (13) that \( F \) is a linear function of \( E \), not \( F = E + \frac{4\pi}{3} E \). For when \( F = E \), i.e. no dipole interaction, then \( t' = t \). It should be noted that the real and imaginary parts of \( \varepsilon^\infty \) in (13) correspond to \( \varepsilon' \) and \( \varepsilon'' \) in the definition \( \varepsilon^\infty = \varepsilon' - i \varepsilon'' \) given at the beginning of this section.

B. Dielectric Material

(a) Application of the Theory to Dielectric Material

If \( \varepsilon' \) be plotted against frequency, we observe dispersion regions in which \( \varepsilon' \) decreases. In this center of these dispersion regions, \( \varepsilon'' \) has a peak. In Fig. 1 we observe two dispersion regions. The higher peak, usually above one megacycle, is due to dipole polarization. The lower peak, usually below one cycle, is attributed to inhomogeneities in the dielectric. At the interfaces of these components, the migrating ions pile up and contribute to the total polarizat-
Fig. 1
tion. This type of polarization is generally called "interfacial".

In many dielectrics, the variation of $\varepsilon'$ is much more gradual and the peak of $\varepsilon''$ much broader. The simple dispersion formulae then, often falls short of adequately expressing experimental data, particularly for non-homogeneous or disperse systems. The broadness of the dipole peak can be explained by postulating a distribution of relaxation times rather than a single value. Maxwell discussed the transient polarization produced by strata of dielectric materials and Wagner gave a general treatment for conducting particles sparsely distributed through a material of comparatively low loss.

In general then we may say that charge carriers and dipoles produce polarization and losses from zero cycles up to the infra-red. The loss peaks will shift with increasing temperature to shorter wavelengths. The simplest way to avoid losses is to choose a dielectric with no charge carriers or unbalanced molecules, unless the charge carriers are trapped and harmless in the temperature range desired and the dipoles are balanced against each other so as to give no net moment.

(b) Electrical and Dielectric Properties of Rubber

Pure natural rubber is non-polar but the process of vulcanization introduces, dipoles originating in the carbon sulphur linkages. The loss peak due to the carbon sulphur dipoles occurs in the one megacycle region. Like other loss
peaks, it can be shifted up the frequency scale by increasing the temperature. The other compounding ingredients of rubber tread, zinc oxide, carbon black, etc., also introduce losses whose effects are most marked in the power frequency region, and are due to an increase in conductivity.

The pure synthetic rubbers can be either polar or non-polar. In the polar group we find the Buna N and Neoprene rubbers. The dipole effect in Buna N arises in the cyanide group and that in Neoprene from the carbon-chlorine bonds. An example of a non-polar synthetic rubber is found in Buna S. The dielectric constants of the non-polar polymers, extrapolated to high frequencies are so close to the square of the refractive index as to indicate the absence of further dispersion in the high frequency region. The relation \( n^2 = \varepsilon \) does not hold true for the polar type polymers and investigation in the ultra short and near infra-red frequency regions will locate the dispersion which should exist there.

<table>
<thead>
<tr>
<th>Stock</th>
<th>Type</th>
<th>( \sqrt{\varepsilon} )</th>
<th>( n_{\text{obs}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gum</td>
<td>non-polar</td>
<td>1.62</td>
<td>1.52</td>
</tr>
<tr>
<td>Buna S gum</td>
<td>non-polar</td>
<td>1.59</td>
<td>1.52</td>
</tr>
<tr>
<td>Buna N gum</td>
<td>polar</td>
<td>1.85</td>
<td>1.52</td>
</tr>
</tbody>
</table>

(Values at room temperature approximately)

It has been previously discussed that the position of the dispersion region depends on the inner viscosity of the polymer. This inner viscosity will determine the mechani-

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1Smith, Schneider, Carter, Mogat - Report from Copolymer Research Branch.
cal hysterisis effect which in turn determines the heat developed when rubber is subjected to mechanical or electrical alternating stresses. The temperature dependence of the inner viscosity is also important, but dielectric properties can be used to estimate the inner viscosity only for the polar type of rubber, such as Buna N.

The dielectric properties of loaded stocks (e.g. rubber-carbon compounds) provide useful information on the degree of dispersion of the carbon black in the rubber. This dispersion determines the mechanical properties of the mixture, and in general, the better the dispersion the better is the reinforcement. As was pointed out by Wiegand, the electrical and dielectric properties of the loaded stocks are also extremely sensitive to the dispersion of the carbon black; a poorer dispersion giving lower values for the dielectric constant and conductivity.

If the volume concentration of carbon black in rubber is less than 25%, a linear relation exists between the ratio of the dielectric constants of the gum stock and the mixture, and the concentration. The theory of spherical conducting particles embedded in a dielectric, was developed by Rayleigh and extended by Guth. A verification of this theory was undertaken at Notre Dame and M.I.T.

