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ELECTRICAL AND MECHANICAL PROPERTIES OF THE SYSTEM BUNA S-GILSONITE

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ABSTRACT

Buna S compounds containing gilsonite have properties that render them suitable for the insulation of communication cables. The principal limitation of these compounds as produced at the time of this investigation was that Buna S contained constituents which caused relatively high water absorption. Electrical measurements were made of gilsonite and of compounds of Buna S containing from 0 to 56 percent of gilsonite by volume, i. e., from 0 to 150 parts by weight per 100 parts of Buna S and 12 parts of other ingredients. The base compound contained, in parts by weight: Buna S, 100; stearic acid, 2; zinc oxide, 5; accelerator, 2; and sulfur, 3. The dielectric constant of this base compound at 1,000 cycles per second was 2.85, and the power factor 30×10^{-4}; the d-c conductivity was 11×10^{-16} mho/cm 1 minute after application of potential. Under the same conditions the dielectric constant of the gilsonite alone was 2.60, the power factor 15×10^{-4}, and the conductivity less than 2×10^{-16} mho/cm. Most of the requirements of the United States Coast Guard specifications for the insulation of submarine cable were met by a compound containing 25.6 percent of gilsonite by volume, or 40 parts of gilsonite by weight per 100 parts of Buna S and 12 parts of other ingredients. This compound had the following properties: dielectric constant at 1,000 cycles per second, 2.78, and power factor, 65×10^{-4}; d-c conductivity, 4×10^{-16} mho/cm; tensile strength, 1,200 lb/in^2; ultimate elongation, 470 percent; tensile stress at an elongation of 200 percent, 560 lb/in^2. At the frequencies at which the measurements were made, namely 100, 1,000, 7,500, and 100,000 cycles per second, the dielectric constant of the base compound decreased from 2.88 to 2.78, and the power factor increased from 15×10^{-4} to 145×10^{-4}. The change with frequency became smaller with additions of gilsonite. Extraction of the Buna S with water before compounding removed about 0.8 percent of water-soluble materials and reduced the absorption of water to about one-third of the value for the commercial material. The change of dielectric constant on immersion in water was reduced by prolonged washing of the Buna S, but the power factor was little affected.

CONTENTS

I. INTRODUCTION

When Buna S, a copolymer of butadiene and styrene, is vulcanized without fillers by the present methods, it has good electrical properties but is too weak and tears too readily to be of much practical use. The addition of carbon black develops mehanical strength at the expense of good electrical properties. By compromising on relatively small amounts of carbon black, e. g., 10 percent, it has been possible to obtain insulating compounds that would serve certain limited uses [1][1]. This loss of electrical quality is avoided when gilsonite is used as a filler instead of carbon black. The gilsonite does not have as much reinforcing action as carbon black, but it imparts sufficient strength and resistance to tear and compression-cutting for the compound to serve many practical purposes.

The use of gilsonite as a compounding material for Buna S was suggested by the fact that it or similar materials have been employed successfully as a compounding ingredient in natural rubber to meet the exacting requirements of the submarine communication cables used by the United States Coast Guard. Gilsonite has the advantage that it is available from domestic sources in quantities adequate for any reasonable demand [2].

Although the present investigation was undertaken for an immediate practical objective, the results constitute at the same time a small contribution to the general subject of heterogeneous dielectrics. A discussion of this problem as applied to rubber-filler systems was given in a recent paper [3].

II. MATERIALS

For this investigation, specimens were prepared having Buna S and gilsonite as their principal constituents. The minor ingredients—stearic acid, zinc oxide, sulfur and accelerator—were used to facilitate the processing and vulcanization of the specimens.

Gilsonite is a natural asphaltlike solid of high softening point [4]. The gilsonite used in this study was ground material of a grade commonly furnished the rubber trade. The fineness was such that 100 percent passed through a No. 100 sieve, and 90 percent was retained on a No. 200 sieve. The softening point as determined by the ring-and-ball method was 153° C, the density at 25° C was 1.0408 g/cm^3. Analytical determinations on the gilsonite by the usual methods gave the following data:

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[1] Figures in brackets indicate the literature references at the end of this paper.

	Percent
Water extract	0. 5
Acetone extract	4. 9
Ash	0. 3
Insoluble in carbon tetrachloride	. 1
Soluble in carbon disulfide	99. 9
Fixed carbon (ASTM D-168-30)	14

The Buna S was obtained from the Standard Oil Co. of New Jersey and was regarded as typical of their production in the spring of 1942. Partial analysis of the Buna S used in this investigation showed

	Percent
Water extract	1. 3
Acetone extract	3. 7
Ash	2. 0
Soap	3. 9

Its density at 25° C was 0.9390 g/cm^3 [5]. This density was about 1 percent higher than the density observed for a sample prepared in the Firestone laboratories by polymerization with a minimum quantity of materials other than butadiene and styrene [5]. In the commercial polymerization of Buna S, catalysts, emulsifying agents, modifying agents, and coagulating agents are used. These materials remain in the manufactured polymer in appreciable quantities and affect the electrical behavior of the polymer, as discussed in a subsequent section of this paper.

III. PREPARATION OF SPECIMENS

Slabs and insulated wires were used for electrical measurements and sheets for mechanical tests.

1. COMPOSITIONS

A series of compounds was prepared by the addition of increasing quantities of gilsonite to a base compound of the following composition:

Base compound A

Ingredients	Parts by weight
Buna S	100. 0
Stearic acid	2. 0
Zinc oxide	5. 0
Sulfur	3. 0
Santocure [2]	2. 0
	112. 0

The successive proportions of gilsonite added to base compound A were 25 parts, 40 parts, 70 parts, and 150 parts by weight per 100 parts of Buna S. Phenyl-beta-naphthylamine was already present as a stabilizer in the Buna S as furnished by the manufacturer. Since this also served as an antioxidant, no other antioxidant was necessary.

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[2] Santocure is an accelerator, described by the manufacturer (Monsanto Chemical Co.) as a "reaction product of cyclohexylamine and mercaptobenzothiazole."

2. COMPOUNDING

The mixing of all constituents except the sulfur and the accelerator was done in an internal mixer of the Banbury type, which was heated by a steam jacket throughout the mixing. The highest temperature obtainable by this method, about 135° C, appeared to give the best dispersion of gilsonite in Buna *S*. In this laboratory-size internal mixer (capacity 550 cm^3 of compound) it was found necessary to masticate the batch for 30 minutes or more to obtain highest values of modulus of elasticity and tensile strength in the vulcanizate. The sulfur and accelerator were added later on the roll mill in the usual way.

