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## DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF THE SYSTEM RUBBER-CALCIUM CARBONATE

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### ABSTRACT

The dielectric constants and power factors of mixtures of calcium carbonate with Vistanex and with natural rubber were determined at 1 and 100 kilocycles per second. There was little difference between the values at the two frequencies. Two different formulas were found to express the dielectric constants of the mixtures as functions of the dielectric constants of the respective components. The dielectric constant of the pure calcium carbonate employed was determined by the method of liquid mixtures. The power factors of the rubber-calcium carbonate mixtures were intermediate between those of the components. The conductivities of the Vistanex-calcium carbonate mixtures measured at the end of 1 minute of electrification were intermediate between those of the components, but the conductivities of the mixtures of natural rubber and calcium carbonate seemed to go through a minimum.

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### I. INTRODUCTION

A study of the electrical properties of rubber-filler systems has been undertaken by the National Bureau of Standards for the purpose of arriving at general relations for the effect of typical fillers on the dielectric constant, power factor, and conductivity of rubber compounds containing the fillers. It is intended that the investigation be comparable in scope to the previous study of the system rubber-sulfur [1].<sup>1</sup> A portion of the work dealing with calcium carbonate

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

as a filler has been completed and is presented here.

The term "rubber" has been rather broadly construed in connection with these studies to include not only conventional vulcanized natural rubber, but also synthetic rubber-like materials. Thus, specimens made from Vistanex, a high molecular weight polymer of isobutylene, have been included in the present work. The experimental compounds which were prepared are simpler than any which would be employed in practice, the aim being to look for general relations rather than to develop practical insulating compounds.

## II. PREPARATION OF THE SPECIMENS

The specimens were made by adding calcium carbonate to the base compounds in a series of amounts up to about 50 percent by volume. The composition was closely controlled and special attention was paid to the molding of the specimens so as to obtain the high degree of uniformity in thickness requisite for the accurate determination of the electrical properties.

### 1. COMPOSITION AND MIXING OF THE EXPERIMENTAL COMPOUNDS

One base compound was made from natural rubber according to the following formula:

Ingredients:	<i>Parts by weight</i>
Blended smoked sheet rubber.....	100
Zinc oxide (Kadox).....	1
Stearic acid.....	2
Tetramethylthiuram disulfide.....	3
	106

The natural rubber had been blended before purchase so as to give a uniform grade of rubber for test purposes. This base compound and the calcium carbonate compounds prepared from it were vulcanized for 30 minutes at 126° C.

The other base compound consisted of high molecular weight Vistanex. Vistanex is a polymer of isobutylene produced in the United States by the Advance Solvents and Chemical Corporation. The Vistanex compounds, of course, required no vulcanization. They were of such consistency that specimens could be molded to precise dimensions. They had the advantage over rubber specimens that they could be remolded repeatedly if they were imperfect or not of the desired shape.

The calcium carbonate used in the investigation was of the reagent grade and of the type low in alkalis.

The maximum limit of impurities was 0.5 percent for magnesium and 0.08 percent for all other impurities. It was assumed that the magnesium carbonate was similar to calcium carbonate in its effect on the electrical properties and that the other impurities were present in too small amount to be of significance.

The compounds were usually mixed in a laboratory internal mixer. The mixer was not perfectly tight, so that some of the calcium carbonate was lost by dusting; batches were weighed before and after the addition of this material and the loss was made up. The vulcaniz-

ing agent, tetramethylthiuram disulfide, was added on a roll mill, as is the usual practice.

The accuracy of the compounding was checked by determining the specific gravity of the finished specimens, and, in the case of the Vistanex compounds, the residue on ignition was determined as a further check. Vistanex, unlike natural rubber, can be driven off at a temperature below red heat, and hence well below the temperature at which calcium carbonate undergoes significant decomposition.

## 2. MOLDING AND VULCANIZING OF THE SPECIMENS

Special care was necessary in order to mold the specimens so that they would be free from entrapped air and would be sufficiently uniform in thickness to permit the determination of dielectric constant to be made to the desired accuracy. Two forms of specimens were used. Some of the specimens were prepared in the form of disks having embedded aluminum electrodes, whereas the rest were prepared in the form of rectangular slabs to which foil electrodes were subsequently applied.

The disk-shaped specimens were similar to those employed in a previous investigation [1], where one embedded electrode was smaller than the other. The present specimens were made considerably thicker in an effort to improve the precision with which the effective thickness could be measured. The method of measuring thickness is described in a subsequent section of this paper. The electrodes were 15 cm and 20 cm in diameter, respectively, and the thickness of the rubber was about 0.6 cm. When these specimens were molded and vulcanized in a single operation they were somewhat thicker at the center than at the edges, or slightly lens-shaped. In order to obviate this difficulty, the stock was first molded in the form of a blank at about 100° C. After the electrodes had been applied, it was again molded at 100° C. The temperature was then raised to 126° C and the specimen vulcanized. By thus separating the molding and vulcanizing operations it was possible to obtain specimens which were highly uniform in thickness.

When specimens having embedded electrodes were being prepared, blanks of the stock were usually made and allowed to stand for several days before they were molded to the final shape. This was done to get rid of air, which is often entrapped in compounds containing large amounts of filler. In forming the blanks, any air pockets present are collapsed by the high pressure and the air is forced into solution. When the pressure is released the air remains in the form of a supersaturated solution which diffuses slowly to the surface and escapes if no electrodes are present. If electrodes have been applied before the air has had time to escape, it accumulates in pockets underneath them.