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2 Lord Rayleigh, Phil. Mag. (5), 34, 481, 1892.
of electrically conducting rubber is also becoming of great practical interest, and for this reason the effect of temperature, elongation, time and percentage concentration of the carbon black on the d.c. conductivity of GR-S has been thoroughly studied.

The change of the dielectric properties of natural rubber with stretch was first investigated by Schiller. For natural rubber, and a stretch of 30%, he observed a decrease in the dielectric constant upon stretching, from 3.67 to 3.51 at 1.2 k.c. Ivey observed in some preliminary work on natural rubber at this University, a decrease in dielectric constant, for 100% stretch, of the same order of magnitude as Schiller.

In the present paper measurements of the dielectric constant and the loss factor of natural rubber are presented at frequencies between 400 cycles and 10 megacycles and at temperatures of 25° and 68°, for stretches to maximum 300%. An apparatus has been built which allows measurements to be undertaken at a wide range of temperature and stress, which will be used for further investigations on natural and synthetic rubber.

2Schiller, Ann der Physik, p. 931, 35, 1911.
III. EXPERIMENTAL PROCEDURE

A. Equipment

The range .4 k.c. to 10 m.c. was covered in the measurements. The equipment used:

(1) .4 to 10 k.c.
   Oscillator - General Radio Type 608A
   Schering bridge - " " 716B
   Null detector - " " 1132A

(2) 50 k.c. to 1 m.c.
   Q-meter - Boonton Type 160A

(3) .5 m.c. to 30 m.c.
   Signal generator - General Radio Type 805C
   Twin-T impedance bridge - " " 821A
   Radio detector - Hammarlund Type HQ-129X

B. Apparatus

The rubber sample was placed between two steel condenser plates C (Fig. 3); the upper plate was three inches in diameter and the lower one five inches. These plates were ground flat to better than 1/1000 of an inch in the workshop at the University of Notre Dame. The upper plate was roughly centered by a pyrex tube and pressed flat on the rubber by
Fig. 2

A ...... Capacitance Bridge  D ...... Twin T Impedance Bridge
B ...... Audio Oscillator  E ...... Signal Generator
C ...... Null Detector  
F ...... Radio Detector  
G ...... Q-Meter
Fig. 3

B ........ Blower
C1C2 .... Clamps
C .......... Condenser
G1G2 ...... Reduction Gears
H .......... Heater
M1M2 ...... Motors

B1B2 .... Air Outlets
R ........ Rubber Sheet
S1S2 .... Screws
t1t2 ...... Thermometers
T .......... Thermostat
TR ......... Thermoregulator
W .......... weight

W ........ Wooden Block
Fig. 4

A ....... Thermostat
B ....... Dial Micrometers
C ....... Coax Lead
D ....... Air Outlet Pipes
A ..... Condenser Plates
B ..... Pyrex Rods to Micrometer
C ..... Clamp
D ..... Rubber Sheet
E ..... Coax Lead
F ..... Shielding

Fig. 5
Fig. 6

Control Circuit
means of a two kilogram lead weight w. The height of the top condenser plate and the thickness of the rubber was determined by three dial micrometers \( g_1 \), \( g_2 \), \( g_3 \), which were externally supported. These dial micrometers read to \( 1/10,000 \) of an inch. They were kept in mechanical contact with the top plate by pyrex rods. Electrical connection to the top plate was made through a piece of coax which projected into the measuring cell and could be plugged in and out of the top plate. The entire cell was surrounded by wire gauze on copper sheathing to afford shielding.

The eccentric clamps \( c_1 \), \( c_2 \) which stretched the rubber, were moved in and out by means of motor-driven screws \( s_1 \), \( s_2 \). The chamber was heated with warm air by a blower B, and the temperature regulated by a mercury thermostat T. It was possible to set the thermostat for any desired temperature between 20°C and 70°C by means of an adjustable reservoir. The thermostat controlled the grid of a thyratron in the thermo-regulator TR, which in turn supplied the power for the heaters H.

C. **Measurements of Dielectric Constant and Loss Factor**

(a) Electrical Measurements

(1) 400 to 10,000 cycles - Schering bridge.

The substitution method was used. If \( C' \) and \( D' \) be the initial readings with the unknown condenser disconnected and \( C \) in \( \mu \mu F \) and \( D (\%) \) the final readings with the unknown condenser connected, the unknown Capacity \( C_x \) and dissipation
factor $D_x$ are

$$C_x = C' - C$$

and

$$D_x = \frac{C'}{C' - C} (D - D')$$

The bridge is of the usual form with ratio arms and a balancing impedance in the arm opposite to the unknown. The resistance balance is made, however, by means of a variable condenser connected across one of the ratio arms. The unknown capacitance is read from the balancing condenser.