Completion of the milling is best judged by pulling a bit of the mixture between the fingers. If the mixture gives a short ragged break, further milling is necessary, but if the mixture gives an easily distinguished long stringy break, the dispersion has progressed enough to produce a strong vulcanizate.

When certain waxes were used, this relatively high degree of dispersion was obtainable in less than half the time required when the Buna *S* and gilsonite were used alone. To keep the composition simple, no wax or softener was used. However, such softeners with low power factor and low dielectric constant are available commercially, and in work not here reported were found to facilitate the mechanical operations of mixing and extrusion.

3. MOLDING AND VULCANIZATION OF SLAB SPECIMENS

To prepare material as nearly free from air as possible, slab specimens for the electrical measurements were formed in the following manner, similar to that described by Scott and McPherson [3]: After the first mixing, the stocks were allowed to stand for a few days and then remilled and sheeted. The sheet was cut into strips about 3 cm wide and 15 cm long. Two such strips were laid, one on top of the other, across the center of a 15× 16×0.6-cm rectangular mold, the cover was pressed down, and the strips were pressed out together. The material was so restrained by the sides and faces of the mold that it could flow only toward the ends of the mold. The cover was removed, another strip was added, and this procedure was repeated until the mold was completely filled. The sheet so formed was cut into strips 15 cm long and 3 cm wide, and the filling process was followed as before by plying the strips up in the center of the mold, and successively pressing out the plies. This process was repeated three or four times. Specimens made in this way were more nearly free from air than those made by any other method that was tried.

The specimens were then vulcanized at 162° C for 60 minutes. Vulcanization was complete in about 20 minutes, but, because of the great recovery or "nerve" of Buna *S*, it was considered desirable to continue heating for the longer period in order to obtain specimens for capacitance measurements that would maintain the requisite uniformity of dimensions. Continued heating beyond the time required for vulcanization did not greatly affect either the mechanical properties or the electrical properties of the finished specimens as much as continued heating would have affected the same properties of natural rubber. This is shown by the fact that a specimen containing 25 parts of gilsonite by weight per 100 parts of Buna *S*, after 20 minutes of vulcanization at 162° C had a dielectric constant of 2.84 (1,000 cycles per second and 25° C) and a power factor of 69×10^{-4}, whereas two specimens vulcanized at 162° C for 60 minutes had dielectric constants of 2.82 and 2.83 and power factors of 64×10^{-4} and 72×10^{-4}, respectively. Furthermore, it is shown in figures 1 and 2 that there is little impairment of tensile strength and elongation with heating beyond the time required for vulcanization.

Dumbbell-shaped specimens for tensile and brittleness tests had a constricted portion 0.25 in. wide and gage marks 2 in. apart. Compression-cutting specimens were 1-in. squares, 0.1 in. thick. Hardness specimens were strips 0.25 in. thick.

4. EXTRUSION ON CONDUCTOR

Since the effect of water absorption on the electrical properties can conveniently be studied with specimens in the form of insulated wire, some wire was insulated with base compound *A* mixed with 40 parts by weight of gilsonite per 100 parts of Buna S. This compound was selected because it had good mechanical properties. The stock contained enough gilsonite so that it could be extruded smoothly, yet not so much that it would be stiff when cold or too tacky when hot, effects which occur when more gilsonite is used. This mixture when vulcanized had approximately the highest tensile strength and elongation obtainable from any compound of the constituents.

For extrusion on wire the stock was preheated on the rolls to about 70° C. It was then extruded around No. 12 AWG (0.205 cm in diameter) aluminum wire by means of a small commercial tubing machine. Thermometers were placed in wells drilled in the head and in the die holder of the machine. The best extrusion of the stock was obtained when the temperature of the stock and the die were held somewhat higher than that required for natural rubber. The die was kept at about 80° to 85° C.

IV. MECHANICAL PROPERTIES

The mechanical properties studied were density, elastic behavior, hardness, and brittleness at low temperatures. These were observed under a variety of conditions. In most respects the mechanical properties were similar to those of compounds of natural rubber containing gilsonite, the chief differences being that the Buna S stocks were stiffer, and when properly vulcanized, gave lower values of the tensile strength. Processing operations such as milling, molding, and extrusion seemed to proceed best at temperatures higher than those used for natural rubber.

1. DENSITY

To compute volume and thickness, density measurements were made by means of hydrostatic weighings on vulcanized specimens prepared for electrical tests. The results of the density determinations are given in table 1. Since the density of gilsonite, 1.0408 g/cm^3, is very near the density of vulcanized base compound *A*, 1.0028 g/cm^3, all of the vulcanized compounds containing gilsonite in the proportions used in this study had about the same density.

TABLE 1.—*Change in volume of Buna S-gilsonite compounds on vulcanization*

Base material	Proportion of gilsonite to Buna S by weight	Gilsonite content of vulcanized specimens	Density at 25° C computed for unvulcanized compounds	Number of specimens examined	Density of specimens measured at 25° C			Shrinkage in volume resulting from vulcanization
					Maximum	Minimum	Mean	
	Parts per 100 parts of Buna S	*Percent by volume*	*g/cm* ^{3}		*g/cm* ^{3}	*g/cm* ^{3}	*g/cm* ^{3}	*Percent*
Base compound *A*[1]	0.00	0.00	0.9948	4	1.0033	1.0023	1.0028	0.80
Do.[1]	25.00	17.70	1.0029	4	1.0110	1.0086	1.0098	0.69
Do.[1]	40.00	25.57	1.0065	4	1.0122	1.0107	1.0114	0.48
Do.[1]	70.00	37.60	1.0120	4	1.0174	1.0170	1.0172	0.53
Do.[1]	150.00	56.30	1.0206	2	1.0241	1.0230	1.0236	0.28
Gilsonite	∞	100.00	----------	3	1.0411	1.0405	1.0408	----------

[1] Base compound *A* contained, in parts by weight: Buna S, 100; stearic acid, 2; zinc oxide, 5; Santocure, 2; and sulfur, 3.

2. REDUCTION IN VOLUME ON VULCANIZATION

The densities of the unvulcanized compounds computed from the densities of the ingredients are shown in the fourth column of table 1. A comparison of these values with the observed densities of the vulcanized compounds given in the eighth column gave the percentage of shrinkage on vulcanization shown in the last column. This reduction in volume is approximately proportional to the volume of Buna S present, and is presumably brought about by the reaction of the Buna S with sulfur. Assuming that all of the sulfur goes into combination, this shrinkage amounts to about 60 percent of the volume of the combined sulfur. A similar shrinkage occurs during the vulcanization of natural rubber [7].

3. STRESS-STRAIN CHARACTERISTICS

Tensile tests of from 3 to 15 dumbbell-shaped specimens of each cure and composition were made in accordance with the procedure described in Federal Specification ZZ–R–601a, Rubber Goods; General Specifications (Methods of Physical Tests and Chemical Analyses).

