

LE3 B7
1948 A8
C6 D4
cop.1

THE DIELECTRIC PROPERTIES OF NATURAL AND SYNTHETIC
RUBBER-SULPHUR COMPOUNDS

by

Robert Smith Codrington

A Thesis submitted in partial fulfilment of
the requirements for the degree of
MASTER OF ARTS
in the department
of
PHYSICS

Approved
April 19/48

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1948

ABSTRACT

The dielectric properties of natural and butyl rubber-sulphur compounds have been investigated at temperatures of 20°C and 60°C and extensions of 0% and 200%, in a frequency range extending from 100 cycles to 20 megacycles. This investigation has shown that the dielectric constant of butyl rubber is less than that of natural rubber and that the dielectric constants of both types of rubber decrease with increasing temperature and increasing extension.

The investigation has also shown that the dielectric behaviour of these rubbers may be explained by the Gevers' extension of the Debye dipole theory. If free sulphur is present in the rubbers, the behaviour must be explained by a combination of the dipole theory and the inhomogeneity theory.

The Kirkwood-Fuoss theory for polar polymers, has been applied to natural rubber with 2% sulphur. The dipole moment per monomer unit obtained from the Kirkwood-Fuoss plot for this sample was 0.41 Debye units.

ACKNOWLEDGEMENT

This work was carried out with the aid of a research grant to Dr. O. Blüh from the Associate Committee on Synthetic Rubber of the National Research Council of Canada.

The author wishes to thank Dr. O. Blüh for his many helpful suggestions, and for his constant interest in the progress of the work.

This investigation is a continuation of the work of Mr. L. V. Holroyd to whom the author is indebted for several valuable suggestions. The author is also indebted to the Research Division of the Polymer Corporation for the samples they have prepared for this research.

The author wishes to express his appreciation to the National Research Council of Canada for the Studentship for 1947/48 which has enabled him to complete this work.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	
1. General Introduction	1
2. Properties of Natural Rubber	2
3. Properties of Butyl Rubber	5
4. Properties of Stretched Rubber	7
II. THEORY OF DIELECTRICS	
1. Definition of the Terms	8
2. The Maxwell-Wagner Theory	9
3. The Debye Theory	10
4. Summary	14
III. APPARATUS	
1. The Measuring Instruments	15
2. Description of the Apparatus	15
IV. EXPERIMENTAL PROCEDURE	
1. General Procedure	21
2. Measurement of the Sample Thickness	23
3. Edge Correction	24
4. Correction for Lead Impedence	25
V. RESULTS	
1. Composition of the Samples	28
2. Tables and Graphs	29
3. Discussion of the Results	37
VI. CONCLUSION	44
VII. BIBLIOGRAPHY	45

PLATES

	Page
I. The Standard Cell	17
II. Front View of the Apparatus	18
III. The Measuring Instruments	19
IV. Cross-section of the Apparatus	20
V. Correction for the Twin-T Bridge	27
VI. Results for Natural Rubber 2% S	31
VII. Results for Natural Rubber 10% S	32
VIII. Results for Natural Rubber 15% S	33
IX. Results for Butyl Rubber 2% S	34
X. Results for Butyl Rubber 4% S	35
XI. Results for Butyl Rubber 10% S	36
XII. Debye and Maxwell-Wagner Curves	40
XIII. Kirkwood-Fuoss Plots for Sample 1-A	41

THE DIELECTRIC PROPERTIES OF NATURAL AND SYNTHETIC RUBBER-SULPHUR COMPOUNDS

I. INTRODUCTION

1. GENERAL INTRODUCTION

The dielectric constant (ϵ') and the dissipation factor ($\tan \delta$) have been shown to be intimately related to the molecular constants of dielectrics. An investigation of the dielectric properties of rubber may therefore provide information which will indicate the structure of the rubber molecule.

The terms "rubber" and "elastomer" are now generally applied to any substance showing the characteristic physical properties of long-range reversible elasticity and anomolous thermoelastic behaviour. This definition may be applied to any substance regardless of its chemical composition. However, the majority of natural and synthetic rubbers have now been shown to be long chain polymers of hydrocarbon groups.

The term polymer refers to a chemical valence combination of small molecules called "monomers" into a large

molecule called a "macromolecule". A copolymer is a substance which has macromolecules composed of two or more different monomers. When the macromolecules are composed of 100 or more monomers the substance is referred to as a high polymer.

2. PROPERTIES OF NATURAL RUBBER

X-ray and chemical analysis have shown that natural rubber is a high polymer composed of isoprene monomers in a cis configuration (see Fig. 1).

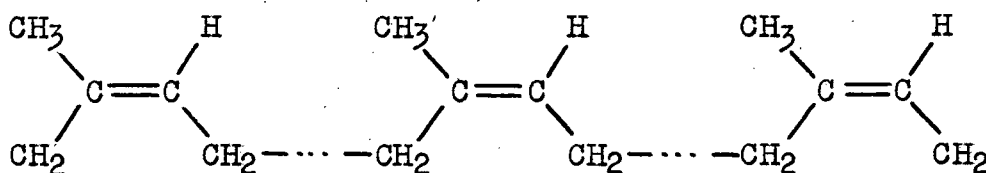


Figure 1.

The number of monomer units composing the macromolecule is believed to be between 2000 and 4000.

James and Guth¹⁾ have shown that a quasi-free rotation about a single carbon-carbon bond in long chain molecules, is sufficient for the development of rubberlike elasticity. This free rotation is responsible for the dielectric losses in vulcanized rubber since it will allow the rubber-sulphur dipoles to follow the oscillations of the electric field.

Vulcanization may be defined to be any treatment which maintains the elasticity of the rubber but reduces its

¹⁾ H. James and E. Guth J. of Chem Phys. 11, 455, 1943.

plasticity. There are a number of vulcanization processes, the most common one being the combination of the rubber with sulphur which introduces rubber-sulphur dipoles into the rubber configuration.

The effect of vulcanization upon the dielectric properties of rubber has been investigated by Boggs and Blake¹⁾, Kitchin²⁾, and Scott Curtis and McPherson³⁾. These investigations show that the dielectric constant of rubber increases with increasing sulphur content and reaches a maximum value for 12% combined sulphur. Boggs and Blake have explained this behaviour by assuming that the sulphur is initially added to the end double bonds of the rubber macro-molecule. This first addition activates the adjacent double bonds which in turn may take on a sulphur atom and activate the next double bond. In this way, the combination with the sulphur proceeds progressively from the ends of the molecule towards the centre (see Fig. 2).

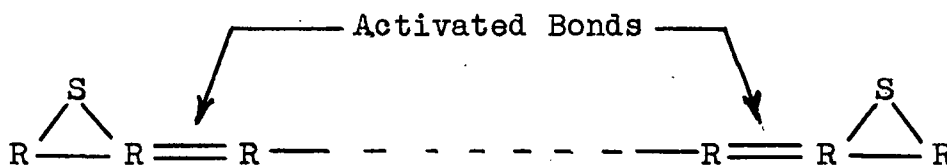


Figure 2.

The molecules of raw rubber are symmetrical and hence are non-polar. However, as sulphur is added the

-
- 1) C.R. Boggs and J.T. Blake Ind. and Eng. Chem 22, 748, 1930.
 2) D.W. Kitchin Ind. and Eng. Chem 24, 549, 1932.
 3) A. Scott H. Curtis and A. McPherson Bur. Stan., J. of Res. 11, 173, 1933.

dissymmetry of the molecule and hence the polarity of the molecule increases until half the double bonds are saturated with sulphur atoms. A further increase in the sulphur content increases the symmetry and hence decreases the polarity of the molecule.

This simple explanation of the dielectric behaviour of vulcanized rubber is complicated by the fact that the addition of sulphur not only alters the dipole moments of the individual molecules, but also changes the physical characteristics of their environment. In particular, Tuckett¹⁾ has suggested that vulcanization introduces cross-linkages between the rubber macromolecules creating intermolecular forces which oppose the free rotation of the dipoles.

The theory of Boggs and Blake does not attempt to explain the nature of the dissymmetry produced by the addition of the sulphur atoms, and it is questionable whether such a dissymmetry actually exists.

The author has suggested that the ϵ' and $\tan \delta$ maxima are due to the formation of the cross-linkages during vulcanization. The function²⁾ which relates the number of cross-linkages (ν) to the concentration of sulphur C_S is such that for $C_S < 12$, ν is small and for $C_S > 12$, ν is large. A small increase in C_S for $C_S < 12$ would therefore

1) R.F.Tuckett Trans.Faraday Soc. 38, 310, 1942.

2) H.James and E.Guth J.of Chem.Phys. 15, 669, 1947.

result in the formation of a large number of dipoles and relatively few cross-linkages, while an increase in C_s for $C_s > 12$ would result in the formation of a large number of cross-linkages and relatively few dipoles.

This explanation of the vulcanization process would therefore require the ϵ' and $\tan \delta$ maxima to occur at a value of C_s such that a small increase in C_s would result in the formation of equal numbers of cross-linkages and dipoles.

3. PROPERTIES OF BUTYL RUBBER

Butyl rubber is a copolymer of isobutylene with small amounts of a diolefin such as isoprene. The number of monomer units composing the butyl macromolecule is between 1200 and 2400. Rehner¹⁾ has shown that the isoprene monomers are distributed at regular intervals of 50 to 200 monomer units in the polyisobutylene chain.

A possible structure for butyl rubber is given in Fig. 3.

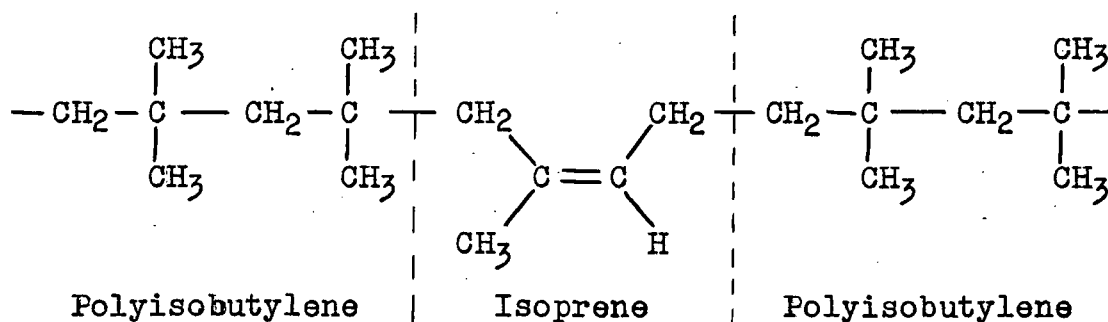


Figure 3.

¹⁾ J. Rehner Ind. and Eng. Chem. 36, 47, 1944.

The isobutylene monomer units contain no double bonds and as a result, are very stable. However when isoprene monomers are introduced into the chain, the molecule becomes less stable or "the degree of saturation" decreases.

The vulcanization of butyl rubber has not been extensively treated in the literature. Flory¹⁾ has shown that the number of cross-linkages between the butyl molecules is proportional to the number of isoprene monomer units in the macromolecule. Since the cross-linkages are formed during vulcanization, Flory's result implies that the sulphur only combines with the isoprene units.

This qualitative explanation of the vulcanization process in butyl rubber shows that there are relatively few rubber-sulphur dipoles formed during vulcanization. It shows, also, that the majority of the dipoles exist in the cross-linkages between the molecules where they are held more or less rigidly by the inter-molecular forces. It is therefore to be expected that the ϵ' and $\tan \delta$ for vulcanized butyl rubber will be less than the ϵ' and $\tan \delta$ for vulcanized natural rubber.