(2) 50 k.c. to 1 m.c. - Q-meter

The substitution method was used. If $C'$ and $Q'$ be the initial readings on the Q-meter and $C$ and $Q$ the final readings, then $C_x$ and $D_x$ are

$$C_x = C' - C$$

and

$$D_x = \frac{100 C'(Q' - Q)}{(C' - C)Q'Q}$$

The Q-meter is a resonant circuit device. The unknown capacity is equal to the capacity subtracted when the circuit is rebalanced. The voltage across the circuit is read by a vacuum tube voltmeter calibrated directly in $Q$.

(3) 1 m.c. to 30 m.c. - Twin-T bridge

Substitution method used. If $C'$ and $G'$ be the initial values of capacitance and conductance, and $C$ and $G$ the final values

$$C_x = C' - C$$

$$D_x = \frac{G}{w(C' - C)}$$

($G'$ made equal to zero on initial adjustment. $w = 2\pi f$ frequency).
The circuit consists of two T networks connected so that they furnish parallel transmission paths. An initial balance is made so that no energy is transferred from generator to detector. The increase in capacity, when the unknown is connected, is compensated for by a decrease in a balancing condenser. A calibrated condenser which restores the phase to its initial value after connection of the unknown gives the conductance.

(b) Calculation of Results

The thickness of the sample was determined initially using a small optical flat and one of the dial micrometers. The bottom plate was given a very thin coat of petroleum jelly, the rubber placed in position and then rolled thoroughly with a roller. The rubber could then be stretched if desired. A metal foil, the same diameter as the top condenser electrode, was pressed in place with a thin coat of petroleum jelly, and rolled until no air pockets were observed. This method gave reproducible results. Since the bottom plate was slightly higher than the clamp, the tension in the rubber pressed it tightly against the plate. The thickness of the rubber was determined before and after electrical measurements were taken. The flat was inserted in turn under each of the connecting rods of the dial micrometers. A second reading was taken with the rubber removed, and the optical flat on the bottom plate. The difference between these readings gave an average value for the thickness. A special soft-material micrometer was also used to serve as a check.
The pyrex rods connected to the dial micrometers, normally rested on the top condenser plate. It was thus possible to observe slip of the plate or changes in thickness of the sample during measurements. Quartz rods were used at first, but were eventually replaced by pyrex rods which proved electrically satisfactory. All the rods were cracked if the rubber broke and the pyrex proved to be quicker and easier to replace than the quartz. The rubber broke frequently when stretched to 300% or more at 68°C. The sheet usually tore in from the edge at a point near the clamp where the curvature and therefore the stress was greatest.

The stray capacity of the measuring cell was determined by using quartz and pyrex spacers of negligible area and of known thickness. The true capacity was calculated using Kirchoff’s formula (to be commented upon below) and this value subtracted from the observed capacity. Two determinations each gave a value of 4.3μf for the stray capacity. The pyrex rods attached to the dial micrometers contributed no observable conductivity losses to the air condenser; the relative humidity was low and therefore we were not troubled with conducting water films. No changes in stray capacity or losses with temperature were observed. The input capacities of the leads were determined and found to remain constant throughout the measurements. The losses in the leads were ignored, since they formed part of the initial balance of the measuring circuits.

The accuracy of the values of dielectric constant
depends more on an evaluation of the "edge effect" rather than instrumental errors. The values for the dielectric constant were calculated from the formula given by Scott and Curtis:\footnote{Edge correction - A. H. Scott and H. L. Curtis, J. of Res. Nat. Bureau of Standards, p.747, Vol. 22, 1939.}

\[
\epsilon' = \frac{C}{C_n + C_e}
\]  

\[
C = \text{measured capacity in } \mu\text{F}
\]

\[
C_n = \text{geometrical capacity in } \mu\text{F}
\]

\[
C_e = \frac{1.113 D^2}{16b}
\]

\[
Z' = f(x') = f\left(\frac{t}{2D}\right)
\]

\[
= (1 + x)\ln(1 + x) - x\ln(x)
\]

The uncorrected value of \(\epsilon'\) will be too high. This formula will over-correct the dielectric constant, i.e. give a value less than the true value, since it assumes that the entire top plate is surrounded by the dielectric. Since the edge correction remains approximately independent of thickness, it becomes, on a percentage basis, smaller, the smaller the thickness. Thus this formula places a lower limit on the edge effect error.

Scott and Curtis also give an empirical formula for
dielectric constant

\[ K = \frac{C - \frac{D}{30} \ln \frac{3.8}{b}}{C_n + 0.0405 \pi D} \]  

(2)

where the symbols in (2) are the same as in (1).