The stress-strain characteristics of the compounds were found to depend on the following factors: (1) dispersion of filler, (2) temperature of vulcanization, (3) length of time of vulcanization, (4) proportion of gilsonite. It was found that the stiffness and tensile strength of the compounds were increased by improving the dispersion of the gilsonite, lengthening the time of cure, and increasing the temperature of vulcanization within limits. The maximum tensile strength was obtained from a composition of 40 parts of gilsonite by weight per 100 parts of Buna S. There is very little danger of overcure, as these compounds may be held at 162° C for an hour or more with very slight loss in either strength or extensibility, as may be seen from figure 1.

The dispersion of gilsonite appears to be affected by the temperature and time of mixing in the internal mixer, as well as by the presence of "fluxing" ingredients, such as stearic acid, waxes, or softeners. These materials may shorten mixing time. However, similar dispersions may be obtained without the addition of fluxing ingredients by prolonged working. With Buna S no deleterious break-down was observed as a result of prolonged working so long as the mixing temperature was kept high. The state of dispersion was judged, as mentioned above, by pulling some of the compound between the fingers to observe whether it pulled out "stringy" or "short." Generally, any gilsonite compound that is stringy is clear and uniform in color when a thin portion is held to the light, whereas a compound which tears short and ragged is often flecked with visible particles of gilsonite. These conditions, which we have interpreted as evidences of good or poor dispersion, have been found to be associated with good or poor mechanical strength. Other evidence of imperfect dispersion in certain batches was found in a flaked structure apparent in broken tensile specimens.

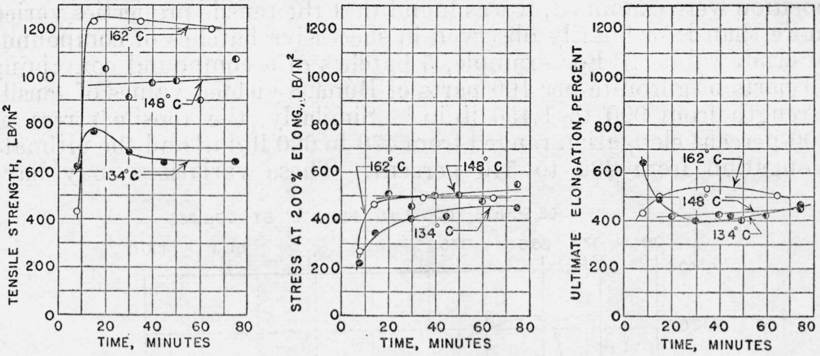

FIGURE 1.—*Effect of temperature and time of vulcanization on the tensile properties of a compound containing 40 parts of gilsonite by weight per 100 parts of Buna S.*

Compounds vulcanized at 162° C, the highest temperature used, had the highest tensile strength, the highest tensile stress at 200-percent elongation, and the highest ultimate elongation of any compounds tested. Irrespective of how long vulcanization was continued at a low temperature, the compound was found not to attain as high a tensile strength as when vulcanized at a higher temperature. This is seen by a comparison of the values of tensile properties obtained from the 162° C cure with values obtained from the cures at 148° and 134° C (figs. 1 and 2) for both of the compounds

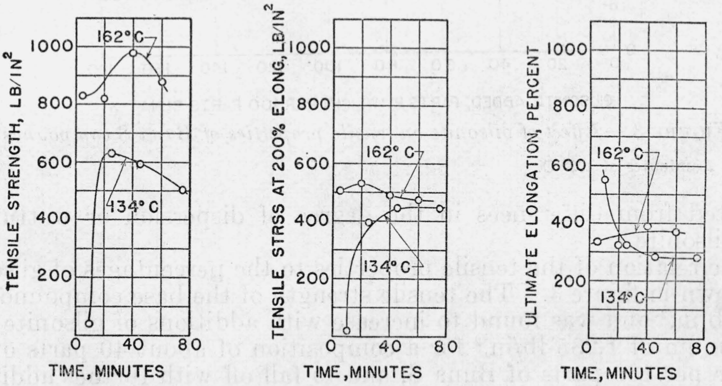

FIGURE 2.—*Effect of temperature and time of vulcanization on the tensile properties of a compound containing 25 parts of gilsonite by weight per 100 parts of Buna S.*

containing 40 parts and 25 parts of gilsonite by weight per 100 parts of Buna S.

Gilsonite softens at 153° C (ball-and-ring test). The greater tensile strength obtained by vulcanization at 162° C may be due to softening of the gilsonite and consequent better interfacial wetting. Flow may occur in the filler phase as well as in the rubber matrix.

When several separately compounded batches of the same composition were examined, it was found that the tensile properties varied more than is ordinarily observed in successive batches of compounds of crude rubber. For example, 5 batches of a compound containing 40 parts of gilsonite per 100 parts of Buna S yielded values of tensile strength from 990 to 1,450 lb/in.^{2} Similarly, the tensile stress at 200-percent elongation ranged from 470 to 620 lb/in.^{2} and the ultimate elongation from 420 to 540 percent. These variations may have resulted from differences in the degree of dispersion or wetting of the gilsonite.

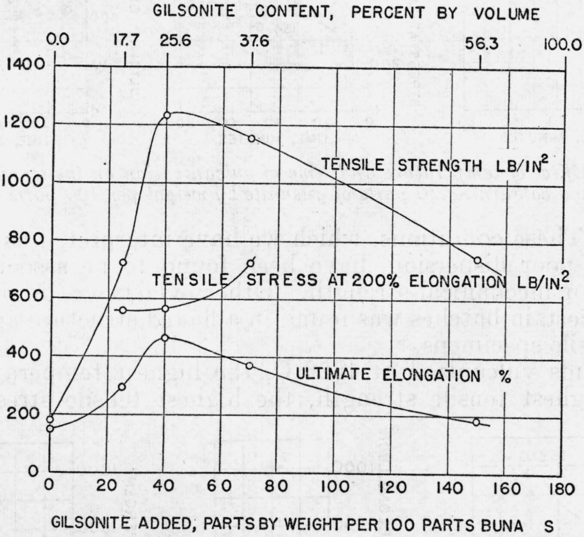

FIGURE 3.—*Effect of gilsonite on tensile properties of Buna S compounds.*

Cure: 20 minutes at 162° C.

The relation of the tensile properties to the percentages of gilsonite is shown in figure 3. The tensile strength of the base compound was 180 lb/in.^{2} and was found to increase with additions of gilsonite to a maximum of 1,235 lb/in.^{2} for a composition of about 40 parts of gilsonite per 100 parts of Buna S, and to fall off with further additions to 745 lb/in.^{2} for 150 parts of gilsonite. The greatest value of ultimate elongation, 465 percent, was also obtained from the composition containing 40 parts of gilsonite.