This result has been verified by the preliminary measurements of Sparks and his co-workers²⁾. However, a more thorough investigation of the dielectric properties of butyl rubber is necessary before any definite conclusions may be drawn.

1) P.J. Flory Rubber Chem. Tech. 19, 552, 1946.

2) W. Sparks, I. Lightbown, L. Turner, P. Frolich, and C. Klebattel Ind. and Eng. Chem 32, 731, 1944.

4. PROPERTIES OF STRETCHED RUBBER

X-ray analysis of stretched natural¹⁾ and butyl²⁾ rubbers have shown that for a given temperature there exists a critical extension above which crystals begin to form in the rubber. For example, in rubber at room temperature the crystals are formed if the extension exceeds 80%. This critical extension increases with temperature. For a given temperature, and for extensions above the critical value, the degree of crystallization is proportional to the extension.

If the dipoles form part of the crystal lattices the degree of free-rotation which may be assigned to them will be small. Hence the formation of crystals in the rubber will result in a decrease in ϵ' . This decrease has been observed in the case of natural rubber by Schiller³⁾ and Holroyd⁴⁾.

1) J.R.Katz Report to Symposium on Rubber; Delft, Oct. 1936.

2) R.Brill and F.Halle Rubber Chem.Tech. 11, 687, 1938.

3) L.Schiller Ann der Phys. 35, 931, 1911.

4) L.V.Holroyd Master's Thesis, U.B.C., May 1947.

II. THEORY OF DIELECTRICS

1. DEFINITION OF TERMS

In dielectric media the dielectric displacement \bar{D} is related to the electric field strength \bar{E} by the equation

$$\bar{D} = \epsilon \bar{E}$$

In the case of isotropic materials where these vectors are parallel

$$D = \epsilon E \quad (1)$$

If E represents an alternating electric field of the form,

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

where E_0 denotes a constant, ω denotes the frequency and t denotes the time, then

$$D = \epsilon E_0 e^{j\omega t} \quad (2)$$

Experimental results show that for most dielectric materials there is a small phase difference between D and E . Hence (2) becomes

$$D = \epsilon_0 E_0 e^{j(\omega t - \delta)}$$

or

$$D = (\epsilon_0 \cos \delta - j \epsilon_0 \sin \delta) E_0 e^{j\omega t} \quad (3)$$

Hence ϵ has the form

$$\epsilon = \epsilon' - j \epsilon'' \quad (4)$$

The real part of the expression (ϵ') is called the dielectric constant. The tangent of the phase angle,

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (5)$$

is referred to as the dissipation factor as it is a measure of the energy dissipated in the dielectric.

2. THE MAXWELL-WAGNER THEORY

In 1864 Von Siemens observed an increase in the temperature of dielectrics when they were placed in an alternating field. Hopkinson¹⁾ assumed that this temperature rise could be attributed to an after-effect of the displacement, and using a principle of superposition he worked out expressions for ϵ' and $\tan \delta$ in terms of an after-effect function $\phi(t)$

$$\epsilon' = \epsilon_{\infty} \left\{ 1 - \int_0^{\infty} \cos \omega t \frac{d\phi(t)}{dt} dt \right\} \quad (6)$$

$$\epsilon'' = -\epsilon_{\infty} \int_0^{\infty} \sin \omega t \frac{d\phi(t)}{dt} dt \quad (7)$$

Pellat²⁾ gave the after-effect function the form

$$\phi(t) = k e^{-t/\tau}$$

where k represented the total fractional dispersion of ϵ' and τ was a time constant called the relaxation time of the after-effect. Substituting for $\phi(t)$ in (6) and (7) gives;

$$\epsilon' = \epsilon_{\infty} \left(1 + \frac{k}{1 + \omega^2 \tau^2} \right) \quad (8)$$

$$\tan \delta = \frac{k \omega \tau}{1 + k + \omega^2 \tau^2} \quad (9)$$

These expressions were found to be too dependent

¹⁾ J. Hopkinson Phil. Trans. 166, 489, 1876.

²⁾ Pellat J. of Physics 9, 313, 1900.

upon the frequency and it was suggested by Von Schweidler¹⁾ that there should be a distribution of relaxation times $G(\tau)$. Wagner²⁾ assumed that $G(\tau)$ should be of Gaussian form; hence, replacing τ by $G(\tau)$ in (8) and (9) and integrating between zero and infinity gives,

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{\sqrt{\pi} \epsilon_{\infty}} \int_0^{\infty} \frac{e^{-(b \ln \tau / \bar{\tau})^2} \epsilon_{\infty}}{1 + \omega^2 \tau^2} d(b \ln \tau / \bar{\tau}) \quad (10)$$

$$\tan \delta = \frac{\epsilon_0 - \epsilon_{\infty}}{\epsilon_{\infty} \sqrt{\pi}} \int_0^{\infty} \frac{\omega \tau e^{-(b \ln \tau / \bar{\tau})^2}}{1 + \omega^2 \tau^2} d(b \ln \tau / \bar{\tau}) \quad (11)$$

where $\bar{\tau}$ denotes the mean relaxation time, and ϵ_0 and ϵ_{∞} are constants such that $\epsilon = \epsilon_0$ when $\omega = 0$ and $\epsilon = \epsilon_{\infty}$ when $\omega = \infty$

Equations (10) and (11) can also be derived by extending the two-layer inhomogeneity theory of Maxwell³⁾ to the case of an infinite number of spheres of one dielectric embedded in another dielectric. These equations satisfactorily predict the dielectric behaviour of such inhomogeneous mixtures: they do not, however, predict the dielectric behaviour of pure dielectrics.

3. THE DEBYE THEORY

A more fundamental theory of dielectrics was developed by Debye⁴⁾ who introduced the concepts of deformation and orientation polarizations. The deformation polarization

1) E. Von Schweidler Ann. der Phys. 24, 711, 1907.

2) K. W. Wagner Ann. der Phys. 40, 817, 1913.

3) C. Maxwell Electricity and Magnetism Vol. I, 328, Oxford.

4) P. Debye Polar Molecules, 1929, Chem. Catalogue Co.

(P_d) is attributed to dipoles which are formed when the dielectric is placed in an electric field. The formation of these dipoles results from the distortion of the electronic orbits within the atoms.

The orientation polarization (P_o) is attributed to permanent molecular dipoles which orientate themselves in the direction of the applied electric field. The rotation of these dipoles under the influence of the electric field is opposed by the thermal agitation of the molecules, and it is this opposition which gives rise to the dielectric loss.

Debye has shown that

$$P_o = \frac{4}{3} \pi N \alpha_o \quad (12a)$$

$$P_o = \frac{4 \pi N \mu^2}{9kT} \quad (12b)$$

where N = Avogadro's number, α_o = the polarizability of the molecule, μ = the dipole moment, k = Boltzman's constant, and T = the absolute temperature. The total polarization P which from the Clausius-Mosotti equation is,

$$P = \frac{\epsilon - 1}{\epsilon + 2} V$$

where V = the molar volume, is given by the sum of P_o and P_d . Hence

$$P = \frac{4}{3} \pi N (\alpha_o + \frac{\mu^2}{3kT}) \quad (13)$$

Equation (13) has the form

$$P = a + \frac{b}{T}$$

which for the variables P and $\frac{1}{T}$, is the equation of a straight

line with slope

$$b = \frac{4\pi N \mu^2}{3k} \quad (14)$$

The dipole moment μ of a substance may therefore be calculated from (14) since k and N are known constants and b may be determined from experimental results.

The Debye theory leads to equations for ϵ' and $\tan \delta$ which are identical to those of Pellat (equations (8) and (9)). However, in the Debye expressions the relaxation time τ refers to the time required for the dipoles to turn through $1/e^{\text{th}}$ of the angle between their directed position and their equilibrium position.

The Debye theory is not applicable to solids or viscous liquids as it does not consider the interaction of the dipoles. Debye¹⁾ and Yager²⁾ have attempted to extend the theory by postulating an interaction energy (q), and a Gaussian distribution of relaxation times. Both of these theories are restricted in their application to solids.

The dielectric behaviour of polymers has been predicted by the theories of Cole and Cole³⁾, and of Fuoss and Kirkwood⁴⁾. The latter theory requires a distribution of relaxation times such that there is a linear relationship between the logarithm of the frequency (ν) and the quantity

$$\psi(\epsilon', \epsilon'') = \cosh^{-1} \frac{\epsilon''_m (2 + 1/\epsilon'^2_m)}{\epsilon'' (2 + 1/\epsilon'^2)}$$

1) P. Debye Phys. Zeits 36, 100, 1935.

2) W. A. Yager Physics 7, 434, 1936.

3) R. Cole and K. Cole J. of Chem. Phys. 9, 341, 1941.

4) R. Fuoss and J. Kirkwood J. of Amer. Chem. Soc. 63, 385, 1941.

where ϵ''_m = maximum dielectric loss and ϵ'_m = the dielectric constant at the frequency of maximum loss.

In the case of polymers, μ^2 is replaced in (12b) by the product of the dipole moment of the isolated monomer μ , and $\bar{\mu}$ which is the vector sum of μ and the moment induced by the molecule in its environment. Substituting for μ^2 in (12b) gives;

$$P_0 = \frac{4 \pi N \mu \cdot \bar{\mu}}{9kT}$$

or $\mu \cdot \bar{\mu} = \frac{9 k T P_0}{4 \pi N}$ (16)

The polarization at zero frequency is given by,

$$P_0(0) = \frac{4 \epsilon''_m}{9 \alpha} V$$

where α is the slope of the straight line given by plotting $\psi(\epsilon', \epsilon'')$ against $\log \nu$. Substituting for P_0 in (16) gives

$$\mu \cdot \bar{\mu} = \frac{k T \epsilon''_m}{\alpha \pi N} V$$
 (17)

The dipole moment per monomer unit can be shown to be

$$\bar{\mu} = \sqrt{\frac{\mu \cdot \bar{\mu}}{n}}$$
 (18)

where n = the number of monomer units per molecule. Substituting for $\mu \cdot \bar{\mu}$ in (18) gives

$$\bar{\mu} = \sqrt{\frac{\epsilon''_m k T V}{\pi \alpha N n}}$$
 (19)

and since $V = nM/\rho$ where M = the molecular weight of the monomer unit and ρ = the density, (19) becomes,

$$\bar{\mu} = \sqrt{\frac{\epsilon''_m k T M}{\pi \alpha \rho N}}$$
 (20)

The Fuoss-Kirkwood theory has been extended by Gevers¹⁾ who considers a distribution of activation energies $G(q)$. The activation energy q is the energy supplied to the dipole to remove it from the potential well in which it normally exists. If $X(q)$ represents the static susceptibility of a dipole having an activation energy q , then;

$$\epsilon' = \epsilon_{\infty} + 4\pi N \int_0^{\infty} \frac{G(q) X(q)}{1 + \omega^2 \tau^2} dq \quad (21)$$

$$\tan \delta = \frac{1}{\epsilon'} 2\pi^2 N G(q_0) X(q_0) kT \quad (22)$$

where q_0 = the critical activation energy.

4. SUMMARY

There are two distinct types of dielectric phenomena; the type associated with inhomogeneous dielectrics and the type associated with polar dielectrics. The ϵ' and $\tan \delta$ of inhomogeneous dielectrics are given by equations (10) and (11) while the ϵ' and $\tan \delta$ of polar dielectrics are given by equations (21) and (22).

The $\tan \delta$ maxima associated with (11) are referred to as Maxwell-Wagner maxima while $\tan \delta$ maxima associated with (22) are referred to as Debye maxima. Schneider, Carter, Magat and Smyth²⁾ have shown that a dielectric may exhibit both types of $\tan \delta$ maxima.