This formula was developed for tinfoil electrodes 11 cm. in diameter and a thickness of .003 cm. The values obtained from (1) and (2) were compared using a slightly modified experimental arrangement. Instead of the steel electrode, foil electrodes .004 cm. in thickness and 11.04 cm. in diameter were used and the values obtained compared with those from the steel plate arrangement. Since none of the 15 minute cure stock was left, some new 20 minute cure stock was used.

The steel plate arrangement gave a value for \( \epsilon' \) of 2.94 at 400 cycles using formula (1). (This is higher than the value 2.90 obtained from the 15 minute cure, due possibly to higher moisture content, inherent variations in stock, or greater sulphur combination). The 11 cm. foil electrode gave a value 3.01, using formula (2). Thus we see that (1) over-corrects by about 2%. The sample contracts too much upon stretching to allow the intercomparison of (1) and (2) for smaller thicknesses. The over-correction would be less and may be estimated to be 1%.

The values of \( \epsilon' \) submitted in the graphs are left over-corrected since any other evaluation of the data might give under-corrected values and cast some doubt on the negative change of \( \epsilon' \) with stretch which was observed at 25°C. If 1% relative accuracy is desired, an investigation of the
edge effect for the particular electrode configuration used, will have to be undertaken.

IV. RESULTS

A. Tables and Graphs
<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>$f$</th>
<th>$C_1$</th>
<th>$D_1Q_1G_1$</th>
<th>$C_2$</th>
<th>$D_2Q_2G_2$</th>
<th>$C$</th>
<th>$C-4.3$</th>
<th>$\varepsilon'$</th>
<th>D.F.%</th>
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<td>13.05</td>
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<td>161.7</td>
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<td>2.88</td>
<td>.55</td>
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<td>13.00</td>
<td>50</td>
<td>354</td>
<td>Q1 75</td>
<td>280</td>
<td>Q2 68</td>
<td>74</td>
<td>70</td>
<td>2.90</td>
<td>.75</td>
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<td>.1 m.c.</td>
<td>462</td>
<td>128</td>
<td>389</td>
<td>108</td>
<td>73</td>
<td>69</td>
<td>2.86</td>
<td>1</td>
</tr>
<tr>
<td>5.36</td>
<td>4</td>
<td>274</td>
<td>170</td>
<td>202</td>
<td>110</td>
<td>72</td>
<td>68</td>
<td>2.82</td>
<td>1.4</td>
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<td>515.2</td>
<td>G1 0</td>
<td>443.8</td>
<td>G2 8</td>
<td>71.4</td>
<td>67.1</td>
<td>2.79</td>
<td>1.9</td>
</tr>
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<td>= .195 cm.</td>
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<td>536.0</td>
<td>0</td>
<td>414.7</td>
<td>116</td>
<td>71.3</td>
<td>67</td>
<td>2.75</td>
<td>2.8</td>
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</table>

$C =$ Capacity in uuf  
$D =$ Dissipation factor  
$Q = \frac{1}{D} $  
$G =$ Conductance in u mhos.
### TABLE II

**Date:** February 3, 1947  
**Sample II:** Natural gum stock 2\% sulphur  
**Unstretched.**  
**Room temperature 25°C**

<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>f</th>
<th>C₁</th>
<th>D₁Q₁G₁</th>
<th>C₂</th>
<th>D₂Q₂G₂</th>
<th>C</th>
<th>C-4.3</th>
<th>ε'</th>
<th>D.F. %</th>
</tr>
</thead>
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<td>12.99</td>
<td>.4 k.c.</td>
<td>235.1</td>
<td>D₁=.015</td>
<td>160.4</td>
<td>D₂ .20</td>
<td>74.7</td>
<td>70.3</td>
<td>2.89</td>
<td>.37</td>
</tr>
<tr>
<td>13.03</td>
<td>1</td>
<td>235.1</td>
<td>-.03</td>
<td>160.6</td>
<td>.06</td>
<td>74.5</td>
<td>70.2</td>
<td>2.89</td>
<td>.38</td>
</tr>
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<td>4</td>
<td>235.1</td>
<td>-.022</td>
<td>160.7</td>
<td>0</td>
<td>74.4</td>
<td>70.1</td>
<td>2.88</td>
<td>.38</td>
</tr>
<tr>
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<td>10</td>
<td>235.4</td>
<td>-.018</td>
<td>161.2</td>
<td>-.005</td>
<td>74.2</td>
<td>69.9</td>
<td>2.87</td>
<td>.56</td>
</tr>
<tr>
<td>13.02</td>
<td>50</td>
<td>354</td>
<td>Q₁ 76</td>
<td>280</td>
<td>Q₂ 70</td>
<td>74</td>
<td>70</td>
<td>2.88</td>
<td>.65</td>
</tr>
<tr>
<td>13.03</td>
<td>.1 m.c.</td>
<td>463</td>
<td>128</td>
<td>390</td>
<td>110</td>
<td>73</td>
<td>69</td>
<td>2.85</td>
<td>.89</td>
</tr>
<tr>
<td>- 5.38</td>
<td>.5</td>
<td>160</td>
<td>188</td>
<td>86</td>
<td>99</td>
<td>72</td>
<td>68</td>
<td>2.80</td>
<td>1.3</td>
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<tr>
<td>7.65</td>
<td>1</td>
<td>509.0</td>
<td>G₁ 0</td>
<td>437.3</td>
<td>G₂ 7.5</td>
<td>71.7</td>
<td>67.4</td>
<td>2.78</td>
<td>1.8</td>
</tr>
<tr>
<td>t = 7.65 x 10⁻² in.</td>
<td>10</td>
<td>514.8</td>
<td>0</td>
<td>443.3</td>
<td>110</td>
<td>71.5</td>
<td>67.2</td>
<td>2.74</td>
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</table>