The rectangular specimens were about 16 cm long, 15 cm wide, and 0.6 cm thick. Tinfoil electrodes were made to adhere to the specimens, using a thin film of vaseline as an adhesive, by rolling the tinfoil down with a narrow roller. This gave tightly adhering electrodes, since the small amount of vaseline left was absorbed by the rubber. One electrode was made to cover an entire face, the opposite one was cut to a rectangle 11 by 12 cm. The vaseline used in applying the tinfoil electrodes probably did not affect the electrical properties of the specimens, since comparative measurements made with embedded

aluminum electrodes and tinfoil electrodes agreed within experimental error.

### 3. EXAMINATION OF SPECIMENS FOR POROSITY

The specimens were carefully examined for porosity, since the presence of voids, or air pockets, would decrease the accuracy of the electrical determinations. Large defects in the specimens having embedded electrodes were usually made evident by a variation in thickness. Typical specimens were cut up after the electrical measurements had been made, and the cut edges of the compound were examined for pores. When defects were found in any specimen, the measurements on that specimen were discarded.

In order to investigate the possibility that the specimens might be more porous than visual inspection would indicate, compressibility measurements were made on strips cut from representative specimens. Volume compressions at 1,500-lb/in.<sup>2</sup> and 3,000-lb/in.<sup>2</sup> pressure were determined. If no air pockets were present, the volume compression at 3,000 lb/in.<sup>2</sup> should be approximately twice that at 1,500 lb/in.<sup>2</sup> Large deviations from this can be attributed to air pockets which are collapsed at the lower pressure.

To make the volume compression measurements, the specimen strips were placed in a Pyrex-glass piezometer having the form shown diagrammatically in figure 1. When this was placed under pressure in a pressure bomb, mercury was forced through the fine capillary in the bottom and dropped off the tip inside, thus being trapped. After the pressure was released, this mercury was weighed. From a knowledge of the weight of the mercury, the volume of the capillary, the compressibility of the glass, the volume of the piezometer, and the volume of the specimen, the volume compression ( $K = \Delta V/V_0$ ) of the specimen could be determined.

After the volume compressions for 1,500-lb/in.<sup>2</sup> and 3,000-lb/in.<sup>2</sup> pressure had been determined, the fraction of the volume ( $U$ ) of the specimen occupied by air pockets was computed from

$$U = K' - \left( \frac{K'' - K'}{P'' - P'} \right) P', \quad (1)$$

where  $K'$  is the volume compression for pressure  $P'$  (1,500 lb/in.<sup>2</sup>) and  $K''$  is the volume compression for pressure  $P''$  (3,000 lb/in.<sup>2</sup>). This assumes that the compressibility of the specimen does not vary with the pressure. Since the compressibility decreases somewhat with pressure, the values thus obtained are higher than the actual values. However, the error is not large, and if the computed value is below the allowable limit, the actual value certainly is. All the

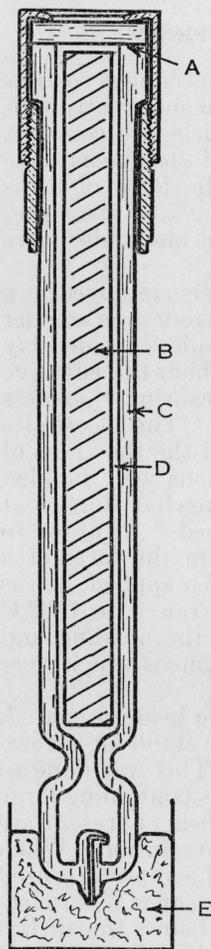


FIGURE 1.—Piezometer for measuring volume compressions of rubber specimens

A, lapped surface; B, specimen; C, Pyrex glass; D, confining liquid; E, mercury.

specimens used in this work that were not discarded as a result of visual inspection contained less than 0.4 percent by volume of air. Since the thickness cannot be measured more closely than 1 percent, it was assumed that air volumes of 1 percent could be tolerated. The specimens were well within this limit.

### III. MEASUREMENT OF DIMENSIONS OF THE SPECIMENS

The thickness of each of the circular specimens having aluminum electrodes was measured by means of the tilting-bar gage described in a previous publication [1]. The over-all thickness was measured at a number of points according to a fixed pattern, and from this the combined thickness of the two electrodes was subtracted. The area of the specimen was taken as the area of the smaller electrode. The diameter of the smaller electrode was measured by means of a steel rule.

The thickness of each of the rectangular specimens was determined from the volume obtained by means of hydrostatic weighings. The edges were cut straight by means of a knife working in a guide, a strip about 0.6 cm wide being cut from each edge. The length and breadth were then measured by means of a steel rule and the area was computed. From the area thus obtained and the volume found by hydrostatic weighing, the average thickness was computed. A few of the specimens were measured for uniformity of thickness, using a gage designed by Holt [2], which applied very light pressures to the specimen. The area used in computing the dielectric constant was that of the smaller electrode, and this was computed from measurements of the length and breadth made with a steel rule.

## IV. ELECTRICAL MEASUREMENTS

### 1. DIELECTRIC CONSTANT AND LOSS TANGENT OF THE RUBBER COMPOUNDS

The capacitance and loss tangent (tangent of the phase difference angle, i. e.,  $\tan \delta$ )<sup>2</sup> of the specimens were measured on a conjugate Schering bridge similar to the one described in the American Society for Testing Materials standard method for measuring capacitance and power factor [3]. A diagram of the bridge is shown in figure 2. The entire bridge, with the exception of the transformer supplying the power, was enclosed in a grounded metallic cage which was large enough to accommodate the operator. The four arms of the bridge are indicated by the subscripts 1, 2, 3, 4, and the Wagner ground is indicated by the subscripts 5 and 6. The variable resistor,  $R_v$ , when

<sup>2</sup> The term "loss tangent" is used throughout this paper rather than "power factor," because the loss tangent comes directly from the bridge equations. For values less than 0.1, the loss tangent and power factor are the same within experimental error.

properly adjusted, aided in the balance of the bridge.<sup>3</sup> The function of this resistance in the bridge balance has been discussed by Astin in his detailed analysis of the bridge [4].