Tensile modulus of elasticity increased with additions of gilsonite; for 40 parts of gilsonite the tensile stress at 200-percent elongation was 565 lb/in.^{2} For the extremes in composition, namely, compounds containing no gilsonite and those containing 150 parts of gilsonite, the ultimate elongations were less than 200 percent, and for this reason the tensile stress at 200 percent elongation, of course, cannot be represented on the curves. The compound containing 70 parts of gilsonite by weight per 100 parts of Buna S had a tensile strength of 1,155 lb/in.^{2}, a tensile stress of 725 lb/in.^{2} at 200-percent elongation, and an ultimate elongation of 370 percent. Since these properties are not greatly inferior to those of a compound containing less gilsonite, the utilization of such a compound might be desirable from the standpoint of extending the supply of Buna S.

4. BEHAVIOR AT LOW TEMPERATURES

The compound containing 40 parts of gilsonite per 100 parts of Buna S was tested for hardness over a range of low temperatures with a Shore Durometer [8]. The values obtained are shown in figure 4. The values of hardness at the three highest temperatures were obtained after the specimens had been held at these temperatures about half an hour and were checked by measurements on the specimens held at the temperatures overnight. The values of hardness at the lower temperatures were observed shortly after the specimens were brought to these temperatures in an alcohol bath cooled by dry ice.

A test for brittleness was made by observing the highest temperature at which a clamped tensile specimen would break when abruptly bent at right angles with pliers. The brittle point was found to be about −53°C. This may be compared with the brittle point of a gum compound of Buna S containing no filler reported as −65.5°C [9]. At the temperature at which brittleness was observed the Shore hardness number had not reached 100, as shown in figure 4.

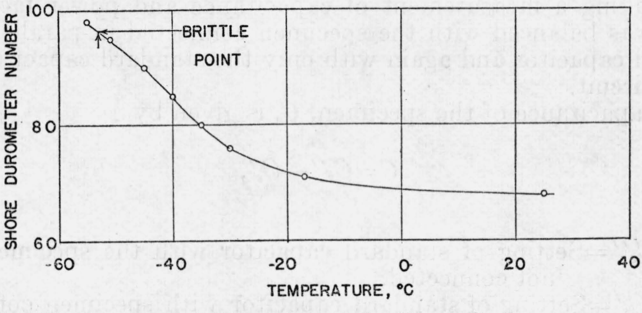

FIGURE 4.—*Hardness and brittle point of the Buna S-gilsonite compound containing 40 parts by weight of gilsonite per 100 parts of Buna S.*

V. ELECTRICAL PROPERTIES

The electrical properties studied were dielectric constant, power factor, and direct-current conductivity. The dielectric strength was determined for one compound for comparison with certain specifications, as described in a later section.

Rectangular specimens prepared as described earlier were used for the study of the electrical properties. Rectangular tinfoil electrodes were applied to the two faces of the specimens by means of a thin film of vaseline and were rolled down by means of a narrow roller. One electrode extended to the edges of the specimen and the other was cut to leave an uncovered margin having a width greater than three times the thickness of the specimen, as recommended in a previous paper [10]. No guard rings were used for either the direct-current conductivity measurement or for the dielectric-constant and power-factor measurements, since tests showed that the same values of conductance were obtained whether or not guard rings were used. The areas of the electrode and of the specimen were measured with a steel scale. Thickness was found by dividing the volume, as determined by means of hydrostatic weighings, by the area of the specimen.

1. DIELECTRIC CONSTANT AND POWER FACTOR

(a) METHOD OF MEASUREMENT

The measurements of capacitance and power factor were made by means of a conjugate Schering bridge, as described in a former paper [3]. This bridge is similar to one described in the ASTM standard method for measuring capacitance and power factor [11].

Two types of detectors were used with this bridge, depending on the frequencies. For 7,500 cycles per second and lower frequencies a tuned amplifier was employed having a galvanometer to indicate the output. For 100,000 cycles per second a regenerative radio receiver was used as the detector. The receiver was set for such regeneration that it oscillated, and then was tuned so that the oscillations produced a beat note of 1,000 cycles per second in the headphones when the current from the bridge was applied to the input of the receiver.

In making a measurement of capacitance and power factor, the bridge was balanced with the specimen connected in parallel with a standard capacitor and again with only the standard capacitor in the bridge circuit.

The capacitance of the specimen, C, is given by

$$C = C_s'' - C_s',$$

where

C_s'' = Setting of standard capacitor with the specimen not connected.

C_s' = Setting of standard capacitor with specimen connected in parallel.

Corrections for edge capacitances were applied as described in a previous paper [10]. Thus dielectric constant is given by

$$K = \frac{C - C_i}{C_n + C_m}$$

where

C = Capacitance of specimen in micromicrofarads,

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

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

$C_m = 0.0405P$,

P = Perimeter of small electrode in centimeters,

b = Thickness of specimen in centimeters,

A = Area of small electrode in square centimeters.

The power factor, *P.F.*, is given by

$$P.F.=\frac{\omega R_4 C_s'(C_4'-C_4'')}{C-C_i},$$

where

$\omega=2\pi f$.

f=Frequency.

R_4=Resistance in parallel with capacitor, C_4 (in arm opposite the standard capacitor).

C_4'=Capacitance of C_4 with the specimen connected into the bridge.

C_4''=Capacitance of C_4 with specimen not connected into the bridge.

The above equations hold with sufficient accuracy for the present purposes if the power factor is less than 0.1, and if the power factor of the standard capacitor can be considered zero. The specimens were measured at frequencies of 100, 1,000, 7,500, and 100,000 cycles per second. For each composition, at least two separately mixed batches were studied to observe any variation in properties between particular batches. All measurements were at room temperature of about 25° C and 50-percent relative humidity or less.

On determinations of dielectric constant at particular frequencies and compositions, an average variation of 0.022 was found with different specimens. Repeated measurements on the same specimens were made in a few cases, and the variation in values from the original determinations was negligible. For power factor the individual determinations showed an average range of 5×10^{-4}. Typical data are cited for determinations of dielectric constant and power factor in table 2. In this instance the variation in dielectric-constant measurements was 0.038 and in power factor, 2×10^{-4}.

TABLE 2.—*Reproducibility of determinations of electrical properties*

[Compound contained 25.6 percent of gilsonite by volume. Measurements were at 1,000 cycles per second and at 25° C.]