\[ C = \text{Capacity in uuf} \quad D = \text{Dissipation factor} \quad Q = \frac{1}{D} \quad G = \text{Conductance in u mhos.} \]
### TABLE III

**Date:** February 20, 1947  
**Sample I:** Natural gum stock, 2% sulphur.  
**Unstretched 68°C**

<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>f</th>
<th>$C_1$</th>
<th>$D_1Q_{1G_1}$</th>
<th>$C_2$</th>
<th>$D_2Q_{2G_2}$</th>
<th>$C$</th>
<th>$C-4.3$</th>
<th>$\varepsilon$</th>
<th>D.F.%</th>
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<tr>
<td>14.15</td>
<td>.4 k.c.</td>
<td>235.5</td>
<td>-0.016</td>
<td>163.4</td>
<td>$D_2$ .30</td>
<td>72.1</td>
<td>67.8</td>
<td>2.84</td>
<td>.55</td>
</tr>
<tr>
<td>14.10</td>
<td>1</td>
<td>235.5</td>
<td>-0.035</td>
<td>163.5</td>
<td>.08</td>
<td>72.0</td>
<td>67.7</td>
<td>2.84</td>
<td>.50</td>
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<td>14.20</td>
<td>4</td>
<td>235.5</td>
<td>-0.020</td>
<td>163.8</td>
<td>.002</td>
<td>71.7</td>
<td>67.4</td>
<td>2.82</td>
<td>.38</td>
</tr>
<tr>
<td>14.18</td>
<td>10</td>
<td>235.8</td>
<td>-0.015</td>
<td>164.2</td>
<td>-0.005</td>
<td>71.6</td>
<td>67.3</td>
<td>2.82</td>
<td>.43</td>
</tr>
<tr>
<td>14.20</td>
<td>50</td>
<td>354</td>
<td>$Q_1$</td>
<td>73</td>
<td>283</td>
<td>$Q_2$</td>
<td>68</td>
<td>71</td>
<td>67</td>
</tr>
<tr>
<td>14.16</td>
<td>.1 m.c.</td>
<td>463</td>
<td>125</td>
<td>392</td>
<td>112</td>
<td>71</td>
<td>67</td>
<td>2.81</td>
<td>.70</td>
</tr>
<tr>
<td>14.17</td>
<td>5</td>
<td>159</td>
<td>185</td>
<td>89</td>
<td>120</td>
<td>70</td>
<td>66</td>
<td>2.76</td>
<td>.89</td>
</tr>
<tr>
<td>- 6.43</td>
<td>1</td>
<td>520.0</td>
<td>$G_1$</td>
<td>0</td>
<td>450.7</td>
<td>$G_{24.5}$</td>
<td>69.3</td>
<td>65.0</td>
<td>2.72</td>
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<tr>
<td></td>
<td>3</td>
<td>170.2</td>
<td>0</td>
<td>101.9</td>
<td>20</td>
<td>68.3</td>
<td>64.0</td>
<td>2.68</td>
<td>1.6</td>
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<tr>
<td>$t = 7.74 \times 10^{-2}$ in.</td>
<td>10</td>
<td>500.8</td>
<td>0</td>
<td>432.1</td>
<td>84</td>
<td>68.7</td>
<td>64.4</td>
<td>2.66</td>
<td>2.1</td>
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</table>

$t = 7.74 \times 10^{-2}$ in. = .197 cm.

C = Capacity in uuf  
D = Dissipation factor  
$Q = \frac{1}{D}$  
G = Conductance in u mhos.
## TABLE IV

Date: February 25, 1947.  
Sample II: Natural gum stock, 2% sulphur.  
Unstretched.  
68°C.