In making a measurement of capacitance and loss tangent several cycles of adjustment were necessary in which the detector was connected first to the bridge and then to ground. The specimen ( $C_x$ ) was connected into the bridge by closing switch  $S_a$  to 1. A cycle of adjustments consisted of closing switch  $S_b$  to 1 and balancing the bridge by adjusting  $C_2$  and  $C_3$ , then throwing switch  $S_b$  from 1 to 2 and balancing

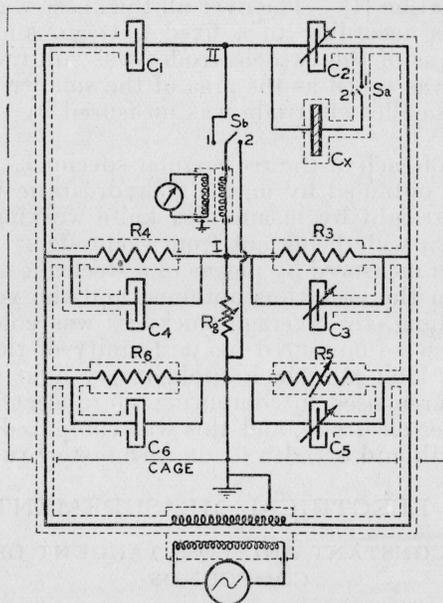


FIGURE 2.—Conjugate Schering bridge for measurements of capacitance and loss tangent.

the bridge by adjusting  $C_5$  and  $R_5$ . This cycle was repeated until throwing switch  $S_b$  from 1 to 2 did not affect the balance.

Convergence to balance was made more rapid by the proper adjustment of  $R_g$ . This adjustment was made after one or two cycles of adjustment, as described above, and needed to be made only once, as long as specimens of about the same capacitance were measured. The

<sup>3</sup> The solution of the generalized bridge equations can be shown to be

$$Y_1 Y_3 - Y_2 Y_4 = \frac{V_1 + V_{II}}{V_1 + V_{II} - 2V_{I4}} (Y_1 Y_2 - Y_{II} Y_3),$$

where  $Y_1, Y_2, Y_3, Y_4$  are the admittances of the four arms of the bridge proper,  $Y_1$  and  $Y_{II}$  are the admittances to ground of the two detector points of the bridge,  $V_1$  and  $V_{II}$  are the potentials of the detector points with respect to ground, and  $V_{I4}$  is the potential of one of the source points with respect to ground. The right-hand side of the equation can be made equal to zero by making  $V_1 = V_{II} = 0$ , which is the object of the Wagner-grounded bridge technique. However, if the balance adjustments of the bridge proper depend appreciably on the values of the admittances in the Wagner ground and in the source, as is often the case for shielded bridges, it may be difficult to adjust  $V_1$  and  $V_{II}$  to zero. This dependence can be materially decreased by the adjustment of either  $Y_1$  or  $Y_{II}$  to make

$$Y_1 Y_2 \approx Y_{II} Y_3.$$

Thus the proper adjustment of  $R_g$  in the present bridge arrangement decreases the dependence of the balance adjustments of the bridge proper on the Wagner ground and source admittances, and materially decreases the effort required to balance the bridge.

adjustment of  $R_g$  was made as follows. With the balance obtained when the switch  $S_b$  was thrown to 1 as described above,  $R_5$  was set sufficiently off balance to give a good indication in the detector.  $R_g$  was then adjusted for a minimum detector indication. The regular cycles of adjustment for balance were then continued.

When the bridge had been properly balanced, readings of  $C_2$  and  $C_3$  were taken. Call them  $C_2'$  and  $C_3'$ , respectively. The specimen was then disconnected by throwing switch  $S_a$  to 2. The bridge was adjusted as before without disturbing  $R_g$ , and the readings of  $C_2$  and  $C_3$  were again taken. Call them  $C_2''$  and  $C_3''$ , respectively. The capacitance,  $C$ , was then computed by means of the equation

$$C = C_2'' - C_2'. \quad (2)$$

The edge capacitances were determined by the method described in a previous paper [5] for computing the edge capacitance from the perimeter of the smaller electrode and the thickness of the specimen. Thus the dielectric constant,  $K$ , of the material is given by

$$K = \frac{C - C_i}{C_n + C_m}, \quad (3)$$

where

$C$  = the measured capacitance of the specimen in micromicrofarads

$$C_i = \frac{P}{30} \ln \frac{3.8}{b}$$

$$C_n = \frac{1.113A}{4\pi b}$$

$$C_m = .0405P$$

$P$  = perimeter of the small electrode in centimeters

$b$  = thickness in centimeters, and

$A$  = the area of the small electrode in square centimeters.

It was shown in the previous paper [5] that  $C_i$  was independent of the dielectric constant of the material and was therefore presumably the capacitance in air at the edge of the electrodes, so the loss tangent of the material,  $\tan \delta_x$ , is given by

$$\tan \delta_x = \frac{\omega R_3 C_2' (C_3'' - C_3')}{C - C_i}, \quad (4)$$

where  $\omega$  is  $2\pi$  times the frequency, and  $R_3$  is the resistance in parallel with  $C_3$ .