¹⁾ N.V. Gevers Philips Res. Rep. 1, 298, 1946.

²⁾ W. Schneider, W. Carter, M. Magat, and C.P. Smyth J. Amer. Chem. Soc. 67, 959, 1945.

III. APPARATUS

1. THE MEASURING INSTRUMENTS

The measuring instruments used in the various frequency ranges were;

(a) 100 cycles to 15 M.c.

Schering Bridge - General Radio type 716-B
Oscillator - General Radio type 608-A
Null Detector - General Radio type 1231-A

(b) 50 K.c. to 1 M.c.

Q-meter - Boonton type 160-A

(c) 500 K.c. to 20 M.c.

Twin-T Impedance
Bridge - General Radio type 821-A
Signal Generator - General Radio type 805-C
Radio Detector - Hammarlund type HQ-129X

2. DESCRIPTION OF THE APPARATUS

The standard cell consisted of two stainless steel plates whose faces were ground flat to better than $1/1000^{\text{th}}$ of an inch. The lower plate (diameter = 5") was mounted rigidly on a maple block and was grounded to the copper shield surrounding the standard cell. The smaller top plate (diameter = 3") was held coaxially with the lower plate by a pyrex tube through which pressure from a 2 kilogram weight

was applied to the sample.

The top plate was connected to the measuring instruments with 1-1/2 feet of 1/2" silvered coaxial line. The connection at the top plate could be broken while the initial bridge balances were being made.

The thickness of the sample was measured with three Starrett dial micrometers type 25-T6 which were connected to the top plate by pyrex rods.

The rubber was held by two eccentric brass clamps (see Plate IV) which were moved in and out by motor-driven screws. The clamps were connected to the grounded copper shield surrounding the standard cell.

The insulated chamber containing the clamps and the standard cell (see Plate IV) was heated by a hot air circulating system. The temperature of the air could be held to within one degree of the desired temperature by the mercury thermostat (T) which controlled the power delivered to the heaters (H).

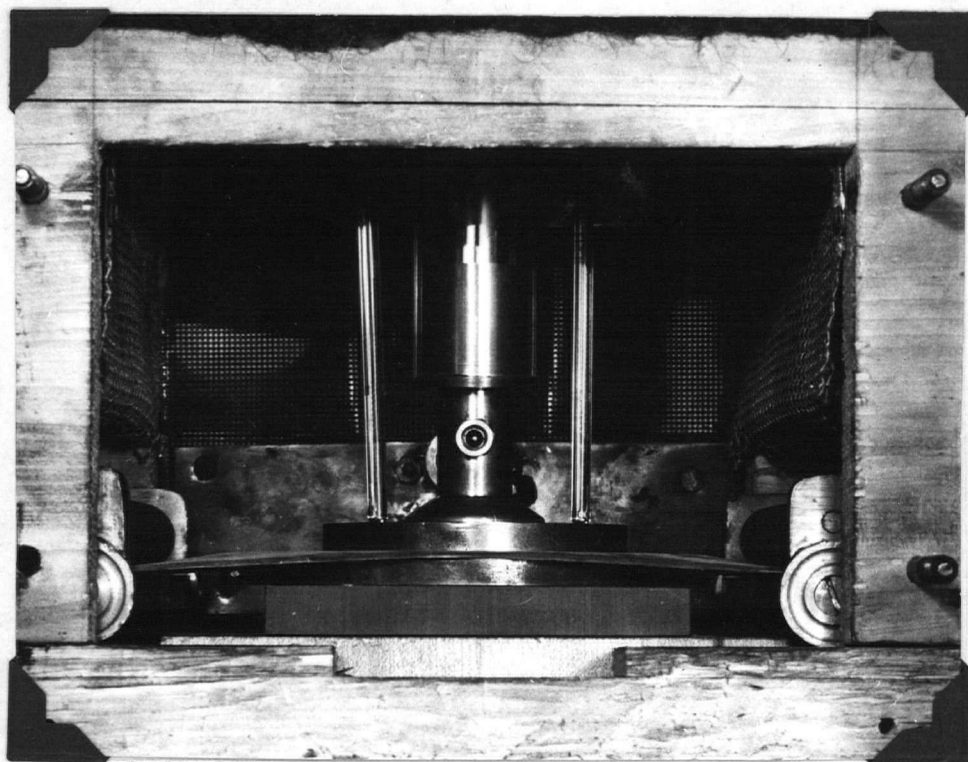


PLATE I
The Standard Cell

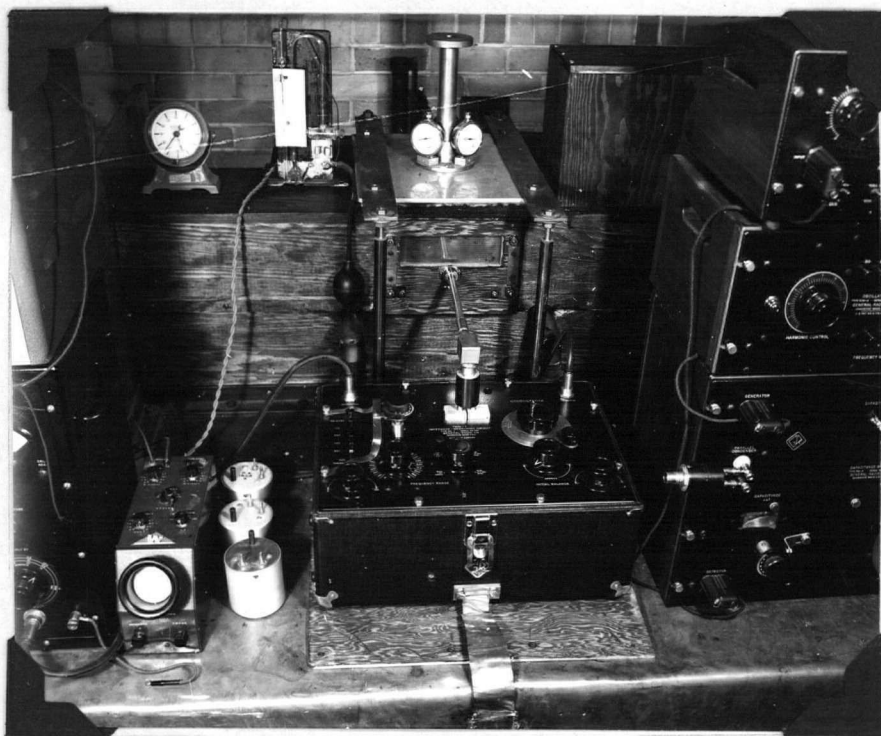


PLATE II

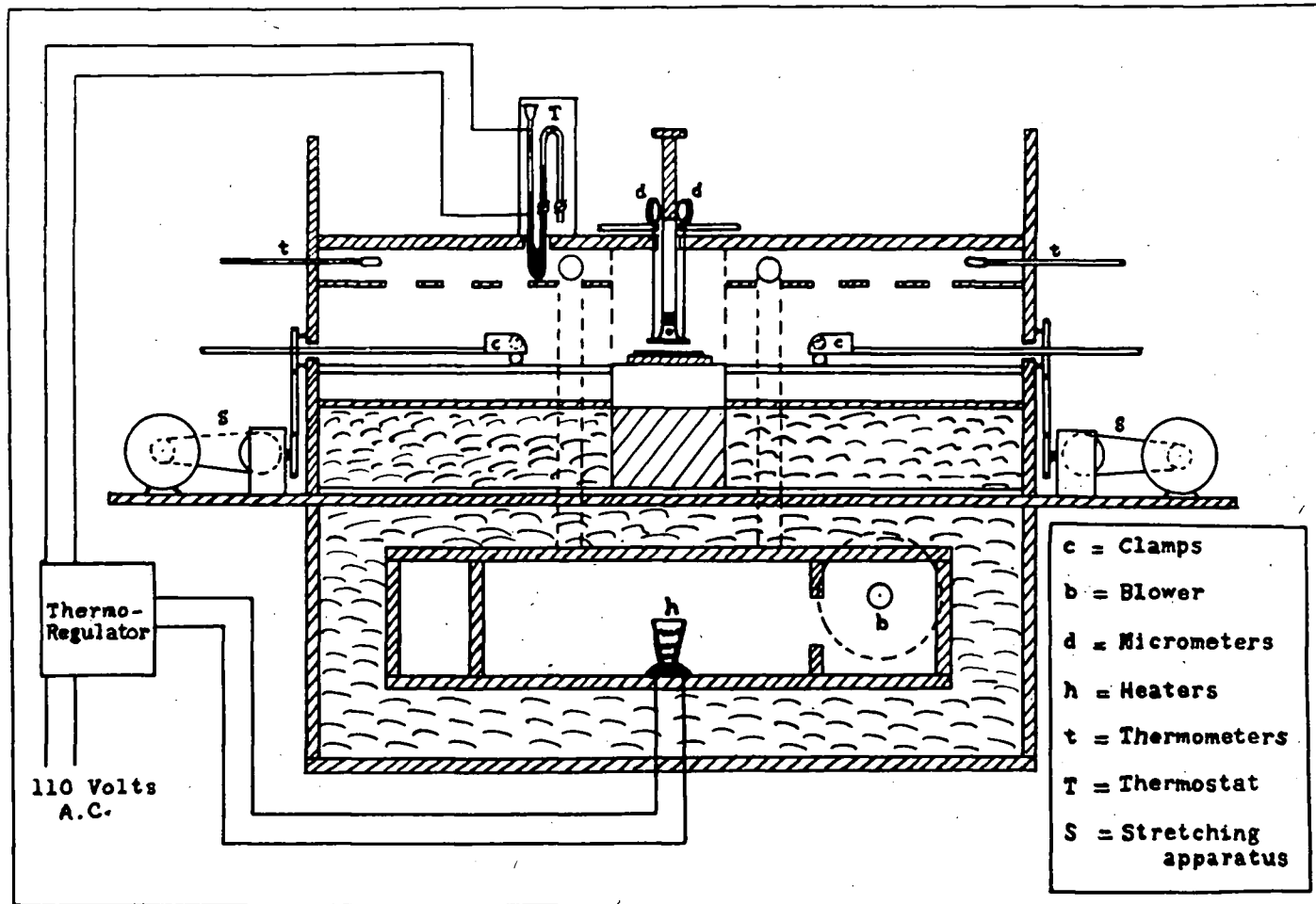
Front View of the Apparatus



PLATE III

The Measuring Instruments

PLATE IV
CROSS SECTION OF THE APPARATUS



IV. EXPERIMENTAL PROCEDURE

1. GENERAL PROCEDURE

The rubber samples were placed between the condenser plates and left under pressure for 24 hours before any readings were taken. It was found that after 24 hours the contact between the rubber and the electrodes was almost as good as was obtained by the foil-electrode method of Holroyd (ref. p. 7). The foil-electrode method was discarded as it was found that the petroleum jelly-carbon black mixture used to secure the electrode to the sample caused the rubber to swell slightly.

Measurement of the cell capacity (C_x) and the dissipation factor (D_x) in the various frequency ranges, were made in the following ways:

(a) 0.1 to 15 K.c.

The standard cell was connected in parallel with a standard condenser which formed one ratio arm of a balanced Schering bridge. The bridge was rebalanced with the standard condenser and a conductance condenser calibrated in terms of the dissipation factor. If C' and C are the initial and final settings of the standard condenser and if D' and D are the initial and final settings of the conductance condenser,

$$C_x = C' - C$$

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

(b) 50 to 700 K.c.