Specimen number	Dielectric constant	Power factor
1	2.771	64×10^{-4}
2	2.801	66
3	2.769	64
4	2.763	65

(b) EFFECT OF COMPOSITION AND FREQUENCY

The dielectric constant and the power factor of gilsonite at all frequencies measured were found to be smaller than for Buna S base compound *A*. In figures 5 and 6 it is seen that additions of gilsonite in general had the favorable effect of lowering the values of the dielectric constant, whereas the power factor increased with small additions, yet decreased with high gilsonite content. In the main the dielectric constant was found to decrease about in proportion to the gilsonite content except in the range from 20 to 35 percent by volume. At 1,000 cycles per second the dielectric constant decreased from 2.85 for Buna S base compound *A* to 2.60 for pure gilsonite, whereas the power factor changed from 30×10^{-4} to 15×10^{-4}, passing through a maximum value of about 72×10^{-4} at 35 percent of gilsonite by volume.

The preparations containing approximately 25 percent of gilsonite by volume were lower in dielectric constant and power factor than

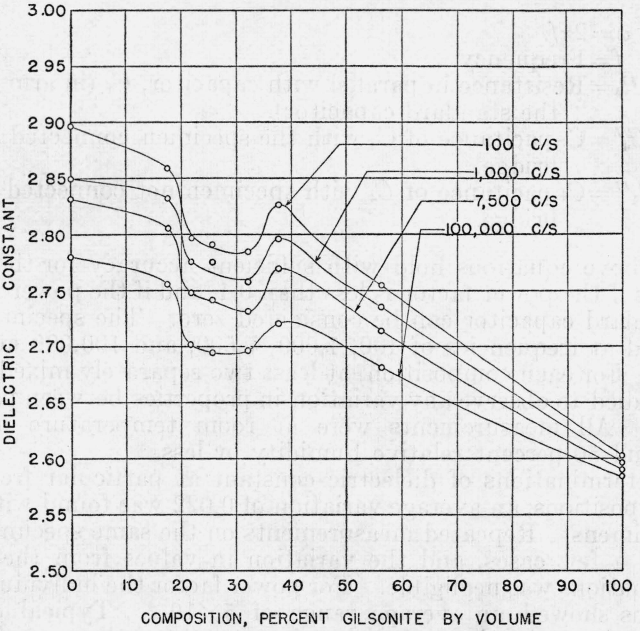

FIGURE 5.—*Effect of composition and frequency on dielectric constant of Buna S-gilsonite compounds.*

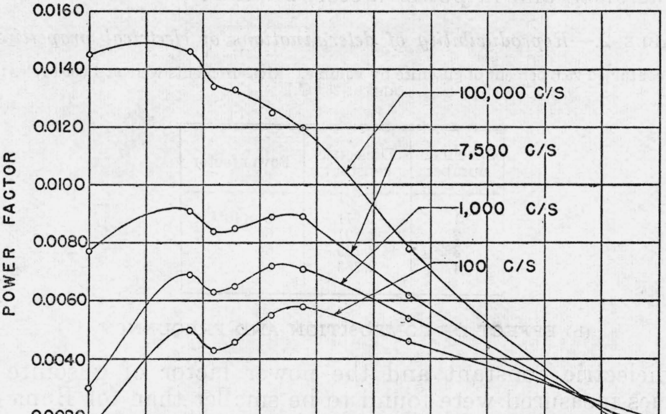

FIGURE 6.—*Effect of composition and frequency on power factor of Buna S-gilsonite compounds.*

might have been expected from the trend of the other observations. This deviation, first observed on duplicate specimens, was again observed on specimens of independently compounded batches. No explanation for this is offered.

The dielectric constants of all the compounds were found to decrease with frequency. For pure gilsonite the change of dielectric constant with frequency is about one-fourth that for base compound *A*. As gilsonite is added to Buna S, there are progressively smaller variations of dielectric constant with frequency and lower absolute values of dielectric constant for all frequencies.

Although the power factor of the base compound increases with frequency the addition of gilsonite reduces the range of variation with frequency. For pure gilsonite this effect of frequency on the power factor is opposite to that for the base compound, the values decreasing slightly with increasing frequency at room temperature.

The effect of lapse of time on electrical properties of two vulcanized specimens containing 37.6 percent of gilsonite by volume (70 parts by weight per 100 parts of Buna S) is shown in table 3. During the intervals between measurements the specimens were stored in a desiccator. After the measurements of the 72d day, a 2-day lapse was allowed in order to make additional measurements to determine whether the slight change represented permanent change in the specimen with time or merely a day-to-day variation in precision of measurement. Table 3 shows there was a change within the specimens with time, although this change was too small to be considered important with regard to performance of the compound as an insulating material.

TABLE 3.—*Electrical properties of two specimens containing 70 parts by weight of gilsonite per 100 parts of Buna S remeasured after a lapse of time*

[Conditions in every case were: frequency, 1,000 cycles per second; temperature, 25° C; humidity, 50 percent.]

Time elapsed	Dielectric constant		Power factor	
	Specimen No. 1	Specimen No. 2	Specimen No. 1	Specimen No. 2
Days:				
0	2.791	2.800	69×10^{-4}	69×10^{-4}
72	2.811	2.822	71	70
74	2.811	2.822	70	70

The dielectric constant and the power factor of four specimens subjected to accelerated aging also showed no significant changes. Comparisons of these properties after aging in air at 70° C for 7 days with properties before aging are shown by the curves in figure 7. The power factor underwent a small increase upon accelerated aging and the dielectric constant decreased a small amount.

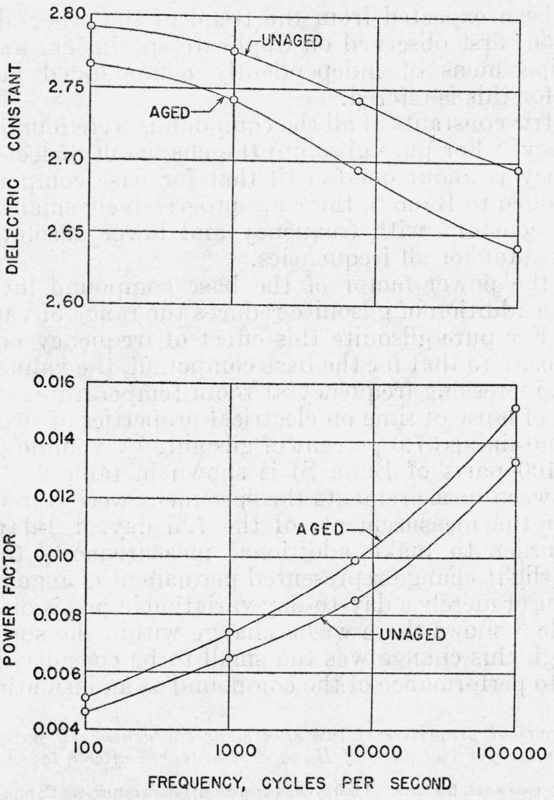

FIGURE 7.—*Effect of accelerated aging on electrical properties of compound containing 40 parts of gilsonite by weight per 100 parts of Buna S.*

Specimens were aged in air at 70° C for 7 days.

2. CONDUCTIVITY

The insulation resistance 1 minute after the application of the potential was measured by means of a highly sensitive galvanometer used as an ammeter [12]. The conductivity, given in table 4, was calculated from the resistance and the dimensions of the specimen. The addition of gilsonite to the base compound *A* reduced conductivity somewhat. (Pure gilsonite had a conductivity less than could be measured with the equipment used, i. e., less than 2×10^{-16} mho/cm.) The values of conductivity are all so small that no conclusion can be drawn as to the effect of varying the composition. Aging may have some effect. Specimens containing 40 parts of gilsonite per 100 parts of Buna S (25.6 percent of gilsonite by volume), after aging in air at 70° F for 7 days, had conductivities less than 2×10^{-16} mho/cm, although conductivities of 4×10^{-16} mho/cm had been determined on these specimens before aging.

TABLE 4.—*Conductivity of compounds of Buna S containing gilsonite*

Base material	Proportion of gilsonite	Number of detn's	"One minute" direct-current conductivity		
			Maximum	Minimum	Mean
	Percent by volume		*Mho/cm*	*Mho/cm*	*Mho/cm*
Base compound *A*[1]	0.0	4	16×10^{-16}	7×10^{-16}	11×10^{-16}
Do.[1]	17.7	4	25	4	12
Do.[1]	21.8	3	4	3	4
Do.[1]	25.6	4	4	3	4
Do.[1]	32.1	3	3	2	3
Do.[1]	37.6	4	8	4	6
Do.[1]	56.3	5	5	3	5
Gilsonite	100.0	4	<2	<2	<2
Washed Buna S compound	0.0	4	20	9	13

[1] Base compound *A* contained, in parts by weight: Buna S, 100; stearic acid, 2; zinc oxide, 5; Santocure, 2; sulfur, 3.

3. EFFECT OF GRAIN OF SPECIMEN ON ELECTRICAL PROPERTIES

A study was made of the effect of grain on the electrical properties as discussed by Scott [13]. For this study, use was made of a typical slab specimen containing 25.6 percent of gilsonite by volume. This slab, 15×16×0.6 cm, was cut into strips 0.6×0.6×15 cm, slicing perpendicular to the grain of the molded sheet. As measured with the capacitor plates parallel to the direction of the grain, the dielectric constant was 2.78 and the power factor was 60×10^{-4} at 1,000 cycles per second. Electrical measurements were then made with the grain of the strips turned perpendicular to the capacitor plates. With the specimen in this position, the dielectric constant was 2.81 and the power factor was 70×10^{-4} at 1,000 cycles per second. It is concluded that for compounds of Buna S and gilsonite the direction of flow in molding has a negligible effect on the electrical properties.

VI. ABSORPTION OF WATER

The effects of the absorption of water in rubber insulating compounds are an important consideration where the stability of the properties of the compounds is essential.

1. QUANTITY ABSORBED AND EFFECT ON ELECTRICAL PROPERTIES

Water absorption and its effect on the electrical properties were studied by the use of specimens in the form of insulated wires, which were kept in water at constant temperature. The rate of absorption of water by the insulation and the changes in dielectric constant and power factor observed over a period of 10 weeks on specimens kept at 25° C and at 70° C are shown in figures 8 and 9. The absorption of water is expressed in milligrams per square inch of exposed surface, as is the custom in cable specifications. Increases in power factor and dielectric constant, as well as weight of water absorbed, were higher than was expected from an essentially pure hydrocarbon matrix. Residual materials remaining in the Buna S after polymerization were probably the cause of increased water absorption. The ash and water extractables found in the Buna S, as mentioned previously, bear out this explanation. It was considered likely that water absorption could, therefore, be reduced by removing water-extractable impurities from the crude Buna S. However, in the water-absorption tests, no appreciable leaching of the insulation took place, since the specimens returned to their original weights after drying.

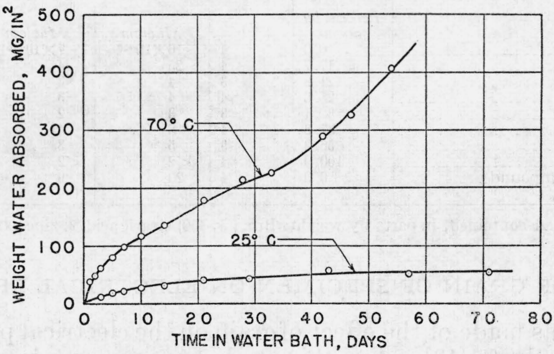

FIGURE 8.—*Absorption of water by the Buna S compound containing 25.6 percent of gilsonite by volume when used as insulation on wire.*

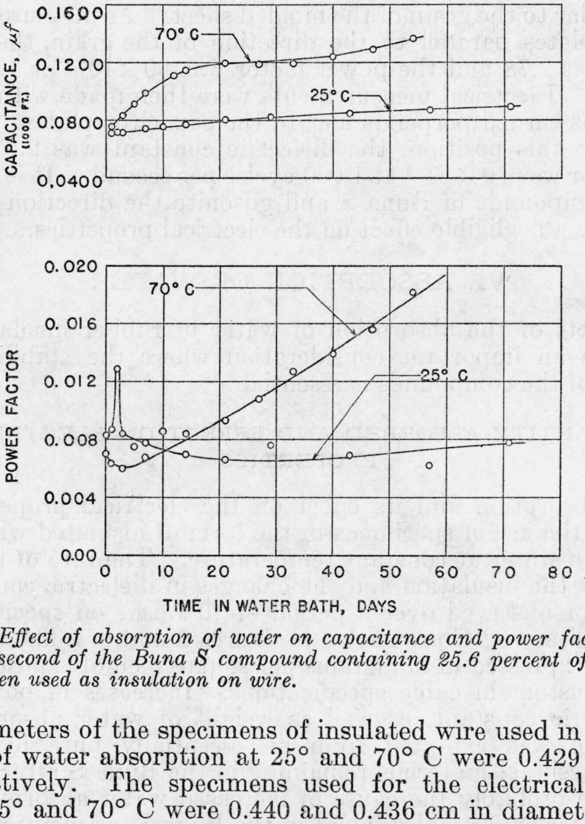

FIGURE 9.—*Effect of absorption of water on capacitance and power factor of 1,000 cycles per second of the Buna S compound containing 25.6 percent of gilsonite by volume when used as insulation on wire.*

The diameters of the specimens of insulated wire used in the measurements of water absorption at 25° and 70° C were 0.429 and 0.436 cm, respectively. The specimens used for the electrical measurements at 25° and 70° C were 0.440 and 0.436 cm in diameter, respectively. The conductor in all cases was 0.205 cm in diameter.

2. FACTORS INFLUENCING THE CHANGE IN ELECTRICAL PROPERTIES OF SPECIMENS IMMERSED IN WATER

In order to isolate the factors influencing the change in electrical properties of specimens immersed in water, slab specimens of three compositions were studied for changes in electrical properties with time of immersion at 90° C. One composition was the base compound *A*. Another composition was that containing the largest quantity of gilsonite used in any of the compounds studied, namely, 56.3 percent by volume or 150 parts by weight of gilsonite per 100 parts of Buna S contained in base compound *A*. The third composition was another "pure gum" compound, prepared in the same manner as the base compound *A* with the exception that the Buna S had been treated to remove part of the water-soluble constituents.

The removal of part of the water-soluble materials was accomplished by soaking the Buna S in distilled water for 2 days, thoroughly rinsing on washing rolls for 30 minutes, soaking in distilled water for 4 days, washing on rolls for 15 minutes, soaking in distilled water for another 9 days, and rewashing for 10 minutes. The polymer was finally dried at 37° C for 4 weeks before compounding. This washing of the crude Buna S caused an 0.8 percent loss in weight.

The electrical properties of the gum compound of washed Buna S at frequencies of 100, 1,000, 7,500, and 100,000 cycles per second are given in table 5. Washing the crude Buna S had only a small effect on its electrical properties. When immersed in water at 70° C the washed Buna S absorbed somewhat less water, and showed somewhat smaller increases in dielectric constant and power factor than the compound of unwashed Buna S, as is shown in figures 10 and 11. Gilsonite is seen (fig. 11) to reduce the changes in electrical properties of specimens of unwashed Buna S kept under water. Conductivity measurements were also made on the slab specimens after immersion in water. Conductivity values were all of the order of 1×10^{-15} mho/cm and showed no significant changes as a result of absorption ofwater.

TABLE 5.—*Dielectric constant and power factor of a pure gum compound prepared from washed Buna S*

Frequency	Number of determinations	Dielectric constant			Power factor		
		Maximum	Minimum	Mean	Maximum	Minimum	Mean
c/s							
100	4	2.874	2.829	2.858	28×10^{-4}	14×10^{-4}	20×10^{-4}
1,000	4	2.863	2.812	2.844	43	37	39
7,500	4	2.844	2.795	2.825	80	71	76
100,000	4	2.790	2.739	2.769	179	174	175

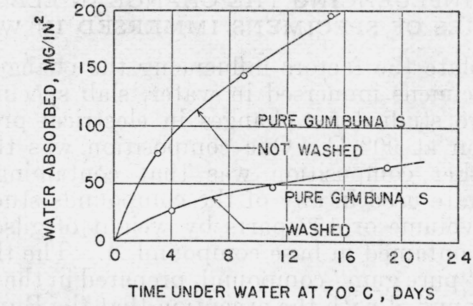

FIGURE 10.—*Absorption of water by slab specimens of Buna S at 70° C.*

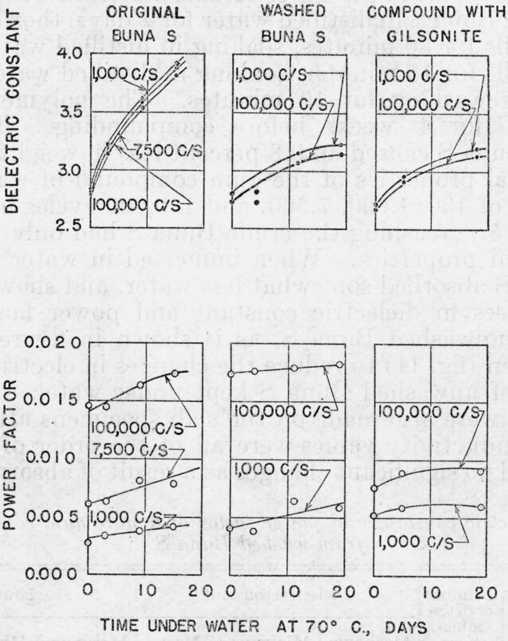

FIGURE 11.—*Effect of absorption of water at 70° C on dielectric constant and power factor of slab specimen.*

The first specimen was prepared from base compound *A* made with the original, unwashed Buna S, and the second with washed Buna S. The third specimen was made from the original base compound *A* and gilsonite, and contained 56.3 percent by volume of the latter.

VII. COMPARISON OF PROPERTIES OF BUNA S-GILSONITE INSULATION WITH SPECIFICATIONS FOR SUBMARINE CABLE

In order to make a practical evaluation of Buna S-gilsonite compounds for electrical insulation, one representative compound was selected and its properties were compared with the requirements of the United States Coast Guard specifications for submarine telephone cable. The compound chosen for this purpose contained 40 parts of gilsonite by weight per 100 parts of Buna S polymer, and possessed as satisfactory mechanical properties as were obtainable with mixtures of these ingredients.

The specifications of the Coast Guard were selected for comparison because they embody nearly all the different types of requirements likely to be included in a specification for rubber insulation. Furthermore, they are based on performance and make no reference to the composition of the insulation other than to refer to it as rubber. The comparison is shown in table 6.

TABLE 6.—*Comparison of a compound of 40 parts of gilsonite by weight per 100 parts of Buna S with United States Coast Guard requirements for the insulation of submarine cable* [1]

Property	Buna S-gilsonite compound	U. S. Coast Guard specifications [1] for submarine telephone cable
Tensile strength, lb/in.^{2}	1,150 to 1,250	2,000 minimum.
Tensile strength after 48 hr in oxygen at 70° C, 300 lb/in.^{2}, percentage of original.	95	75 minimum.
Tensile strength after 7 days in air at 70° C, percentage of original	90	75 minimum.
Ultimate elongation, percent	450 to 475	500 minimum.
Ultimate elongation after 48 hr in oxygen at 70° C, 300 lb/in.^{2}, percentage of original.	95	80 minimum.
Ultimate elongation after 7 days in air at 70° C, percentage of original	85	80 minimum.
Tensile stress at 200-percent elongation, lb/in.^{2}	540 to 580	300 minimum.
Compression-cutting, lb	1,000	650 minimum.
Compression-cutting after 48 hr in oxygen at 70° C, 300 lb/in.^{2}, percentage of original.	80	80 minimum.
Compression-cutting after 7 days in distilled water at 70° C, percentage of original.	45	80 minimum.
Absorption of water after 7 days at 70° C, mg/in.^{2}	98	20 maximum.
Dielectric constant after 24 hr in water at 70° C, 1,000 c/s	3.29	3.20 maximum.
Increase in capacitance after 7 days in water at 70° C, percentage of original capacitance.	31	3.5 maximum.
Increase in capacitance after 28 days in water at 70° C, percentage of original capacitance.	58	10 maximum.
Power factor after 7 days in water at 70° C, 1,000 c/s	0.007	0.010 maximum.
Dielectric constant after 24 hr in water at 60° F, 1,000 c/s	2.89 to 2.98	3.00 maximum.
Resistivity,[2] 1-minute direct current, 60° F, ohm-cm	3×10^{15}	1 to 6×10^{15}.
Voltage test,[3] 5-minute application of potential	23,000 to 38,000 i. e. 330 volts per mil.	3,000 to 5,000 minimum. i. e. 25 to 105 volts per mil.

[1] Most of the requirements have been taken from Specification No. S–218–37, *Rubber Insulation for Telephone Cables. Underground and Submarine Service in Temperate Waters.*

[2] Requirements for the insulation resistance of different sizes and types of conductors are based on different values for the resistivity as well as wall thickness.

[3] Voltage tests were on insulations of thicknesses comparable to that of the specifications.

Most of the requirements given in this table were taken from United States Coast Guard Master Specification S–218–37, which covers rubber insulation for telephone cables intended for underground and submarine service in temperate waters. Some of the requirements of the specification were expressed in different terms from the original in order that the properties might be stated in the same way as elsewhere in this paper. For example, insulation resistance for 1,000 feet of insulated conductor has been converted to resistivity on the basis of the nominal dimensions of the conductor and the average wall thickness of the insulation. Also, the properties not been dealt with previously in the paper were measured by methods described in the Coast Guard specifications.

The Buna S-gilsonite compound exceeds the requirements of the specification in respect to several properties. The change during accelerated aging is considerably less than that permitted by the specification; the tensile stress at an elongation of 200 percent is nearly double that required by the specification, and the load required to produce compression-cutting is 1,000 lb, as compared with the requirement of 650 lb.

The Coast Guard specifications make no stipulation as to resistance to tear for insulation, since the outside jacket of a cable really bears the brunt of tearing and scraping in service. Nevertheless, it is of interest that the addition of 40 parts of gilsonite by weight per 100 parts of Buna S polymer was found to increase the resistance to tear of base compound *A* from 8 lb/in. to 28 lb/in.

In certain other properties the Buna S-gilsonite compound does not meet the specifications, but the deficiency does not seem to be serious. For example, the ultimate elongation is 470 percent instead of 500 percent as specified, and the tensile strength is only 1,200 lb/in.^{2} instead of 2,000. High values of the tensile strength and ultimate elongation are not in themselves necessary for satisfactory performance of a cable, but rather serve merely as indexes of quality when applied to a single variety of rubber.

The serious deficiency of the Buna S-gilsonite compound lies in the change of its properties on immersion in water. The amount of water taken up in the usual 7-day test is about five times that permitted by the specification, and this absorption of water reduces the load under which compression-cutting takes place to 45 percent of the original value, as compared with the minimum of 80 percent called for by the specification.

The absorption of water, as has been shown in an earlier portion of this paper, is accompanied by significant changes in electrical properties. This undesirable quality need not condemn Buna S for use in electrical insulation, since the high absorption may be the result of the presence of residual soap and other chemical agents added in the manufacturing process. The fact that Buna S polymer is a hydrocarbon indicates that if it were available in sufficiently pure form it would be little affected by water. Some improvement in commercial Buna S could be effected by thorough washing or extraction with water, but a more logical method of approach would seem to be through the production of a special type of Buna S low in soap and other polar impurities.

Work in process at the time this paper went to press indicated that samples of commercial Buna S containing no soap were less affected by water than the product used in this investigation.

VIII. REFERENCES

[1] H. Roelig, *Buna in the manufacture of cables,* Rubber Chem. Tech. **13**, 948 (1940). Translated from Kautschuk **16**, 26 (1940).

[2] A. H. Redfield, *Asphalts and related bitumens,* in Bureau of Mines, "Minerals Yearbook, Review of 1940," 1093 (1941).

[3] A. H. Scott and A. T. McPherson, *Dielectric constant, power factor, and conductivity of the system rubber-calcium carbonate,* J. Research NBS **28**, 279 (1942) RP1457; Rubber Chem. Tech. **15**, 879 (1942).

[4] H. Abraham, Asphalts and Allied Substances, 4th ed., 227 (1938) D. Van Nostrand Co., Inc., New York, N. Y.

[5] L. A. Wood, N. Bekkedahl, and F. L. Roth, *Density measurements on synthetic rubbers,* Ind. Eng. Chem. **34**, 1291 (1942); J. Research NBS **29**, 391 (1942) RP1507; Rubber Chem. Tech. **16**, 244 (1943).

[6] A. H. Scott, *Specific volume, compressibility, and volume thermal expansivity of rubber-sulphur compounds,* J. Research NBS **14**, 99 (1935) RP760. Rubber Chem. Tech. **8**, 401 (1935).

[7] A. T. McPherson, *Density and electrical properties of the system, rubber-sulphur. Part I. Density of rubber-sulphur compounds*, B. S. Sci. Pap. **22**, 383, (1927) S560.

[8] L. Larrick, *The standardization of Durometers*, Rubber Age **47**, 287 (1940); Proceedings, ASTM, **40**, 1239 (1940); Rubber Chem. Tech. **13**, 969 (1940).

[9] M. L. Selker, G. G. Winspear, and A. R. Kemp, *Brittle point of rubber on freezing*, Rubber Chem. Tech. **15**, 243 (1942); Ind. and Eng. Chem. **34**, 157 (1942).

[10] A. H. Scott and H. L. Curtis, *Edge correction in the determination of the dielectric constant*, J. Research NBS **22**, 747 (1939) RP1217.

[11] *Tentative methods of testing electrical insulating materials for power factor and dielectric constant*, ASTM Tentative Standard, Designation D 150–41T (1941).

[12] A. H. Scott, A. T. McPherson, and H. L. Curtis, *Effect of temperature and frequency on the dielectric constant, power factor, and conductivity of compounds of purified rubber and sulfur*, BSJ. Research **11**, 173 (1933) RP585; Rubber Chem. Tech. **2**, 342 (1934).

[13] A. H. Scott, *Effect of flow in molding on the dielectric constant and loss tangent of rubber-filler systems*, Annual Report, page 16, 1941 Conference on Electrical Insulation, Division of Engineering and Industrial Research, National Research Council.

WASHINGTON, June 21, 1943.