Equations 2 and 4 are not exact but give the values with sufficient approximation if the loss tangent of the specimen is less than 0.1 and if the loss tangent of the standard capacitor,  $C_2$ , can be considered to be zero. The specimens were measured at two frequencies, namely, 1 kilocycle per second and 100 kilocycles per second.

## 2. DIELECTRIC CONSTANT OF CALCIUM CARBONATE

The dielectric constant of the calcium carbonate was found by two different methods. One method, which is described in another paper [6], consisted in making direct measurements on specimens of white marble in the form of flat disks. In the other method, various mixtures of two liquids, one of which had a higher dielectric constant and

the other a lower dielectric constant than the powder to be measured, were prepared. The powder was added to these liquid mixtures and the effect of the powder on the dielectric constant of the mixtures determined. The dielectric constant of the powder is the same as that of the liquid when the dielectric constant of the mixture of powder and liquids is the same as that of the liquid mixture alone. Some of the more recent descriptions of this method are given by Luca, Campbell, and Maass [7], Whitehead and Hackett [8], Cheng [9], and Wachholtz and Franceson [10]. Actually, the liquid mixture having a dielectric constant exactly that of the calcium carbonate was not prepared, as this would have been too tedious. The value of the dielectric constant of the calcium carbonate was obtained by interpolation.

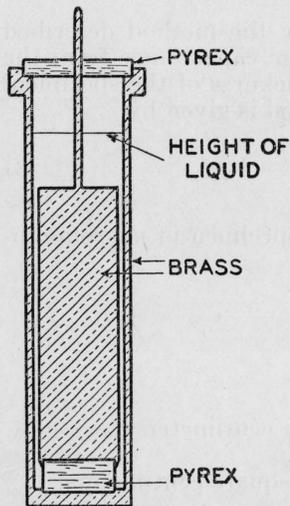


FIGURE 3.—Cylindrical cell for measuring the dielectric constants of powders.

A number of liquid mixtures were prepared, each having a different proportion of the two liquids, benzene, and nitrobenzene. The dielectric constants of these liquid mixtures were determined by means of a cylindrical cell, which is shown in cross section in figure 3. This cell was calibrated by means of benzene, the dielectric constant of which is known. The level of the liquid in the cell was kept to a mark on the inside of the cell. After the dielectric constant of the liquid mixture had been determined, 20 grams of calcium carbonate powder was added to the liquid mixture in the cell. The excess liquid was removed from the cell to bring its level again to the mark, and the change in capacitance of the cell was determined. The percentage changes in capacitance were then plotted against the dielectric constants of the liquid mixtures, and a curve was drawn through the points, as shown in figure 4. The point where the curve crosses the zero ordinate line gives the dielectric constant of the calcium carbonate.

### 3. CONDUCTANCE

The conductance of the specimens was determined from measurements made either with a highly sensitive galvanometer used as an ammeter, as described in a previous paper [1], or by means of an electrometer tube circuit similar to the one described by Penick [11]. In the latter case, a Western Electric electrometer tube was used.

A diagram of the electrometer tube circuit is shown in figure 5. The circuit is so arranged that effects of fluctuations in the filament current are minimized. The circuit was balanced to give zero deflection of the galvanometer,  $G$ , in the following way. The current through the filament was adjusted to the rated value (0.27 ampere) by adjusting  $R_4$ . Resistor  $R_5$  had been so chosen that this current flowing through it gave the proper negative bias (3 volts) to the grid. The resistance of  $R_3$  was so chosen that a potential difference of about 8.5 volts existed between  $A$  and  $B$ . With the grid at  $-3$  volts and the galvanometer,

$G$ , disconnected, the slider on  $R_3$  was adjusted until the potential between  $A$  and  $C$  was about 5.3 volts.  $R_1$  was then adjusted until the

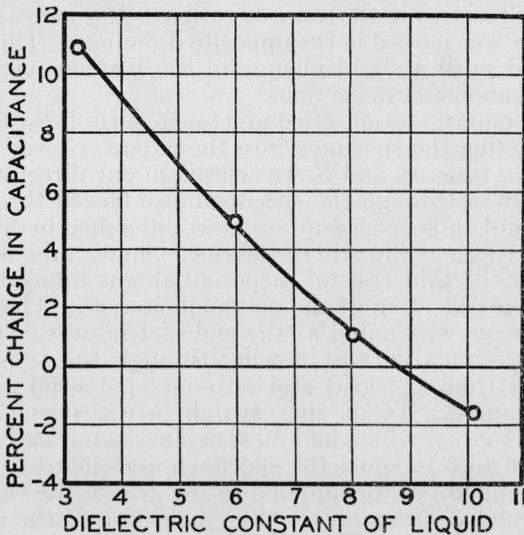


FIGURE 4.—Curve for determining the dielectric constant of calcium carbonate powder. The points are values of the percentage change in the capacitance of the cell when the powder was added to the liquid. The dielectric constant of the powder was taken as that of the liquid where the curve crossed the zero line.

potential between  $A$  and  $D$  was about 4 volts. Next, the galvanometer was connected and  $R_2$  was adjusted until the galvanometer deflection was zero.  $R_4$  was then changed so that the filament current