The standard cell was connected in parallel with a standard condenser forming the capacitative element of a tuned circuit. The circuit was re-tuned with the standard condenser, and the Q of the circuit was measured with a thermocouple voltmeter. If C' and C are the initial and final settings of the standard condenser, and if Q' and Q are Q 's of the circuit before and after the cell was connected into the circuit,

$$C_x = C' - C$$

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

(c) 0.5 to 20 M.c.

The standard cell was connected in parallel with a standard condenser in one section of a balanced parallel-T network. The network was then rebalanced with the standard condenser and a conductance condenser. If C'_b and C''_b are the initial and final settings of the standard condenser, and if G' and G are the initial and final settings of the conductance condenser, then since $G' = 0$

$$C_x = C'_b - C''_b$$

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

Before each set of readings were taken, a quantity of silica gel was placed in the circulating system in order

to keep the humidity as low as possible. In this way the relative humidity of the cell was kept below 40% at 20°C and below 35% at 60°C.

2. MEASUREMENT OF THE SAMPLE THICKNESS

The three Starrett dial micrometers were set to zero with the condenser plates clamped together. The sample was then placed between the plates and a slight pressure was applied. The thickness was then taken to be the mean of the three dial micrometer readings when both plates were making good contact with the sample. The thickness of the sample was also measured with an Ames soft material dial micrometer and a Gaertner cathetometer.

Changes in the sample thickness due to temperature and stress changes, were measured with the three dial micrometers. A correction term had to be subtracted from the measured thickness change since the bottom plate support and the dial micrometer mounting had different coefficients of expansion.

The correction was found by clamping the top and bottom plates together and plotting the mean dial reading (R) against the temperature (T) (see Fig. 4).

The correction for a given temperature change is found by subtracting the values of R corresponding to the initial and final temperatures.

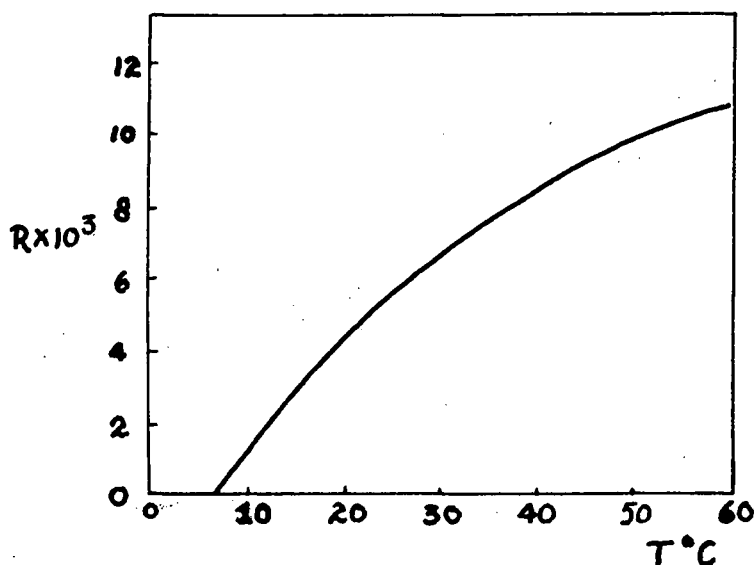


Figure 4.

3. EDGE CORRECTION

The edge correction was found by separating the standard cell plates with small quartz blocks of the same thickness, and measuring the capacity of the cell (C_X) with the 716-B bridge. The edge correction (C_e) is given by,

$$C_e = C_X - C_a$$

where C_a is the capacity of the cell calculated from Kirchoff's formula,

$$C_a = \frac{A}{4\pi d}$$

A = the area of the top plate, and d = the plate separation. The mean value of C_e found by this method was 4.3 $\mu\mu\text{f}$.

A number of pure paraffin samples of different thicknesses were prepared and the values of the edge correction of the cell containing the different samples was measured with the 716-B bridge. It was found that in the range of plate separations investigated, (0.8 to 2.5 mm.), the change

in the edge correction was less than 0.2 $\mu\mu\text{f}$. The edge correction was therefore assumed to be constant with respect to the plate separation.

The edge correction calculated from the empirical formula of Scott and Curtis¹⁾

$$C_e = 1.113 \frac{D}{4\pi} \left\{ \ln\left(\frac{4\pi D}{d}\right) - 3 + Z' \right\}$$

where D = diameter of the top plate of thickness t , d = plate separation, and Z' = a function of $t/2d$, was found to be 3.4 $\mu\mu\text{f}$. An additional correction due to the capacity of the top plate to the copper shield was calculated to be 0.7 $\mu\mu\text{f}$. The total correction is therefore 4.1 $\mu\mu\text{f}$ which is in agreement with the measured value of 4.3 $\mu\mu\text{f}$.

4. CORRECTION FOR LEAD IMPEDENCE

At high frequencies a coaxial line has an appreciable impedance. It was therefore found necessary to re-solve the twin-T network in order to obtain the null conditions when an impedance of the type shown in Fig. 5 was connected across the "unknown" terminals

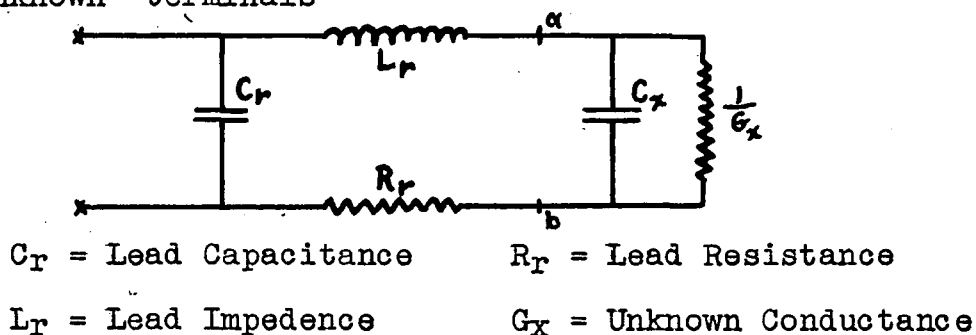


Figure 5.

¹⁾ A.H.Scott and H.L.Curtis Nat.Bur.Stan. J.of Res. 22, 747, 1939.

Actually the capacitance of a coaxial line should not be lumped at the input end. However, for the 1/2" silvered coax, this approximation is justified at frequencies below 25 M.c. At 25 M.c. the error involved is about 4%.

If the impedance in Fig. 5 is connected in parallel with the standard condenser of the twin-T, and if the initial balance is made with the circuit open at points a and b, the bridge equations become

$$C_X = (C_b' - C_b'') \{ 1 + L_T(C_b' - C_b'') \omega^2 \}^{-1} \quad (23)$$

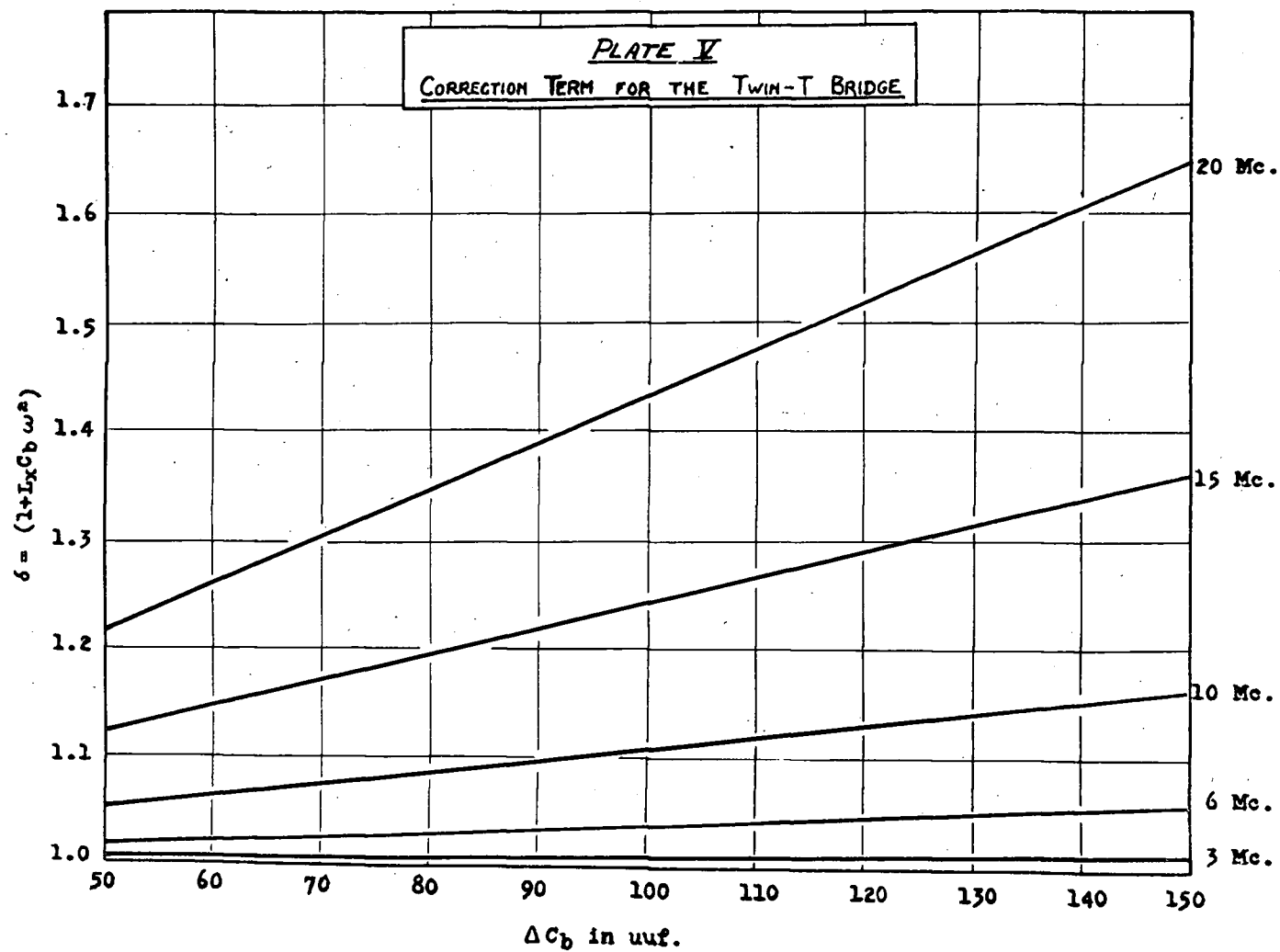
$$G_X = -R_T C_X^2 \omega^2 + (1 - L_T C_X \omega^2)^2 G \quad (24)$$

Since $G = 10^{-7}$, $C_X = 10^{-10}$, and $R_T = 0.08 \Omega$, the first term in (24) may be neglected. If $\delta = (1 + L_T C_b \omega^2)$ where $C_b = \Delta C_b = (C_b' - C_b'')$, and if $\gamma = (1 + L_T C_X \omega^2)$, equations (23) and (24) become

$$C_X = (C_b' - C_b'') \delta^{-1} \quad (25)$$

$$G_X = (2 - \gamma)^2 G \quad (26)$$

The inductance of the line ($L_T = 0.27 \mu\text{h}$) was measured with the 160-A Q-meter and the values of δ calculated at each frequency used in the measurements, were plotted against ΔC_b (see Plate V). The values of γ may be found from the same curves if ΔC_b is replaced by C_X .