<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>f</th>
<th>C_1</th>
<th>D_1G_1</th>
<th>C_2</th>
<th>D_2G_2</th>
<th>C</th>
<th>C-4.3</th>
<th>ε'</th>
<th>D.F.%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>.4</td>
<td>235.5</td>
<td>-016</td>
<td>162.7</td>
<td>.29</td>
<td>72.8</td>
<td>68.5</td>
<td>2.84</td>
<td>.54</td>
</tr>
<tr>
<td>14.52</td>
<td>1</td>
<td>235.5</td>
<td>.035</td>
<td>162.8</td>
<td>.07</td>
<td>72.7</td>
<td>68.4</td>
<td>2.84</td>
<td>.48</td>
</tr>
<tr>
<td>14.57</td>
<td>4</td>
<td>235.5</td>
<td>.020</td>
<td>163.0</td>
<td>.002</td>
<td>72.5</td>
<td>68.2</td>
<td>2.83</td>
<td>.39</td>
</tr>
<tr>
<td>14.45</td>
<td>10</td>
<td>235.8</td>
<td>-.015</td>
<td>163.5</td>
<td>-.005</td>
<td>72.3</td>
<td>68.0</td>
<td>2.82</td>
<td>.42</td>
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<tr>
<td>14.50</td>
<td>50</td>
<td>354</td>
<td>100</td>
<td>282</td>
<td>Q_1</td>
<td>73</td>
<td>282</td>
<td>2.82</td>
<td>.6</td>
</tr>
<tr>
<td>14.50</td>
<td>.1</td>
<td>462</td>
<td>124</td>
<td>390</td>
<td>112</td>
<td>72</td>
<td>68</td>
<td>2.82</td>
<td>.7</td>
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<tr>
<td>14.60</td>
<td>5</td>
<td>158</td>
<td>186</td>
<td>87</td>
<td>123</td>
<td>71</td>
<td>67</td>
<td>2.78</td>
<td>.88</td>
</tr>
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<td>0</td>
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<td>69.9</td>
<td>65.6</td>
<td>2.72</td>
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<td>0</td>
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<td>2.0</td>
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</table>

\( t = 7.72 \times 10^{-2} \) in.  
\( = .196 \) cm.

C = Capacity in uuf  
D = Dissipation factor  
\( Q = \frac{1}{D} \)  
G = Conductance in u mhos.

35
**TABLE V**

Date: March 5, 1947.
Sample II: Natural gum stock, 2% sulphur.

Stretched 280%.
Room temperature 25°C.

<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>f</th>
<th>C₁</th>
<th>D₁Q₁G₁</th>
<th>C₂</th>
<th>D₂Q₂G₂</th>
<th>C₁</th>
<th>C-4.3</th>
<th>ε'</th>
<th>D.F.%</th>
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</thead>
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<tr>
<td>8.71</td>
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<td>235.2</td>
<td>D₁-.02</td>
<td>111.9</td>
<td>D₂ .43</td>
<td>123.3</td>
<td>119.0</td>
<td>2.83</td>
<td>.45</td>
</tr>
<tr>
<td>4.47</td>
<td>4</td>
<td>235.2</td>
<td>-.02</td>
<td>108.3</td>
<td>.45</td>
<td>126.9</td>
<td>122.6</td>
<td>2.84</td>
<td>.46</td>
</tr>
<tr>
<td>4.24</td>
<td>1</td>
<td>235.2</td>
<td>-.025</td>
<td>112.2</td>
<td>.13</td>
<td>123.0</td>
<td>118.7</td>
<td>2.83</td>
<td>.39</td>
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<tr>
<td>3.19</td>
<td>4</td>
<td>235.2</td>
<td>-.02</td>
<td>112.4</td>
<td>.02</td>
<td>122.8</td>
<td>118.5</td>
<td>2.82</td>
<td>.40</td>
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<tr>
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<td>10</td>
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<td>-.015</td>
<td>112.8</td>
<td>.005</td>
<td>122.7</td>
<td>118.4</td>
<td>2.81</td>
<td>.50</td>
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<td>10.60</td>
<td>50</td>
<td>357</td>
<td>Q₁ 76</td>
<td>235</td>
<td>Q₂ 65</td>
<td>122</td>
<td>118</td>
<td>2.81</td>
<td>.77</td>
</tr>
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<td>6.39</td>
<td>.1 m.c.</td>
<td>461</td>
<td>130</td>
<td>340</td>
<td>96</td>
<td>121</td>
<td>117</td>
<td>2.79</td>
<td>1.2</td>
</tr>
<tr>
<td>4.21</td>
<td>.5</td>
<td>157</td>
<td>190</td>
<td>37</td>
<td>72</td>
<td>120</td>
<td>116</td>
<td>2.76</td>
<td>1.6</td>
</tr>
<tr>
<td>t = 4.20 x 10⁻² in.</td>
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<td>G₁ 0</td>
<td>422.2</td>
<td>G₂ 16</td>
<td>118.8</td>
<td>114.5</td>
<td>2.73</td>
<td>2.2</td>
</tr>
<tr>
<td>= .1065 cm.</td>
<td>3</td>
<td>265.0</td>
<td>0</td>
<td>146.5</td>
<td>60</td>
<td>118.5</td>
<td>114.2</td>
<td>2.72</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>260.2</td>
<td>0</td>
<td>137.1</td>
<td>65</td>
<td>123.1</td>
<td>118.8</td>
<td>2.74</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>479.6</td>
<td>0</td>
<td>360.4</td>
<td>250</td>
<td>119.2</td>
<td>114.9</td>
<td>2.71</td>
<td>3.5</td>
</tr>
</tbody>
</table>