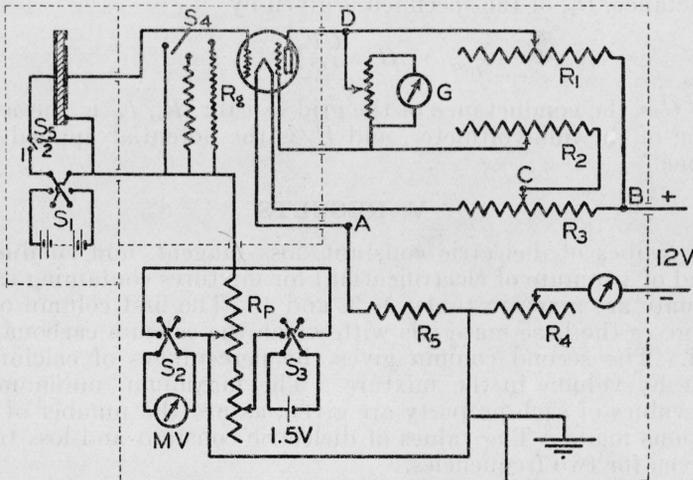


FIGURE 5.—Electrometer tube circuit for measuring conductance.

was slightly altered. If this deflected the galvanometer, the slider on  $R_3$  was not in the correct position, and it therefore was moved

slightly in one direction. The galvanometer deflection was again brought to zero by adjusting  $R_2$ . If this decreased the effect of a slight change of  $R_4$  on the galvanometer deflection, the slider on  $R_3$  was moved still farther in the same direction. If it increased the effect, then the slider was moved in the opposite direction. This adjustment was continued until a slight change in the filament current did not affect the galvanometer deflection.

To make a determination of conductance, switch  $S_5$  was thrown to 1, thus connecting the specimen into the circuit,  $S_4$  was connected to the proper grid resistor, and  $S_1$  was closed in one direction. The current which flowed through the specimen also flowed through the grid resistor,  $R_g$ , and thus caused a potential difference between the ends of the resistor. Since the grid of the electrometer tube was connected to one end of the grid resistor, a potential was applied to the grid, which caused a deflection of the galvanometer,  $G$ . The deflection of the galvanometer was noted at the end of 1 minute. The potential due to the specimen current flowing through the resistor,  $R_g$ , was then removed from the grid and an equal potential applied which could be measured. To do this, switch  $S_1$  was opened and  $S_4$  was turned to the contact which had no resistance connected to it. Switch  $S_5$  was thrown to 2 to short the specimen and guard to the opposite electrode. A potential was applied to the grid of the tube by closing switch  $S_3$  in such a direction that the deflection of the galvanometer was the same as before. The potentiometer,  $R_p$ , was then adjusted until the magnitude of the deflection was the same as before, which indicated that the potential applied to the grid of the tube was the same as before. This potential was measured by means of a millivoltmeter connected to switch  $S_2$ . After the specimen had been shorted at least 2 minutes, a second measurement was made with switch  $S_1$  closed in the opposite direction. An average of the two readings of the millivoltmeter was taken for computing the conductance. The conductance,  $G_x$ , of the specimen is given by

$$G_x = \frac{GE_g}{E_x}, \quad (5)$$

where  $G$  is the conductance of the grid resistor,  $R_g$ ,  $E_g$  is the average reading of the millivoltmeter, and  $E_x$  is the potential applied to the specimen.

## V. RESULTS

The values of dielectric constant, loss tangent, and conductivity (at end of 1 minute of electrification) for mixtures containing calcium carbonate are given in tables 1, 3, and 4. The first column of each table gives the base materials with which the calcium carbonate was mixed. The second column gives the percentages of calcium carbonate by volume in the mixture. The maximum, minimum, and mean values of each property are given, as are the number of determinations made. The values of dielectric constant and loss tangent are given for two frequencies.

TABLE 1.—Dielectric constant of mixtures containing calcium carbonate as a filler

Base material	Volume of calcium carbonate	Number of determinations	Dielectric constant at—					
			1,000 c/s			100,000 c/s		
			Maximum	Minimum	Mean	Maximum	Minimum	Mean
Natural rubber.....	%	8	2.54	2.49	2.52	2.54	2.48	2.51
Do.....	10.2	2	2.91	2.90	2.91	2.89	2.88	2.89
Do.....	23.3	6	3.47	3.44	3.46	3.44	3.42	3.43
Do.....	32.1	3	3.92	3.90	3.91	3.88	3.86	3.87
Do.....	49.6	3	4.84	4.83	4.83	4.80	4.78	4.79
Vistanex.....	0	4	2.29	2.29	2.29	2.29	2.29	2.29
Do.....	10.0	3	2.63	2.62	2.63	2.63	2.61	2.62
Do.....	24.6	3	3.26	3.24	3.25	3.25	3.22	3.23
Do.....	35.7	4	3.85	3.84	3.85	3.84	3.83	3.84
Do.....	47.7	2	4.58	4.56	4.57	4.55	4.53	4.54
Marble <sup>a</sup> .....		8	8.64	8.55	8.57			
Calcium carbonate powder.....					8.75			

<sup>a</sup> Values taken from former paper [6].

### 1. DIELECTRIC CONSTANT

The values of dielectric constant given in table 1 were plotted against the percentages of calcium carbonate by volume, as shown in figure 6 where the measured values are represented by circles. Only the values at 1 kilocycle per second are shown in the figure, since there is only a small difference between the values at the two frequencies.

The value 8.75 used for the dielectric constant of the calcium carbonate is the one obtained for the powder by the method of liquid mixtures. This value is about 2 percent higher than the value (8.57) obtained for the dielectric constant of the white marble [6]. The value 8.75 was used in spite of the fact that it was determined by a less precise method because it was obtained on a sample of the powder that was used in preparing the specimens.

Many formulas have been proposed for representing the dielectric constants of mixtures. Lichtenecker [12] and also Wachholtz and Franceson [10] have considered most of them and have given comprehensive discussions of their limitations. A few of the most promising of these were tested to see if they would fit the present data. Two formulas agreed with the data sufficiently well to warrant consideration.