V. RESULTS

1. COMPOSITION OF THE SAMPLES

(a) Natural Rubber¹⁾

Cure: 30 min at 296°F

COMPOSITION	Parts by Weight		
	Sample 1-A	Sample 1-B	Sample 1-C
Smoked Sheet	100	100	100
Combined Sulphur	1.8	3.9	4.4
Free Sulphur	0.2	6.1	10.6
Zinc Oxide	1.0	1.0	1.0
Zinc Dibutyldithio- carbamate	0.1	0.1	0.1
Total Parts by Weight	103.1	111.1	116.1

(b) Butyl Rubber²⁾

Cure: 60 min at 307°F

COMPOSITION	Parts by Weight		
	Sample 2-A	Sample 2-B	Sample 2-C
Butyl	100	100	100
Combined Sulphur	1.6	3.0	4.4
Free Sulphur	0.4	1.0	5.6
Zinc Oxide	1.0	1.0	1.0
Tetramethylthiuram Disulfide	1.0	1.0	1.0
Total Parts by Weight	104.0	106.0	112.0

All the rubber samples were specially prepared for

¹⁾ L.A. Wood and F.L. Roth J. of App. Phys. 15, 781, 1944.

²⁾ P.J. Flory Rubber Chem. Tech. 19, 552, 1946.

this research by the Research Division of the Polymer Corporation at Sarnia. The samples were 6 inches square and had been carefully molded to ensure plane parallel faces.

The amounts of free sulphur in the samples were determined by the acetone extraction method. (A.S.T.M. Procedure D-297-43T).

2. TABLES AND GRAPHS

A sample set of calculations for sample 2-A at 20°C and 0% extension, is given in Table I. The results for this sample at higher temperatures and extensions, and the results for the other samples are given in the form of graphs (see Plates VI to XI).

In Table I, C' represents the initial setting of the standard condenser, and C_x represents the measured capacity of the standard cell containing the sample. In the capacitance bridge range, ΔD represents the difference in the dissipation factor readings for the initial and final balances; in the Q-meter range ΔD represents the difference of the Q's of the initial and final tuned circuits; and in the twin-T range ΔD represents the conductance of the samples in μ mhos.

The probable errors given for ϵ' and $\tan \delta$, are the mean errors from ten measurements of the ϵ' and $\tan \delta$ of a wax sample. The large errors involved in the Q-meter measurements should be noted.

TABLE I

Sample 2-A: 20.2°C, 0% Extension.

Average Thickness = 0.1867 cms.; $C_a = 23.29 \mu\mu f.$

		Frequency	C' $\mu\mu f$	C_x $\mu\mu f$	ΔD	$C_x - C_e$ $\mu\mu f$	$\epsilon' = \frac{C_x - C_e}{C_a}$		tan δ percent	
Capacitance Bridge		0.1 K.c.	340.9	64.3	.033	60.0	2.58	± .01	.175	± .015
		0.2 "	341.1	64.3	.033	60.0	2.58	± .01	.175	± .015
		0.4 "	341.2	64.3	.038	60.0	2.58	± .01	.201	± .015
		0.75 "	341.2	64.2	.042	59.9	2.57	± .01	.223	± .015
		1 "	341.2	64.1	.053	59.8	2.57	± .01	.282	± .015
		1.5 "	341.3	64.1	.060	59.8	2.57	± .01	.319	± .015
		2 "	341.3	64.1	.062	59.8	2.57	± .01	.330	± .015
		4 "	341.4	64.0	.072	59.7	2.56	± .01	.384	± .015
		7.5 "	341.6	64.0	.097	59.7	2.56	± .01	.517	± .015
		10 "	341.9	63.9	.110	59.6	2.55	± .01	.589	± .020
Q-meter		15 "	342.7	63.8	.135	59.5	2.55	± .02	.725	± .030
		50 K.c.	354.4	64.1	7	59.8	2.57	± .05	.54	± .10
		80 "	347.4	63.8	10	59.5	2.55	± .05	.32	± .10
		100 "	454.6	62.3	9	58.0	2.49	± .05	.35	± .10
		150 "	175.1	62.9	21	58.6	2.52	± .05	.24	± .10
Twin-T Bridge		400 "	271.8	63.0	14	58.7	2.52	± .04	.20	± .10
		0.7 M.c.	250	62.9	0.69	58.6	2.52	± .01	.249	± .022
		1 "	250	62.9	1.0	58.6	2.52	± .01	.253	± .024
		1.5 "	600	62.9	1.8	58.6	2.52	± .01	.303	± .028
		2 "	250	62.9	1.9	58.6	2.52	± .01	.239	± .030
		3 "	250	62.8	2.8	58.5	2.51	± .01	.237	± .030
		6 "	250	62.8	6.4	58.5	2.51	± .01	.270	± .030
		10 "	250	62.7	15.0	58.4	2.51	± .02	.381	± .035
		15 "	350	61.8	32.2	57.5	2.47	± .02	.553	± .040
		20 "	250	61.6	59.3	57.3	2.46	± .02	.764	± .070

PLATE VI
Results for Sample 1-A
Natural Rubber 2% Sulphur

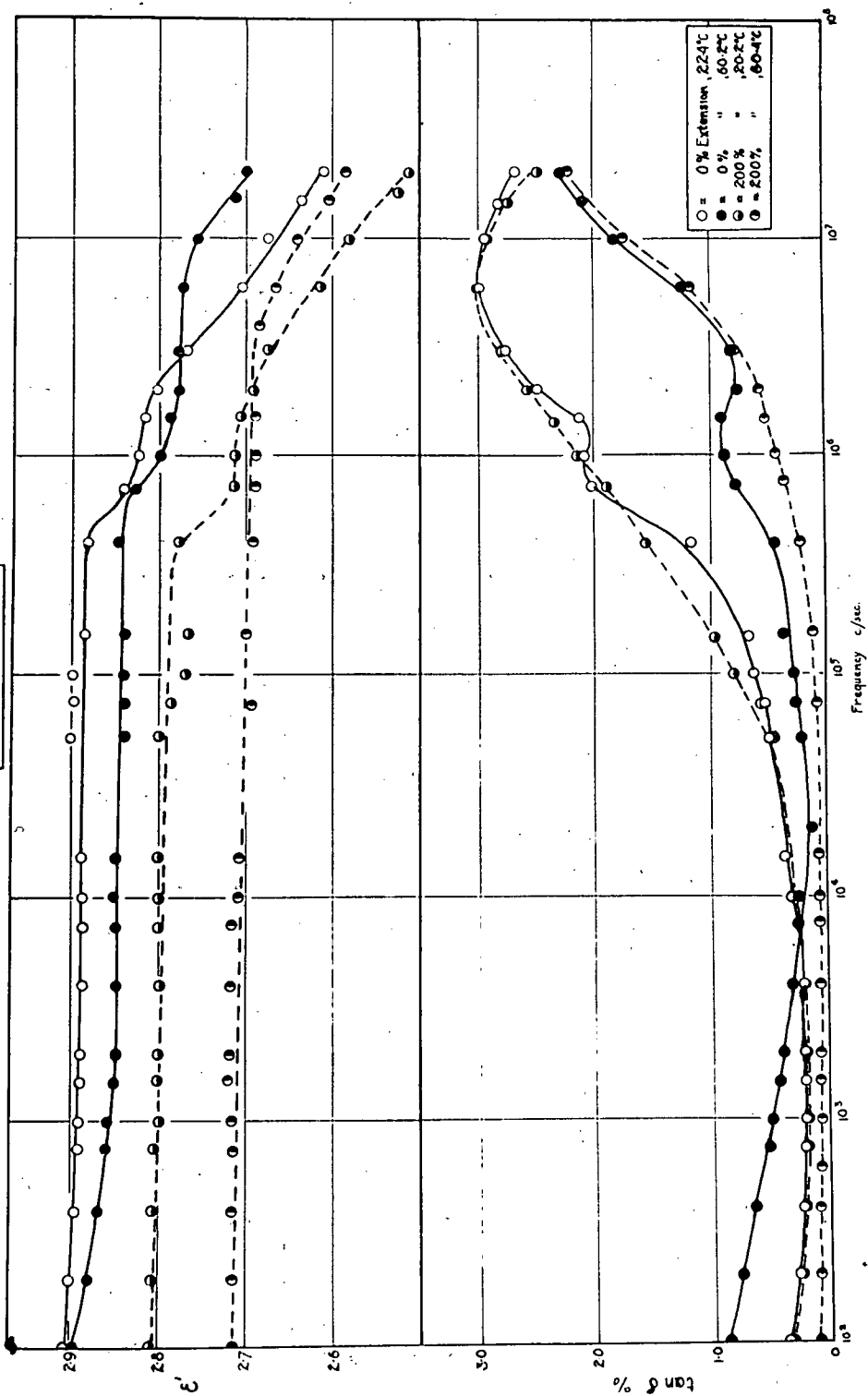


PLATE VII
 Results for Sample 1-B
 Natural Rubber, 10% Sulfur

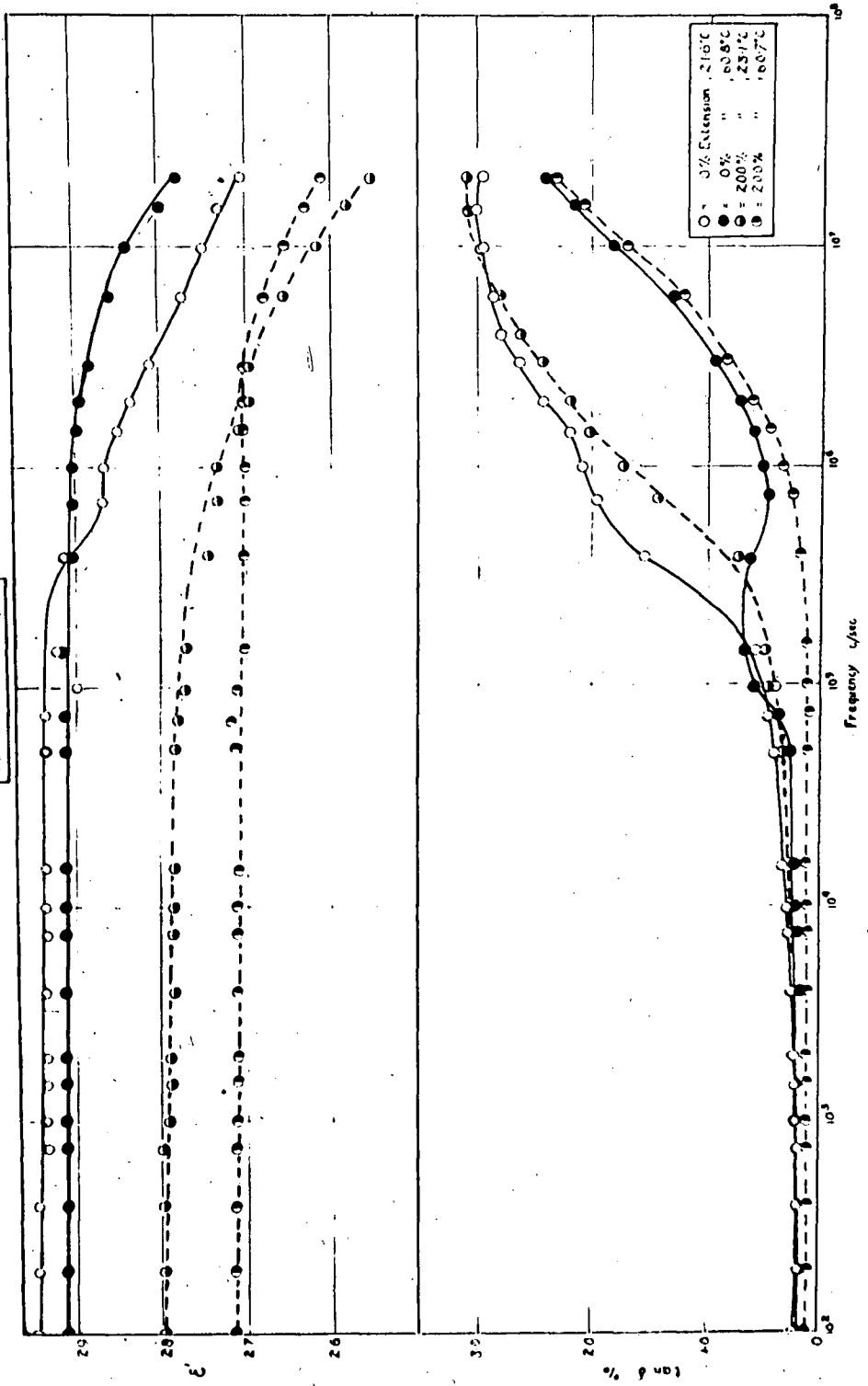


PLATE VIII
 Results for Sample 1-C
 Natural Rubber 15% Sulphur

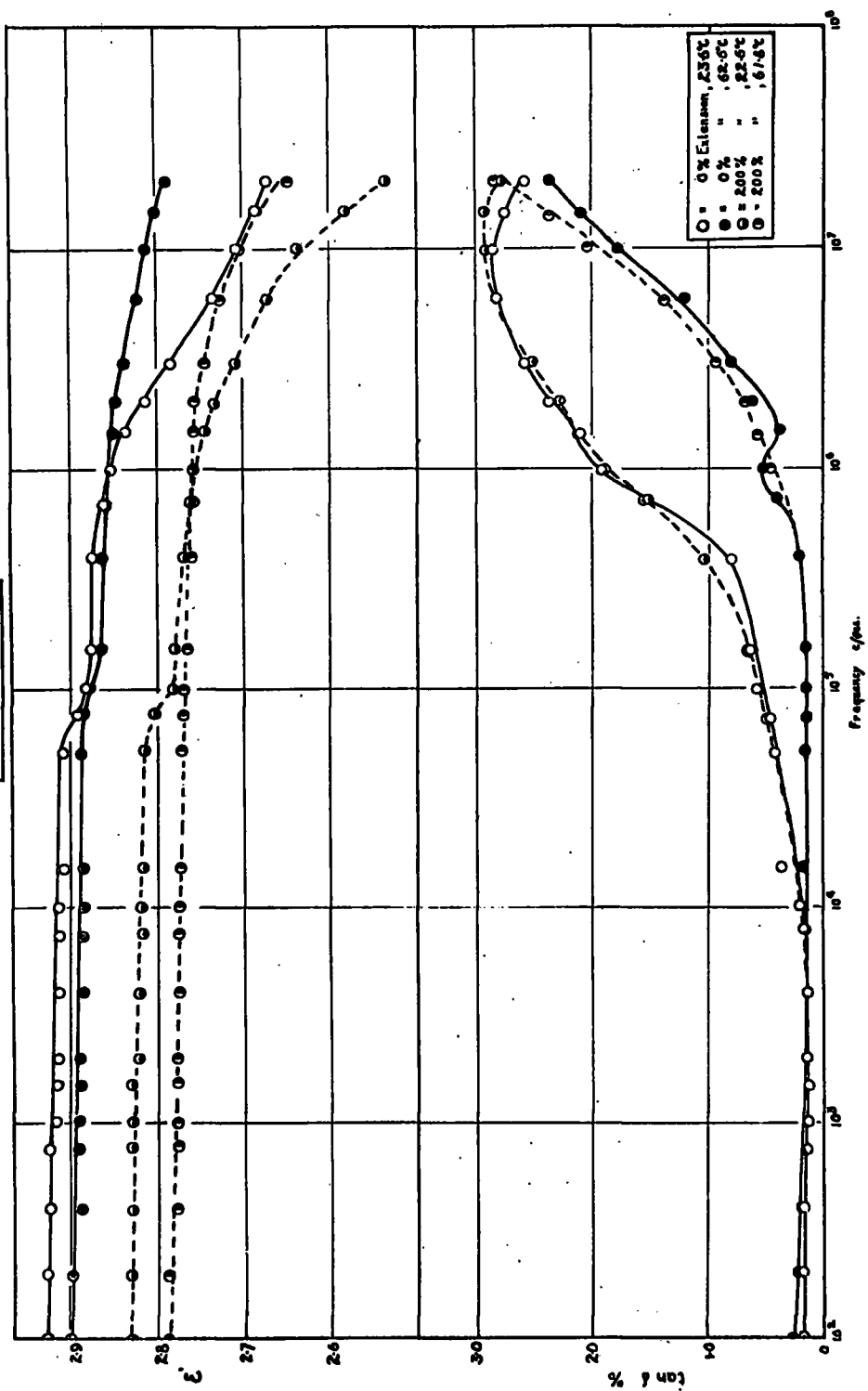


PLATE IX
 Results for Sample 2-A
 Butyl Rubber 2% Sulfur

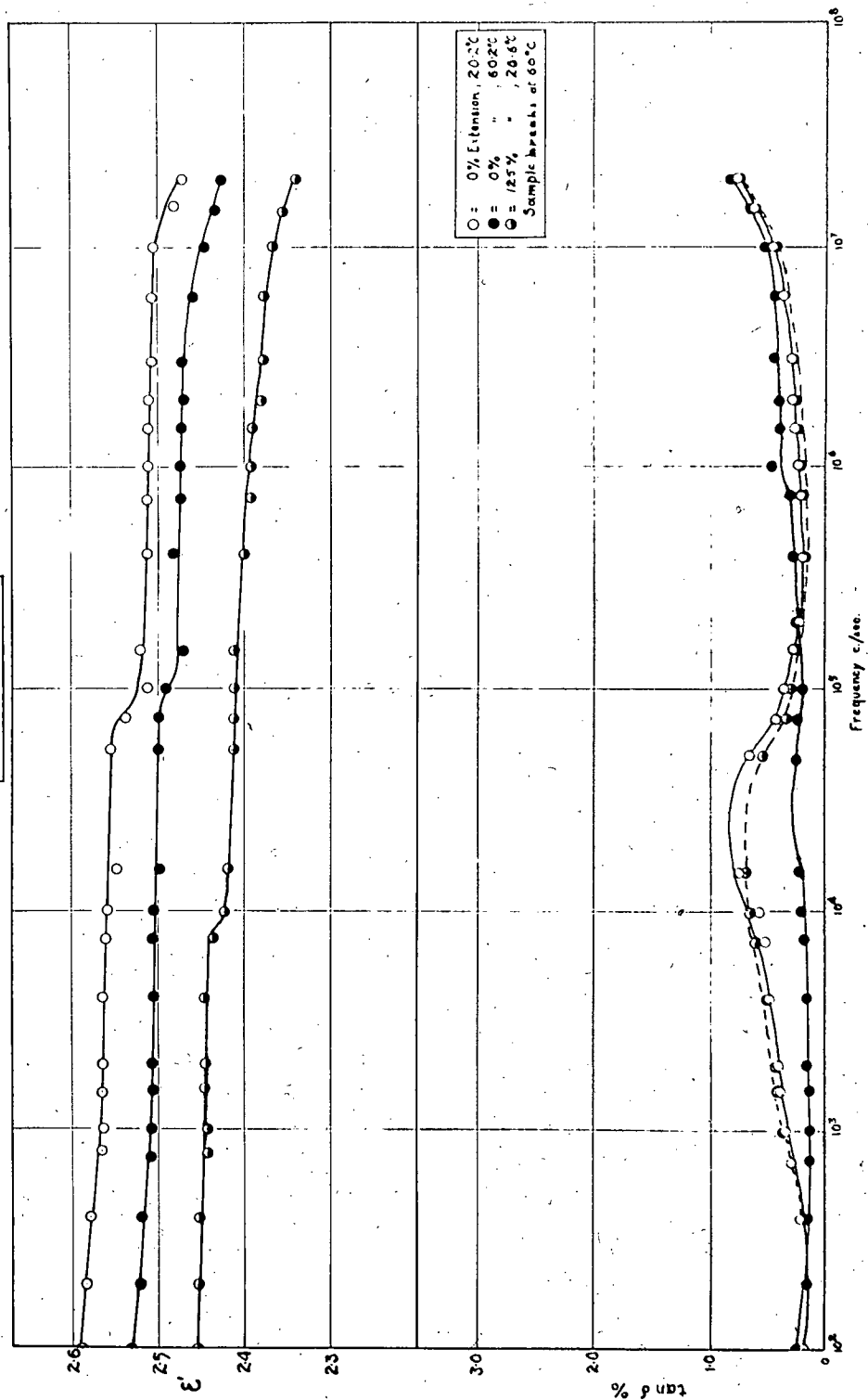


PLATE X
 Results for Sample 2-B
 Butyl Rubber 4% Sulphur

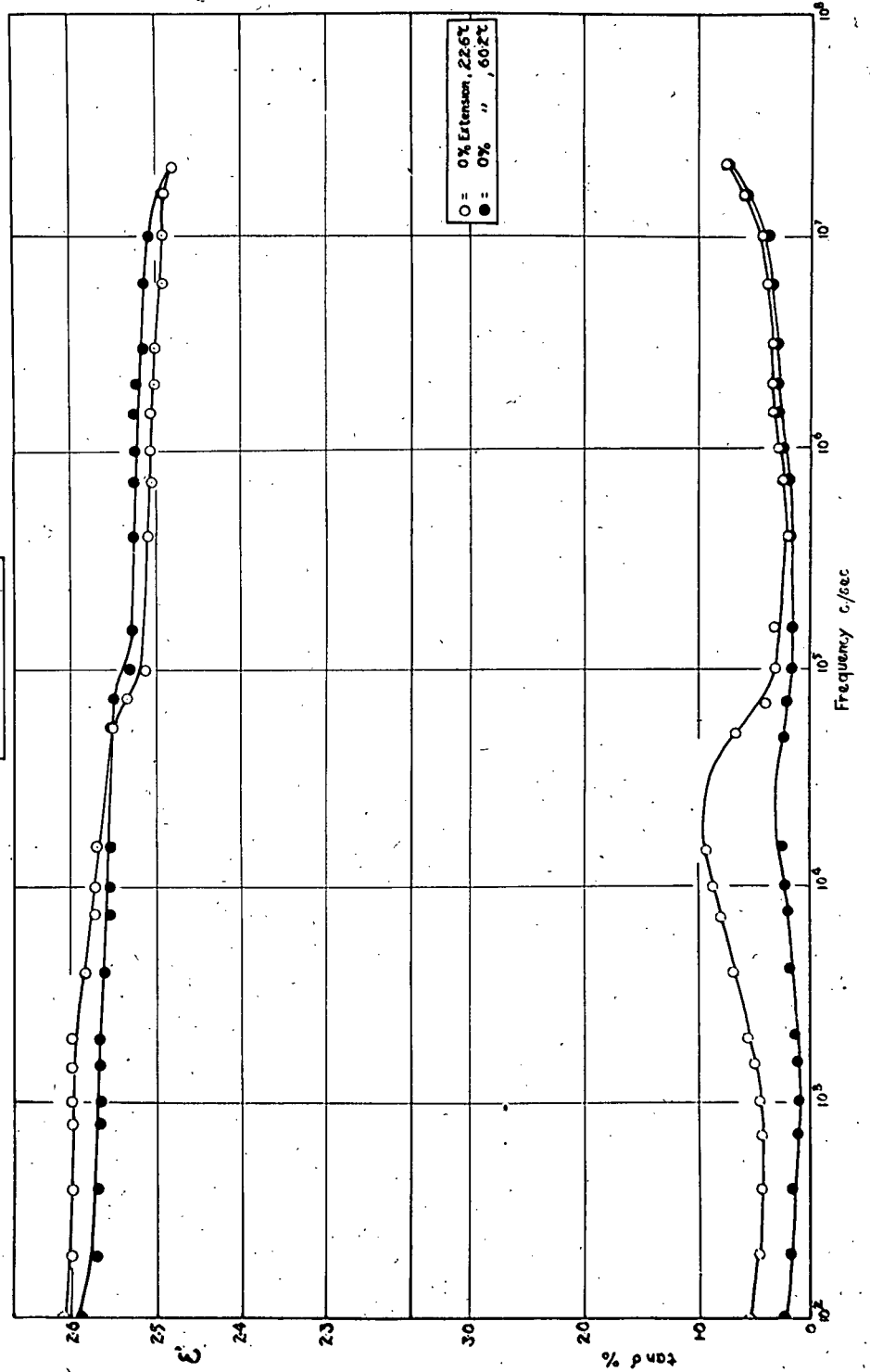
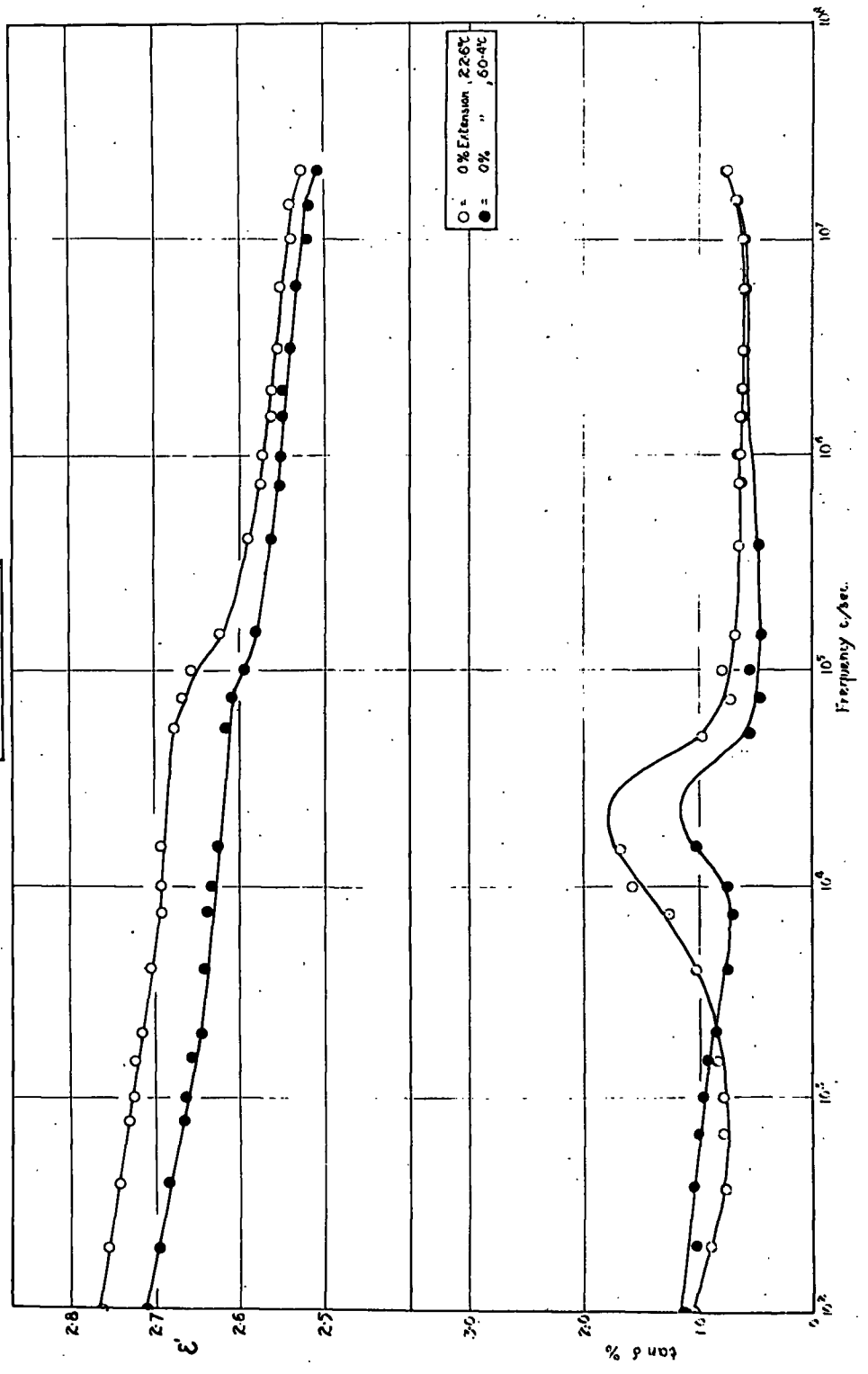


PLATE XI
 Results for Sample 2-C
 Butyl Rubber 10% Sulfur



3. DISCUSSION OF RESULTS

(a) Natural Rubber

The results for the natural rubber samples are given in Plates VI, VII, and VIII. The results for the samples at room temperature were calculated from two separate sets of measurements. At higher temperatures, however, only one set of measurements was taken for each sample.

Values of ϵ' and $\tan \delta$ measured after a high temperature run were found to be slightly lower than the corresponding values measured before the run. These lower values of ϵ' and $\tan \delta$ probably resulted from a reduction in the moisture content of the rubber at the high temperature since the ϵ' and $\tan \delta$ returned to their initial values after 24 hours.

The graphs of " ϵ' vs. $\log \nu$ " show that in the frequency range extending from 500 cycles to 200 K.c., the dielectric constant of the rubber is approximately independent of the frequency. For sample 1-A, the average value of ϵ' in this range is 2.89. This value is in agreement with the values found by previous experimenters.

A comparison of the results for natural rubber with the results of Scott Curtis and McPherson (Ref. 3), p. 3) shows that increases in the dielectric constant of vulcanized rubber which correspond to the differences in the dielectric constants of samples 1-A, 1-B, and 1-C, require an increase in the sulphur concentration which corresponds to the in-

crease in combined sulphur concentrations of the samples. The dielectric constant of vulcanized rubber is therefore a function of the combined sulphur concentration and is independent of the amount of free sulphur in the rubber.

It is shown that in general the dielectric constant of natural rubber decreases with increasing temperature and with increasing extension. This result is not in agreement with the results of Holroyd (Ref. 4), p. 7) who found that at 300% extension, the dielectric constant of rubber increased with increasing temperature.

A comparison of the " ϵ' vs. $\log \nu$ " and " $\tan \delta$ vs. $\log \nu$ " curves at 20°C and 60°C shows that an increase in the temperature causes the anomolous portions of the curves corresponding to the maximum dissipation factor, to be moved to a higher frequency. This large temperature dependence of the $\tan \delta$ maximum is characteristic of polar substances and it can therefore be assumed that rubber-sulphur dipoles are present in vulcanized rubber. The temperature dependence also shows that the $\tan \delta$ maximum is of the Debye type. The ϵ' and $\tan \delta$ of the rubber may therefore be represented by equations (21) and (22).

An interesting result is the appearance of a secondary maximum superimposed upon the Debye curve at 0.9 M.c. The small temperature dependence of this maximum indicates that it is of the Maxwell-Wagner type and is probably due to the presence of free sulphur which acts as a filler in the rubber. The observed $\tan \delta$ curves must therefore be the

resultants of the Debye curves and the Maxwell-Wagner curves (see Plate XII).

As the amount of free sulphur in the rubber is increased, the Maxwell-Wagner maximum becomes less pronounced, and the Debye curve is flattened. The $\tan \delta$ maximum is also observed to decrease. .

<u>Sample</u>	<u>% Free Sulphur</u>	<u>$\tan \delta$ max.</u>
1-A	0.2	0.031
1-B	6.1	0.030
1-C	10.6	0.028

These results are in agreement with the theory of Gevers (Ref. 1), p. 14) who has shown that as a mixture becomes more inhomogeneous, the distribution of the activation energies is broadened and as a result the $\tan \delta$ curve is flattened.

Plate XIII shows plots of the Kirkwood-Fuoss function $\psi(\epsilon', \epsilon'')$ vs. the logarithm of the frequency (ν) for sample 1-A at 20°C and 0% extension, and at 20°C and 200% extension. The resultant curves are very nearly straight lines with slopes of 0.769 for the unstretched sample and 0.812 for the stretched sample. This result is rather unexpected as the Kirkwood-Fuoss theory applies to polymers having a dipole in each monomer unit and hence having a large dipole interaction.

Since natural rubber can contain 32% combined sulphur, sample 1-A with 1.8% sulphur would only have one

PLATE XII
Dissipation Factor Curves for Sample I-A

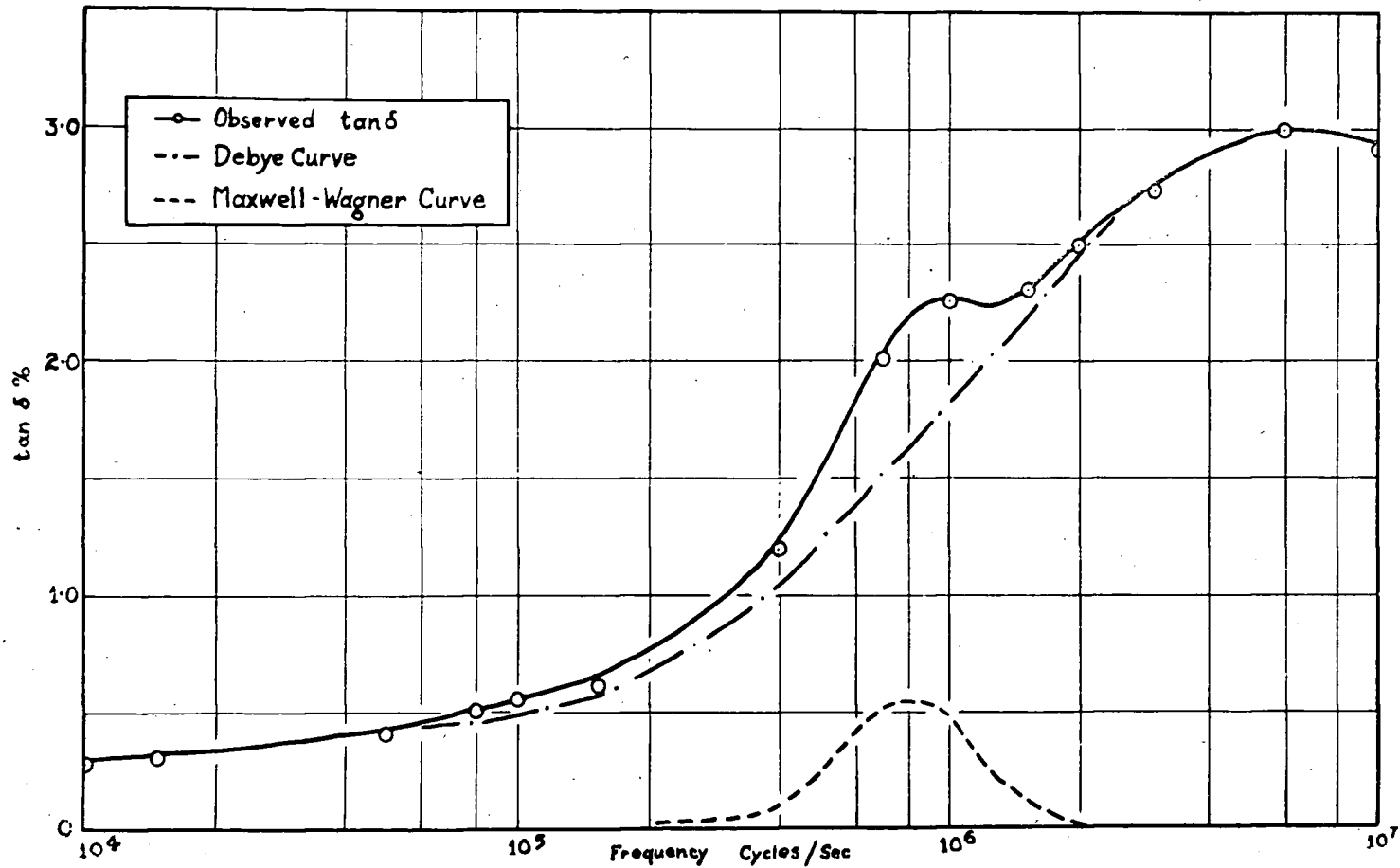
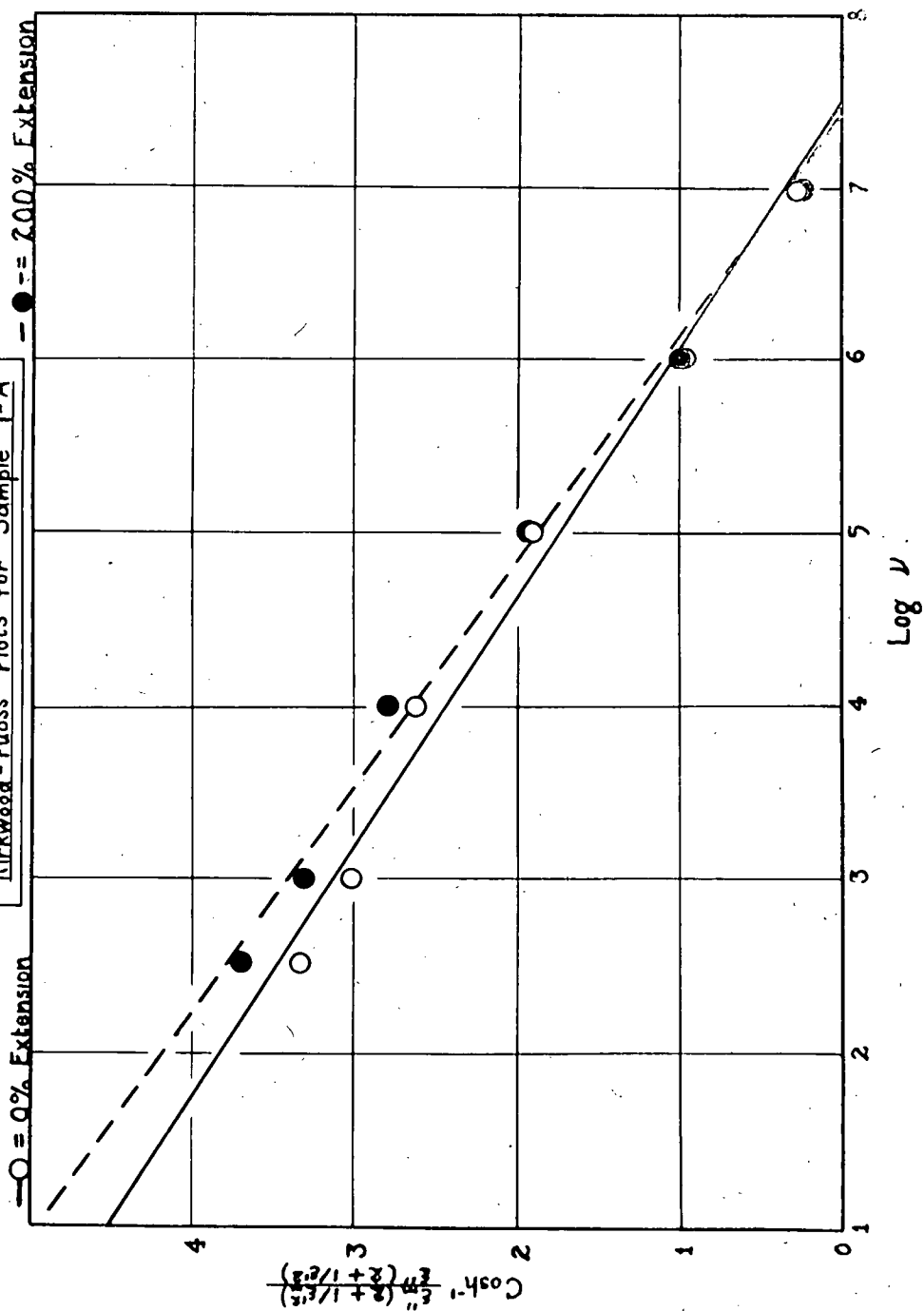


PLATE XIII
Kirkwood-Fuoss Plots for Sample I-A



dipole for every 18 monomer units and hence should have a relatively small dipole interaction. It has of course been assumed that for 32% combined sulphur, every monomer unit contains one dipole. This is not strictly correct as it has been shown that more than one sulphur atom may be associated with a single monomer unit¹⁾.

The dipole moments per monomer unit calculated from equation (20), and the mean relaxation times calculated from $\tau_0 = 1/\omega_m$, where ω_m = the frequency corresponding to the maximum loss, are given in the following table for sample 1-A.

<u>Temp.</u> <u>°C</u>	<u>Extension</u> <u>Percent</u>	<u>Dipole Moment</u> <u>per Monomer</u>	<u>$\tau_0 \times 10^8$</u> <u>sec.</u>
20°C	0	0.41 D	2.04
20°C	200	0.40 D	3.96

1 D = 1 Debye unit = 10^{-18} e.s.u.

The larger relaxation time of the stretched sample shows that the activation energy is greater for stretched rubber than for unstretched rubber.

If again it is assumed that there is only 1 dipole for every 18 monomer units in sample 1-A, the average moment of the carbon-sulphur dipole must be $\mu_{av} = \bar{\mu} \sqrt{18}$, and since $\bar{\mu} = 0.41$ D for the unstretched sample, $\mu_{av} = 1.7$ D. This value corresponds to the moment of 1.6 D observed for the diethyl sulphide dipole²⁾.

¹⁾ M.L.Selker and A.R.Kemp Ind.Eng.Chem. 39, 895, 1947.

²⁾ R.LeFevre Dipole Moments, Menthuen Co., 1938.

(b) Butyl Rubber.

The results for butyl rubber are given in Plates IX, X, and XI. The curves for samples 2-B and 2-C at 125% extension and the curve for sample 2-A at 60°C and 125% extension could not be obtained as the sample broke under these conditions.

In general, the dielectric constant of butyl rubber is less than that of natural rubber and is shown to decrease with increasing temperature and with increasing extension. The temperature dependence of the dielectric constant shows that butyl rubber is a polar substance. The butyl dipoles are probably formed by carbon-sulphur linkages in the isoprene monomer units.

The " ϵ' vs. $\log \nu$ " curves for butyl rubber are very flat in the range investigated, although a loss maximum is indicated at a frequency greater than 20 M.c. The temperature dependence of ϵ' shows that this should be a Debye maximum. If this maximum does exist, the mean relaxation time of the butyl dipoles will be less than the mean relaxation time of the natural rubber dipoles. It may therefore be assumed that butyl rubber has a smaller dipole interaction than natural rubber.

The maximum which occurs in the $\tan \delta$ curve of butyl rubber at 30 K.c. is assumed to be of the Maxwell-Wagner type since it has a very small temperature dependence. This maximum may be attributed to the presence of the free sulphur in the rubber.

VI. CONCLUSION

The dielectric properties of natural and butyl rubbers have been investigated at temperatures of 20°C and 60°C, and at extensions of 0% and 200%, in a frequency range extending from 100 cycles to 20 M.c. The results obtained are as follows:

(1) The dielectric constants of butyl and natural rubbers decrease with increasing temperature and with increasing extension.

(2) In general, the dielectric constant of butyl rubber is less than that of natural rubber.

(3) The relaxation time and hence the dipole interaction of the butyl dipoles are less than the relaxation time and dipole interaction of the natural rubber dipoles.

(4) The distribution of relaxation times of natural rubber-sulphur dipoles may be represented by the Kirkwood-Fuoss distribution function.

(5) The dipole moment per monomer unit is slightly greater for unstretched rubber than for stretched rubber.

(6) The relaxation time of stretched rubber is greater than that of unstretched rubber.

(7) Both butyl and natural rubber-sulphur compounds exhibit Maxwell-Wagner maxima. These maxima are superimposed on the Debye curves and may be attributed to the presence of free sulphur in the rubbers.

VII. BIBLIOGRAPHY

BOOKS

1. Alexander, J. T. Colloid Chemistry, Vol. V,
Reinhold Publishing Co., 1944.
2. Barron, H. Modern Synthetic Rubbers, Chapman
and Hall, 1943.
3. Davis, C. and
Blake, J. Chemistry and Technology of Rubber,
Reinhold Publishing Co., 1937.
4. Debye, P. Polar Molecules, Chemical Cata-
logue Co., 1929.
5. Le Fevre, R. Dipole Moments, Menthuen Co., 1938.
6. Mark, H. and
Whitby, G. S. Advances in Colloid Science, Vol. II,
Interscience Publishers, 1946.
7. Smyth, C. P. Dielectric Constant and Molecular
Structure, Chemical Catalogue
Co., 1931.
8. Weissberger, A. Physical Methods of Organic Chemistry
Vol. II, Interscience Pub-
lishers, 1946.

PAPERS

1. Boggs C. R. and
Blake J. T. Ind.Eng.Chem. 22, 748, 1930.
2. Cole K. S. and
Cole R. H. J.of Chem.Phys. 9, 341, 1941.
3. Debye P. Phys.Zeits. 36, 100, 1935.
4. Flory P. J. Rubber Chem.Tech. 19, 552, 1946.
5. Fuoss R. and
Kirkwood J. J.Amer.Chem.Soc. 63, 385, 1941.

6. Gevers N. V. Philips Res.Rep. 1, 298, 1946.
7. Holroyd L. V. Master's Thesis, U.B.C., May 1947.
8. James H. and Guth E. J.of Chem.Phys. 11, 455, 1943.
9. James H. and Guth E. J.of Chem.Phys. 15, 669, 1947.
10. Katz J. R. Report to the Rubber Symposium, Delft, 1936.
11. Kitchin D. W. Ind.Eng.Chem. 24, 549, 1932.
12. Pellat E. J.of Physics 9, 313, 1900.
13. Rehner J. Ind.Eng.Chem. 36, 47, 1944.
14. Schneider W.,
Carter W., Magat M.,
and Smyth C. P. J.Amer.Chem.Soc. 67, 959, 1945.
15. Schweidler E. von Ann.der Phys. 24, 711, 1907.
16. Scott A. H.,
McPherson A. T. and
Curtis H. L. U.S.Bur.Std., J.of Res. 11, 173,
1933.
17. Scott A. H. and
Curtis H. L. U.S.Bur.Std., J.of Res. 22, 747,
1939.
18. Selker M. L. and
Kemp A. R. Ind.Eng.Chem. 39, 895, 1947.
19. Wagner K. W. Ann.der Phys. 40, 817, 1943.