* Sample I: Stretched 300%.
Room temperature 25°C.

C = Capacity in uuf
D = Dissipation factor
Q = \( \frac{1}{D} \)
G = Conductance in u mhos.
TABLE VI

Date: March 11, 1947.
Sample I: Natural gum stock, 2\% sulphur. Stretched 300\%.

<table>
<thead>
<tr>
<th>Det. of Thickness</th>
<th>f</th>
<th>C₁</th>
<th>(D₁G₁)</th>
<th>C₂</th>
<th>(D₂G₂)</th>
<th>C</th>
<th>C-4.3</th>
<th>ε'</th>
<th>D.F.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.96</td>
<td>.4 k.c.</td>
<td>235.5</td>
<td>-.015</td>
<td>109.7</td>
<td>.40</td>
<td>125.8</td>
<td>121.5</td>
<td>2.88</td>
<td>.41</td>
</tr>
<tr>
<td>2.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>1</td>
<td>235.5</td>
<td>-.033</td>
<td>109.8</td>
<td>.11</td>
<td>125.7</td>
<td>121.4</td>
<td>2.88</td>
<td>.36</td>
</tr>
<tr>
<td>4.40</td>
<td>4</td>
<td>235.5</td>
<td>-.018</td>
<td>111.2</td>
<td>.017</td>
<td>125.3</td>
<td>121.0</td>
<td>2.87</td>
<td>.36</td>
</tr>
<tr>
<td>4.14</td>
<td>10</td>
<td>235.8</td>
<td>-.015</td>
<td>111.0</td>
<td>.005</td>
<td>124.8</td>
<td>120.5</td>
<td>2.86</td>
<td>.5</td>
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<td>4.26</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.08</td>
<td>1 m.c.</td>
<td>510.1</td>
<td>0</td>
<td>387.6</td>
<td>12.5</td>
<td>122.5</td>
<td>118.2</td>
<td>2.80</td>
<td>1.7</td>
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<tr>
<td>3.85</td>
<td>3</td>
<td>269.3</td>
<td>0</td>
<td>147.1</td>
<td>45</td>
<td>122.2</td>
<td>117.9</td>
<td>2.79</td>
<td>2</td>
</tr>
<tr>
<td>4.13</td>
<td>10</td>
<td>501.0</td>
<td>0</td>
<td>378.2</td>
<td>176</td>
<td>122.8</td>
<td>118.5</td>
<td>2.78</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\[ t = 4.18 \times 10^{-2} \text{ in.} \]
\[ = .106 \text{ cm.} \]

C = Capacity in uuf  \quad D = \text{Dissipation factor}  \quad Q = \frac{1}{D}  \quad G = \text{Conductance in u mhos.}

37.
Fig. 7

○ unstretched rubber 25°C  ● unstretched rubber 68°C

Fig. 8

○ unstretched rubber 25°C  ● stretched (280%) rubber 25°C

$F = \text{Frequency}$  $DF = \text{Dissipation Factor}$

$\varepsilon' = \text{Dielectric Constant}$
Fig. 9

- ○ unstretched rubber 68°C
- • stretched (300%) rubber 68°C

Fig. 10

- ○ stretched (280%) rubber 25°C
- • stretched (300%) rubber 68°C
B. Discussion of Results

The results presented in the preceding tables and graphs are for natural gum stock, prepared by the Physical Testing Laboratory of the Polymer Corporation. The recipe for the stock was that used by Lawrence and Wood\(^1\).

<table>
<thead>
<tr>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoked Sheet</td>
</tr>
<tr>
<td>Sulphur</td>
</tr>
<tr>
<td>Zinc Oxide</td>
</tr>
<tr>
<td>Zinc Dibutyldithiocarbamate</td>
</tr>
<tr>
<td>(Cured 15 minutes at 292°F)</td>
</tr>
</tbody>
</table>

The tables give the results for two samples. Any difference between the data from the two samples is well within the limits of experimental error. (cf. Tables I and II). Data on only one sample is given for 300% and 68°C since the rest of the samples available at the time of the measurements, broke under those conditions of strain and temperature. There was no permanent deformation (set) observable in the samples when returned to 0% stretch from 300% stretch at 25°C and no measureable change in electrical characteristics from the initial unstretched state. A permanent set of about 2% was observed in the samples returned to 0% and 25°C from 300% and 68°C. There was a slight general decrease in \(f'\) and dissipation factor upon return to initial conditions, but this may have been caused by the drying out of the rubber at 68°C or

by the absorption of the small amount of petroleum jelly applied under the foil electrodes.