One of these formulas was developed by Wiener [13] for the conductivity of mixtures. Since the formula for the conductivity involves the dimensions of the specimens in the same way as the formula for the dielectric constant, either may be used in the Wiener formula. Using the dielectric constant, the formula becomes:

$$\frac{K-K_1}{K+FK_1} = V_2 \frac{K_2-K_1}{K_2+FK_1} \quad (6)$$

or

$$K = \frac{K_1[K_2+FK_1+V_2F(K_2-K_1)]}{K_2+FK_1-V_2(K_2-K_1)} \quad (7)$$

where  $K$ ,  $K_1$ , and  $K_2$  are the dielectric constants of the mixture, continuous phase (rubber), and the dispersed phase (calcium carbonate),

respectively,  $V_2$  is the volume fraction of the dispersed phase, and  $F$  is a characteristic constant. If  $F=0$ , we have the series distribution of the components, as shown diagrammatically in figure 7 (a). If  $F=\infty$ , we have the parallel distribution of the components, as shown diagrammatically in figure 7 (b). If  $F=2$ , we have the formula developed by Maxwell for spheres embedded in a continuous medium, as illustrated in figure 7 (c).

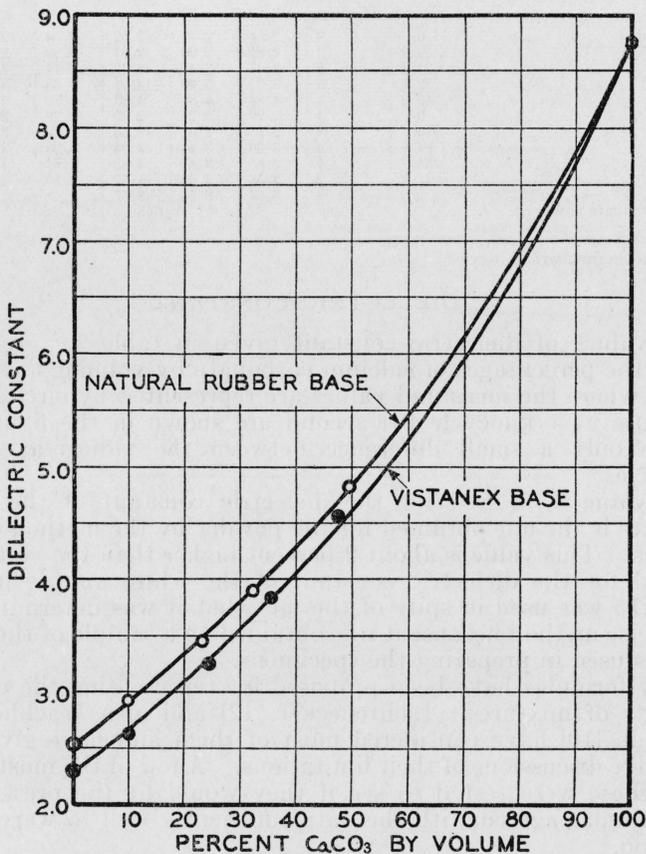


FIGURE 6.—Dielectric constant of rubber containing calcium carbonate at 1 kilocycle per second.

The points represent experimental values and the curves are given by equation 7, page 289.

Formula 6 was developed independently by Fricke [14], who computed the values that  $F$  should have for certain ellipsoidal shapes of the embedded particles. If the particles are flattened and their short axes are parallel to the field,  $F$  will have a value less than 2 but greater than 0, whereas if the short axes are perpendicular to the field,  $F$  will have a value greater than 2.

Wachholtz and Franceson [10] investigated the dielectric constants of mixtures of paint pigments in linseed oil. They found that the shape of the particles had a decided effect on the dielectric constant of the mixture. They also found that  $F$  was essentially constant with

variations in the powder content for those powders whose particle shapes did not differ too radically from the symmetrical shape. Since the particles had random orientation, they found that  $F$  was always larger than 2 if the particle deviated from the symmetrical shape. Thus for barite which had cubical particles (the space arrangement is not very different for spheres and cubes) the value of  $F$  was 2, but for zinc sulfide, which had elongated particles, the value of  $F$  was 3.8.

Applying eq 6 to our present data, we can solve for  $F$  and get values of  $F$  for the various percentages of the calcium carbonate in the rubber. Thus we have

$$F = \frac{V_2 K (K_2 - K_1) - K_2 (K - K_1)}{K_1 (K - K_1) - V_2 (K_2 - K_1)} \quad (8)$$

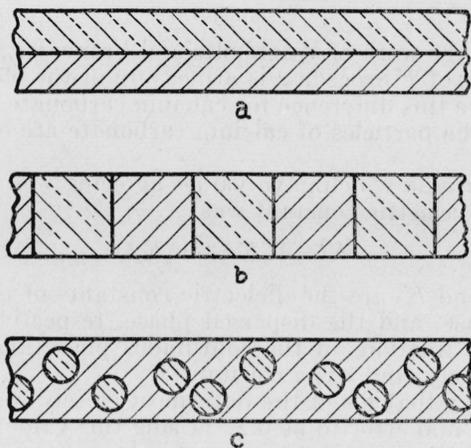


FIGURE 7.—Distribution of components for formula (7).

- (a) Series distribution,  $F=0$ .  
 (b) Parallel distribution,  $F=\infty$ .  
 (c) Spheres embedded in continuous phase,  $F=2$ .

The two components are distinguished in each case by the different slopes of the cross hatching.

The values of  $F$  computed by means of formula 8, using the data in table 1, are given in table 2. The values of  $F$  for the rubber base are probably constant within experimental error, but there is a definite increase with filler content for the Vistanex base. By giving more weight to the values obtained with higher filler contents, it seems that 2.7 is the most probable value of  $F$ . Using this value of  $F$ , the values of dielectric constant were computed for varying percentages of calcium carbonate for both Vistanex and natural-rubber bases. The curves shown in figure 6 represent the computed values. The points represent the measured values. The values of dielectric constant for the percentages of fillers used in the specimens are given in the fifth column of table 2. The agreement between the measured and computed values for the specimens having the natural-rubber base is very good, the difference being less than 1 percent. The agreement is not quite so good for the specimens having the Vistanex base, but the differences between the measured and computed dielectric constants are less than 2 percent.

TABLE 2.—Computed values of  $F$  and  $K$  for 1,000 cycles per second

Base material	Volume of calcium carbonate	$K$ , measured	$F$ , computed by eq 8	$K$ , computed by eq 7, using $F=2.7$	$K$ , computed by eq 9, using $x=0.2$
Natural rubber	% 0	2.52	-----	2.52	2.52
Do	10.2	2.91	2.5	2.92	2.90
Do	23.3	3.46	2.5	3.48	3.47
Do	32.1	3.91	2.8	3.90	3.89
Do	49.6	4.83	2.7	4.83	4.85
Vistanex	0	2.29	-----	2.29	2.29
Do	10.0	2.63	1.7	2.67	2.66
Do	24.6	3.25	1.9	3.30	3.30
Do	35.7	3.85	2.8	3.84	3.85
Do	47.7	4.57	3.2	4.49	4.54
Calcium carbonate powder	-----	8.75	-----	8.75	8.75

According to the work of Wachholtz and Franceson, the amount by which the value of  $F$  exceeds 2 is a measure of the elongation of the particles. Since this difference for calcium carbonate is 0.7, the indication is that the particles of calcium carbonate are elongated somewhat.

The other formula which gave values agreeing well with the measured values of dielectric constant was

$$K^x = V_1 K_1^x + V_2 K_2^x, \quad (9)$$

where  $K$ ,  $K_1$ , and  $K_2$  are the dielectric constants of the mixture, the continuous phase, and the dispersed phase, respectively,  $V_1$  and  $V_2$  are the volume fractions of the continuous phase and the dispersed phase, respectively, and  $x$  is a constant.

The value of  $x$  that fitted the data most closely was found by the method of trial and error to be 0.2. Using this value of  $x$ , the values of the dielectric constant were computed by means of formula 9 for the percentages of calcium carbonate used in the specimens. These values, which are given in the sixth column of table 2, agree with the measured values as well as did the values computed by means of formula 7. Although formulas 7 and 9 give values which agree about equally well with the measured values, formula 7 may be preferred, since it gives some indication of the shape of the particles and state of dispersion of the powder.

## 2. LOSS TANGENT

The values of loss tangent at 1,000 cycles per second given in table 3 are plotted in figure 8 against the percentages of calcium carbonate by volume. The vertical lines through the points indicate the spread in values. Since the data in table 2 indicate practically no change with frequency for the specimens containing a natural rubber and a small decrease with frequency for the specimens containing Vistanex, values for only the one frequency have been plotted. The loss tangent appears to increase directly with the percentage of calcium carbonate by volume. The straight lines drawn through these points and extended to 100-percent calcium carbonate would indicate a value for the loss tangent of calcium carbonate higher than the average value obtained for the marble. However, the extrapolated values lie within the range of values obtained, so that it can be assumed that the loss tangent is directly proportional to the calcium carbonate content.

TABLE 3.—Loss tangent of mixtures containing calcium carbonate as a filler

Base material	Volume of calcium carbonate	Number of determinations	Loss tangent at—					
			1,000 c/s			100,000 c/s		
			Maximum	Minimum	Mean	Maximum	Minimum	Mean
Rubber	%							
Do	0	8	$26 \times 10^{-4}$	$19 \times 10^{-4}$	$22 \times 10^{-4}$	$34 \times 10^{-4}$	$30 \times 10^{-4}$	$32 \times 10^{-4}$
Do	10.2	2	27	27	27	24	23	24
Do	23.3	6	32	26	28	33	27	30
Do	32.1	3	36	35	36	37	36	36
Do	49.6	3	34	33	34	30	29	30
Vistanex	0	4	2	1	2	4	3	3
Do	10.0	3	4	3	3	4	4	4
Do	24.6	4	20	11	13	7	6	6
Do	35.7	4	16	11	14	9	8	9
Do	47.7	2	19	14	17	11	11	11
Marble <sup>a</sup>	47.7	8	56	10	22			

<sup>a</sup> Values taken from a former paper [6].

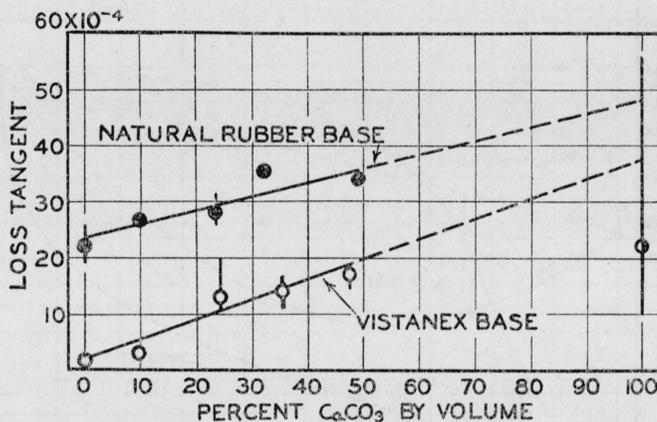


FIGURE 8.—Loss tangents of rubber containing calcium carbonate at 1 kilocycle per second.

The vertical lines through the points show the spread of values.

### 3. CONDUCTIVITY

The conductivity was determined at the end of 1 minute of electrification and is called the "1-minute" conductivity. The logarithms of the values of the 1-minute conductivity given in table 4 are plotted in figure 9 against the calcium carbonate content. The vertical lines through the points indicate the spread of the values. The conductivities of the two base compounds are quite different, that of the natural rubber compound being about 50 times that of Vistanex. The curves of the two (solid lines) are also quite different. The conductivity of the specimens containing natural rubber passes through a minimum, whereas that for Vistanex increases continuously with increasing calcium carbonate content.

TABLE 4.—Conductivity of mixtures containing calcium carbonate as a filler

Base material	Volume of calcium carbonate	Number of determinations	"One-minute" conductivity, in mho-cm <sup>-1</sup>		
			Maximum	Minimum	Mean
Natural rubber	Percent	8	160×10 <sup>-17</sup>	39×10 <sup>-17</sup>	88×10 <sup>-17</sup>
Do	23.3	6	37	23	28
Do	32.1	3	22	22	22
Do	49.6	3	28	23	26
Vistanex	0	2	2.0	2.0	2.0
Do	10.0	7	7.2	3.5	4.9
Do	24.6	2	170	148	92
Do	35.7	2	320	190	260
Marble <sup>a</sup>		8	4,800	290	990

<sup>a</sup> Values taken from another paper [6].

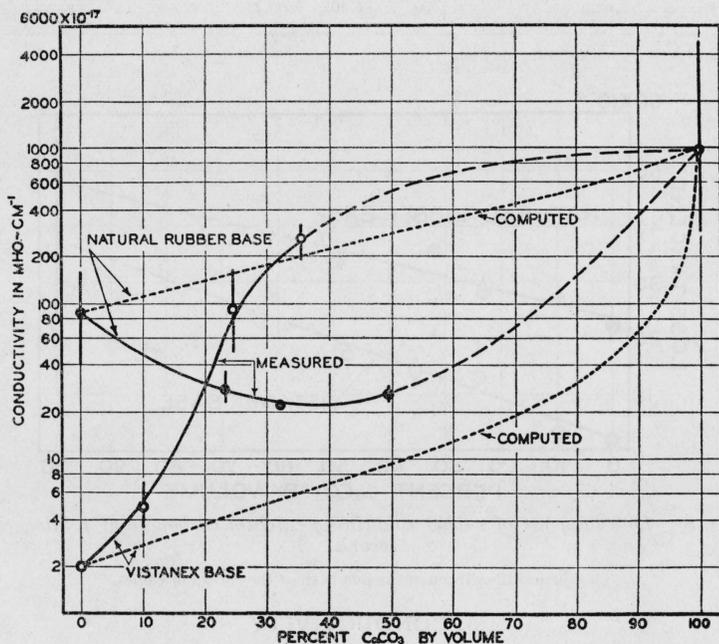


FIGURE 9.—Conductivity of rubber containing calcium carbonate.

The vertical lines through the points show the spread of values.  
The solid line curves were obtained from equation 10, page 294.

Since eq 7, which fitted the dielectric-constant data so well, was originally developed for conductivity, it is of interest to see how it fits the measured values of conductivity. Substituting conductivities for dielectric constants,

$$\frac{\gamma - \gamma_1}{\gamma + F\gamma_1} = V \frac{\gamma_2 - \gamma_1}{\gamma_2 + F\gamma_1}, \quad (10)$$

where  $\gamma$  is the conductivity of the mixture,  $\gamma_1$  is the conductivity of the rubber,  $\gamma_2$  is the conductivity of the calcium carbonate,  $V$  is the volume fraction of the calcium carbonate, and  $F$  is a characteristic constant. The dashed curves of figure 9 represent the values com-

puted by means of eq 10, using the value of 2.7 for  $F$ . These values do not agree with the data for 1-minute conductivity. The conductivities for specimens containing Vistanex were much higher than the computed values, while for those containing natural rubber they were much lower. It is apparent that the 1-minute conductivity is not a direct result of structure but is caused by secondary effects.

In considering the conductivity of a dielectric, it must be kept in mind that the conductivity at the end of 1 minute is a purely arbitrary determination. Rubber compounds usually have considerable electrical absorption, which means that the current flowing through the specimen under constant potential decreases with time, rapidly at first, then more slowly. Thus the conductance which is determined will depend on the time at which the current was measured. Since different specimens may exhibit different electric absorption curves, the conductances determined for a fixed time of electrification may not be comparable. This may explain why the measured values do not agree with the computed values.

## VI. SUMMARY

The results obtained in this investigation indicate that either the formula developed by Wiener (formula 7) or the exponent formula (formula 9) may be used for the computation of the dielectric constants of mixtures of calcium carbonate and rubber. Formula 7 may be preferred, since it gives some indication of the shape of the particles and state of dispersion of the powder.

There was little difference between values of the dielectric constant and loss tangent at 1 kilocycle per second and at 100 kilocycles per second.

The change of the loss tangent with the content of calcium carbonate was not large, but a direct relationship between loss tangent and percentage of calcium carbonate was indicated.

The 1-minute-conductivity values increased continuously with increasing content of calcium carbonate when Vistanex was used as the base but passed through a minimum when natural rubber was used.

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