We may summarize the results as follows:

(a) The dielectric constant of our unstretched gum stock is lower at 68°C than at 25°C (Fig. 7). The loss peak seems to be shifted up the frequency scale by an increase in temperature.

The decrease in dielectric constant is understandable under the assumption that dipoles are present in vulcanized rubber, and that these are kindered in their orientation at high temperature by the random motion of the molecules. If the lowering of the loss peak leaves the position of the maximum unchanged (which cannot be observed without a larger frequency range), the relative decrease in losses can be explained in the same way. A shift of the maximum toward higher frequencies would indicate a decrease in the relaxation time due possibly to changes in viscosity, either because of volume expansion or changes in structure.

(b) The dielectric constant decreases (Fig. 8) and the slope of the loss peak is increased if rubber be stretched 300% at 25°C.

Again the dielectric constant falls because of the hindrance the dipoles experience through the orientation and crystallization (page 2) in a direction normal to the electric field brought about by stretch. The loss curve of stretched rubber at 25°C shows a behaviour contrasting with that in Fig. 7 for unstretched material at 68°C. Now the losses are
increased for equal frequencies in the range observed. The likely explanation will be that, by stretching, structural changes are made which shift the peak to the left (the maximum is brought towards lower frequencies); i.e. the relaxation time is increased because the extended molecules exert greater friction on each other.

(c) In Fig. 9 stretched and unstretched rubber is compared both at 68°C. The dielectric constant curve is shifted to higher values by stretching. The loss curve, however, shows the same behaviour as before (Fig. 8).

Here we must determine the result of our overcorrection of edge effect. (See page 29). Comparison of unstretched and stretched material makes the application of different percentage corrections necessary, because with stretch the thickness of the samples is reduced to about one half. The overcorrection for the unstretched sample is (page 30) between 2 and 3%, whereas for the stretched sample it is only about 1 to 2%.

Comparing the dielectric constant curves in Fig. 8, the corrections, e.g. of the first point on the left, will make the dielectric constant increase; for the lower point from 2.83 (overcorrected) (+ 0.04) to 2.87 (correct) and for the higher point 2.9 (overcorrected) to 2.98, leaving a difference of 0.11. If the same corrections are applied to the dielectric constant curves in Fig. 9, the higher point (stretched) is increased from 2.88 to 2.92 (adding, as before, 0.04), and the lower point is increased from 2.84 (+ 0.08) to
2.92, and we get a difference 0. This would mean that at 68° stretching has no or very little effect on the dielectric constant, at least for the lower frequencies.

The change in the loss curve at 68° is in the same direction as for 25°.

(d) In Fig. 10 we compare the curve for stretched material at temperatures 68°C and 25°C. No edge correction is necessary because the material has approximately the same thickness in both these cases. The dielectric constant increases apparently with temperature in the stretched material, and the losses are smaller for the higher temperature.

The result on the dielectric constant is opposite to the expectation under the dipole theory, and there must be another influence which brings this result about. Stretching at 25° (room temperature) causes orientation and crystallization (page 2). The orientation of the dipoles is lost at higher temperature, and the dielectric constant should, therefore, be lowered. The crystals will melt when the temperature is raised from 25 to 68°, that means the number of free dipoles is increased, which would explain the increase in the dielectric constant.

A further discussion seems to be only worthwhile on basis of more experimental data.

The experimental results make no claim to a higher degree of accuracy of dielectric constant than 3% and of dissipation factor than 10%. The necessity of a study of the edge effect has already been pointed out. Surface irregulari-
ties prove to be a source of difficulties, especially for the smaller thicknesses, although this effect could be eliminated by using thicker samples and by carefully preparing and selecting the specimens. The advantages of a wider frequency range are obvious.

It would prove interesting to measure the dielectric constant and dissipation factor over the complete range of temperature and stretch and attempt to correlate the results with data on percentage crystallization and melting point temperatures obtained from stress-strain and X-ray observations. The effects at below zero temperatures should also be investigated.

One may also vary the natural gum stock by changing the amount of combined sulphur and the type and quantity of loading. The above mentioned line of investigation must also be followed in the case of each of the commoner synthetic rubbers.


V. BIBLIOGRAPHY

Books:
5. Van Vleck, J.H., Theory of Electric and Magnetic Susceptibilities, Oxford University Press.

Papers:


