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SYNTHETIC AND NATURAL RUBBER COMPOSITIONS CONTAINING WAX AND HEAT-TREATED GILSONITE

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This invention relates to the production of electrical insulating compounds, and particularly to the production of electrical insulating compounds having low dielectric constants and in which rubber or a synthetic, rubber-like material, such as Buna S, is the vulcanizable constituent.

In many types of communication equipment, it is desirable that the electrical conductors used therein be insulated with materials having low dielectric constants in order that the resulting insulated conductors will have low capacitances. Thus, for example, conductors used in carrier current telephone systems, underground telephone distribution wires, and various field wires and cables employed in military communication systems are insulated with low capacity, vulcanized insulating compounds in which rubber or a synthetic, rubber-like material is the vulcanizable constituent.

The usual vulcanized electrical insulating compounds generally are applied to electrical conductors by extruding them over the conductors while in the unvulcanized state and then vulcanizing the resulting coverings. The unvulcanized compounds contain natural rubber, or a vulcanizable synthetic, rubber-like material, or a mixture of both, together with suitable fillers, plasticizers, accelerating agents, vulcanizing agents and oxidation retarders. The fillers usually employed in such compounds are carbon black, mineral rubber, zinc oxide, clay, talc, whiting and the like. While these fillers improve the mechanical properties of the compounds materially, most of them have the undesirable characteristic of raising the dielectric constants of the compounds, which for high quality insulating compounds is extremely undesirable. As a result, it has been the practice to make high quality, low dielectric constant insulating compounds of mixtures having high contents of vulcanizable materials.

It is desirable to minimize the amount of rubber or vulcanizable, rubber-like materials used in insulating compounds in order to lower the cost of these compounds and to decrease the working necessary to break down the rubber or rubber-like material to a consistency suitable for easy and smooth extrusion of such compounds.

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Consequently, it is extremely desirable to provide fillers or spreaders that will give desirable mechanical properties to insulating compounds but will not raise materially the dielectric constants of the resulting compounds.

Hard, natural asphalts, such as gilsonite and the like, have been suggested for use as fillers or spreaders in insulating compounds. Such materials are relatively inexpensive and those of the best quality have properties that render them suitable for use in high grade, low capacity insulating compounds. Gilsonite is among the best of the hard, natural asphaltic materials for use as a filler or spreader for rubber or vulcanizable, synthetic, rubber-like materials. Gilsonite has desirable electrical characteristics and also has the desirable property of acting at low temperatures as a filler and reinforcing agent in insulating compounds, while at relatively high temperatures it acts as a plasticizer for rubber or synthetic, rubber-like compounds.

These facts had been recognized previously, but the use of such materials has been limited in the past by the extreme difficulty encountered in incorporating them in insulating compounds. The principal objection to the use of gilsonite is that its softening point is too high to permit it to be incorporated readily in insulating compounds. It is even more difficult to incorporate gilsonite in insulating compounds containing a synthetic, rubber-like material, such as Buna S, than is the case with compounds made with natural rubber. In view of the present extensive use of buna compounds, particularly Buna S compounds, this is an especially serious drawback. Furthermore, different lots of gilsonite, especially those from different localities, vary in their physical properties, and it is difficult to produce uniform insulating compounds containing them.

When vulcanizable compounds containing gilsonite in its native state were employed heretofore as insulation for electrical conductors and such an insulating compound was vulcanized on a conductor by vulcanization processes known to the art, such as by continuous vulcanization in high pressure steam, the gilsonite was heated to a temperature at which a substantial quantity of volatile matters was distilled therefrom. The

evolution of such distilled materials had a deleterious effect upon the insulating compound, since it tended to produce porosity and to cause blistering in the compound.

This invention has for its objects the provision of new and useful electrical insulating compounds, and the provision of new and useful methods of making electrical insulating compounds.

Another object of the invention is to provide new and improved bituminous compositions for use in electrical insulating compounds.

In accordance with the invention, low capacity insulating compounds may be made by incorporating a derivative of a hard, natural asphaltic material, such as gilsonite, in a vulcanizable compound in which rubber, a vulcanizable, synthetic, rubber-like material, or a mixture of the two is the vulcanizable constituent, and vulcanizing the resulting compound. The gilsonite derivative employed is obtained by removing from gilsonite a predetermined quantity of the original volatile constituents thereof. Before the gilsonite derivative is introduced into the vulcanizable compound, it preferably is blended with waxy material, such as microcrystalline waxes and paraffin, to form a bituminous composition embodying certain features of the invention.

In the copending application of K. N. Yellott, Serial No. 657,353, filed March 26, 1946, as a continuation-in-part of application Serial No. 571,547, filed January 5, 1945, by K. N. Yellott, now abandoned, there are described and claimed methods of making certain bituminous compositions consisting of derivatives of natural, hard asphaltic materials, such as a gilsonite derivative, admixed with microcrystalline waxes with or without paraffin. These bituminous compositions are especially suitable for incorporation in vulcanizable insulating compounds, particularly Buna S insulating compounds. Such bituminous compositions were described and claimed in the abandoned application of T. K. Cox, Serial No. 657,339, filed March 26, 1946, as a continuation-in-part of application Serial No. 571,541, filed January 5, 1945, now abandoned. Electrical insulating compounds embodying the invention and prepared in accordance with methods embodying the invention include such bituminous compositions.

The invention will be clearly understood from the following specific examples of insulating compounds embodying the invention and methods of making them. These examples are illustrative only, and the invention embraces all compounds and methods covered by the annexed claims.

Example I

One specific type of insulating compound embodying the invention was prepared by mixing the following ingredients in accordance with recognized practices in the types of equipment usually employed to make vulcanizable insulating compounds:

Ingredients	Composition Range, Parts	Preferred Composition
GR-S (Buna S)	35.00–55.00	41.35
Carbon Black	1.50– 3.00	2.02
Zinc Oxide	1.50– 3.00	2.02
Whiting	25.00–40.00	28.25
Bituminous Composition A	18.00–30.00	21.68
Selenium diethyl dithiocarbamate	0.65– 1.60	0.82
Mill Sulphur	0.60– 1.60	0.82
Plasticisers, softeners, accelerating agents, oxidation retarders, etc.	2.25– 5.67	3.04
Total		100.00

This compound exhibits strong resistance to deterioration caused by exposure to ozone and sunlight and has a low dielectric constant. Such a compound is useful for insulating conductors used in military communication lines.

The bituminous composition employed consisted of the following ingredients in the proportions indicated:

Bituminous composition A

Gilsonite derivative	86.45
Microcrystalline waxes (M. P. 152°–156° F.)	5.55
Paraffin	8.00
Total	100.00

The gilsonite derivative used in this bituminous composition may be prepared and the several constituents of the bituminous compositions may be blended by processes described fully and claimed in the aforementioned copending application of K. N. Yellott, Serial No. 657,353. The gilsonite derivative is obtained by heating naturally occurring gilsonite to a temperature in excess of about 450° F. for a period of time sufficient to distil therefrom a predetermined quantity of volatile constituents thereof not exceeding about 5% by weight of the original gilsonite. Each batch of gilsonite treated is subjected to substantially the same conditions in order that all of the batches of gilsonite derivative obtained therefrom will have substantially the same properties.

One suitable method of blending these ingredients is that in which the mass of gilsonite derivative is heated to a temperature of about 625° F., and simultaneously stirred, making certain that no portion thereof is overheated. The gilsonite derivative then is allowed to cool to about 580° F., at which time the microcrystalline waxes are added. The microcrystalline waxes melt and are stirred thoroughly into the gilsonite derivative. When the temperature of the resulting mixture drops to about 475° F., the paraffin is added, and, since it melts at that temperature, it is stirred thoroughly into the mixture. The thus-blended mass is placed in suitable containers while still molten and is allowed to solidify.

The resulting bituminous composition is a uniform blend of its several constituents and has a softening point of about 210° F. It may be incorporated easily in the above-outlined and other usual types of insulating compounds containing rubber or vulcanizable, synthetic, rubber-like materials, such as Buna S, together with the other usual ingredients employed in making high quality, low capacity insulating compounds.

Bituminous compositions of this nature have a number of other important advantages. For example, since the gilsonite derivative used therein has a dielectric constant substantially equal to that of rubber or similar materials used in electrical insulating compounds, it may be used as a filler or spreader in unlimited quantities without raising the dielectric constant of the resulting insulating compound. The paraffin and microcrystalline waxes, which are blended with the gilsonite derivative, also serve useful functions in the resulting insulating compounds, since both types of waxes act as lubricants during processing and the microcrystalline waxes also serve to retard cracking of the vulcanized insulating compounds caused by exposure to ozone and sunlight.

Still another advantage of using these bituminous compositions in insulating compounds is that they improve the mechanical properties of such

compounds. In particular, they increase the resistance of buna compounds, especially Buna S compounds, to deformation at relatively high temperatures, that is, at temperatures up to about 160° F.

A further advantage of using such a bituminous composition as a filler or spreader instead of the usual hard hydrocarbon (blown asphalt) is that compounds containing such compositions have rates of vulcanization up to about 20% higher than those of compounds containing an equal percentage of hard hydrocarbon and which are otherwise identical. In addition, insulating compounds including such bituminous compositions possess marked resistance to cracking when exposed to ozone and sunlight.

Example II

Another insulating compound embodying the invention consisted of the following ingredients in the proportions outlined:

Ingredients	Composition
GR-S (Buna S)	35.83
Carbon Black	10.52
Zinc Oxide	35.05
Bituminous Composition A	10.50
Mill Sulphur	1.40
Plasticizers, softeners, accelerating agents, oxidation retarders, etc	6.70
Total	100.00

The Buna S employed in compounds of this nature may vary from about 30 to about 55 parts per 100 parts of compound, and the other constituents of the compound may be varied within similar ranges. This type of compound also exhibits marked resistance to the action of ozone and sunlight and has a low dielectric constant. It is suitable for insulating telephone drop wires.

Example III

A further insulating compound possessing the features of the invention has the following formula:

Ingredients	Composition
GR-S (Buna S)	43.86
Carbon Black	21.93
Aluminum Hydrate	9.21
Zinc Oxide	2.19
Bituminous Composition A	13.16
Mill Sulphur	1.75
Plasticizers, softeners, accelerating agents, oxidation retarders, etc	7.90
Total	100.00

If desired, the Buna S component of the mixture may range from about 35 parts to about 55 parts per 100 parts of compound, and the other ingredients may be varied within similar ranges. This compound also exhibits great resistance to cracking when exposed to ozone or sunlight, and its dielectric constant is low. It is an excellent material for use as an insulator for drop wire.

One of the outstanding features of this invention is the fact that insulating compounds embodying the invention in which such bituminous compositions have been incorporated exhibit remarkable resistance to ozone and sunlight. Thus, for example, an insulating compound ("sample A") was prepared having substantially the composition of the preferred embodiment of Example II and containing "Bituminous composition A." This compound was compared with another compound ("sample B") as nearly like it as possible, but not containing such a bituminous composition. "Sample B" was identical in all respects with "sample A" except that in making it natural gilsonite, microcrystalline waxes of the type used in "Bituminous composition A" and paraffin were added separately in such amounts that the finished product contained quantities thereof equal respectively to the amounts of gilsonite derivative, microcrystalline waxes and paraffin present in "sample A." Except for these differences, both compounds were prepared in an identical manner.

These compounds were extruded on #18 A. W. G. conductors to an outside diameter of 0.107", and were cured for 25 seconds at 200° C. in open steam. The cured compounds were evaluated for mechanical properties with the following results:

Compound	Tensile Strength, Lbs./in.	Elongation, Per Cent	Load Required to Stretch 200%, Lbs./in.	Compression Resistance, Lbs.	Adhesion to Conductor, Lbs.
A	2,220	570	435	1,235	9.3
B	1,905	555	405	1,255	9.5

These results indicate that the compound of "sample A" was superior to "sample B" from the standpoint of mechanical properties, although the difference between the two samples was not great.

Each of the samples was wrapped around a ¼" mandrel (30% elongation), and exposed to an ozone concentration of 25 parts per 100,000,000 parts of air at a temperature of 120° F. for periods of 10 hours and 24 hours, respectively. After each of these intervals the samples were examined, and it was found that after 10 hours' exposure "sample A" had no evident cracks such as are caused by exposure to ozone, while "sample B" had cracked appreciably. After 24 hours' exposure to this concentration of ozone, "sample A" exhibited slight cracking, while "sample B" showed extensive cracking due to the action of the ozone thereon. Since the conditions under which these samples were tested represent what is considered to be a good accelerated technique for predicting outdoor serviceability of insulated conductors, it is evident that the compound of "sample A" should give service far superior to that obtainable by the use of the compound of "sample B."

In order to make further comparisons, weather resistance tests were made on two Buna S compositions of the type suitable for use in insulating telephone drop wire. These compounds were identical in all respects except that one, "sample C," contained 50 parts of "Bituminous composition A," while the other, "sample D," contained 25 parts of "Bituminous composition A," 25 parts of mineral rubber (blown asphalt) and 1.5 parts of microcrystalline waxes.

Wires insulated with these compounds were exposed simultaneously for 10 hours in a "Weatherometer," in which the compounds were exposed to heat, water sprays and an atmosphere high in ozone. At the end of this period, "sample C" was substantially unaffected, but "sample D" had clearly evident cracks such as are typical of those caused by exposure to ozone.

Other samples like "sample C" and "sample D" were subjected to atmospheres containing higher concentrations of ozone, but in which they were not subjected to heat or water sprays. In one test the samples were subjected to an atmosphere containing 10 parts of ozone to 100,000,000 parts of air, while in another test they were subjected

to an atmosphere containing 100 parts of ozone to 100,000,000 parts of air. These concentrations are greatly in excess of those found in the air under normal circumstances. In both of these tests, the compound of "sample C" was far superior to that of "sample D" in its resistance to ozone.

Two other similar Buna S compounds were tested under the same conditions to determine the relative effects of weathering and ozone on a buna rubber compound embodying the invention containing "Bituminous composition A" and one containing mineral rubber. The first, "sample E," contained 50 parts of the "Bituminous composition A," while in the second, "sample F," this bituminous composition was replaced by 30 parts of mineral rubber and 3 parts microcrystalline waxes, the compounds being otherwise identical. The cracking due to exposure to weathering and to ozone was very slight in the case of "sample E," but was quite marked in "sample F."

The bituminous composition employed in preparing the insulating compound of Example I is typical or such compositions that are useful in practicing the invention. However, other related bituminous compositions may be substituted therefor. For example, another bituminous composition which may be used in these insulating compounds was prepared by blending the following materials in the proportions indicated:

Bituminous composition B

Gilsonite derivative	83.8
Microcrystalline waxes (M. P. 152°–156° F.)	3.7
Paraffin	12.5
Total	100.0

These materials were prepared and blended in a manner substantially identical with that described hereinabove in connection with Example I. This material had a softening point of about 198° F.

Still another bituminous composition that may be used in insulating compounds embodying the invention was prepared by blending in substantially the same manner the following materials in the following proportions:

Bituminous composition C

Gilsonite derivative	83.80
Microcrystalline waxes (M. P. 152°-156° F.)	5.55
Paraffin	10.65
Total	100.00

This material had a softening point of about 214° F.

An additional bituminous composition that is useful in making insulating compounds embodying the invention was made by blending in substantially the manner described the following ingredients in the ratios indicated:

Bituminous composition D

Gilsonite derivative	85.3
Microcrystalline waxes (M. P. 152°–156° F.)	3.7
Paraffin	11.0
Total	100.0

This composition had a softening point of about 200° F., and may be incorporated readily in vulcanizable insulating compounds.

The method of preparing the gilsonite derivative employed in making these bituminous compositions and the manner in which this gilsonite derivative and the waxes are uniformly blended will be thoroughly understood from the following description of a process of making "Bituminous composition A":

The gilsonite derivative may be prepared and the other ingredients may be blended uniformly therewith by introducing a mass of gilsonite into a melting kettle large enough to hold a quantity thereof substantially in excess of a predetermined weight. The gilsonite used preferably is a commercial grade containing only a small amount of extraneous matter, since such a material is easier to treat than are materials of lower quality. A suitable material is the product known as "Gilsonite selects," or one having comparable properties, although almost any commercial variety of gilsonite can be employed.

Assuming, for example, that it is desired to make a 1,000 pound batch of "Bituminous composition A," a kettle large enough to hold at least 1700 pounds of gilsonite is filled about half full of solid processed gilsonite. Heat is gradually applied to the kettle to melt the gilsonite and the heating is continued until the mass reaches a temperature of about 625° F. The mass is stirred constantly by means of a suitable mechanical stirrer to avoid overheating or burning of the gilsonite.

When the temperature of the mass is about 625° F., approximately 865 pounds of cold gilsonite are added to the molten gilsonite in the kettle. The temperature of the molten gilsonite is reduced by the addition of this cold material and the heating is continued until the whole is brought to a temperature of about 625° F., the material being stirred thoroughly in the meanwhile. As soon as the temperature again reaches about 625° F., a batch of the molten material weighing about 865 pounds is drawn off into a blending kettle and a second charge of gilsonite weighing approximately 865 pounds is added to the melting kettle. The heat supplied to the melting kettle is so controlled that it requires about 70 minutes to raise the temperature of each cold charge of gilsonite to about 625° F. This treatment drives off a desired amount of volatile materials from the gilsonite and produces a gilsonite derivative having properties somewhat different from those of the original gilsonite.

The molten gilsonite derivative that is drawn off into the mixing kettle is allowed to cool to a temperature of about 580° F., when a batch of the microcrystalline waxes weighing about 55 pounds is added. The waxes melt at that temperature and as soon as the added batch melts it is stirred into the molten gilsonite until a uniform mixture results. This mixture is allowed to cool to a temperature of about 475° F. and about 80 pounds of paraffin then are added thereto. Since the melting point of the paraffin is below that temperature, it melts rapidly and, when molten, it is stirred thoroughly into the other ingredients. The resulting blended product is placed in suitable containers while still molten and permitted to cool and solidify therein. These steps are repeated for each batch of molten gilsonite derivative withdrawn from the kettle to prepare successive batches of bituminous compositions.

When this procedure is followed, the respective components of the bituminous composition are blended together uniformly and the resulting composition may be incorporated readily in vulcanizable compounds, such as vulcanizable insulating compounds containing rubber or synthetic rubber-like materials. Such bituminous compositions are dispersible in buna insulating

compounds, particularly those made of Buna S, much more easily than natural, untreated gilsonite, the gilsonite derivative described hereinabove, or other bituminous mixtures, can be incorporated therein. Also, bituminous compositions of this nature, which have been blended in accordance with the invention possess uniform physical properties despite some lack of uniformity that occurs in the individual ingredients thereof.

One reason for the uniformity in the quality of these blended bituminous compositions is the fact that the heating cycle of each batch of gilsonite is so controlled that the same amount of the volatile portions of the gilsonite is driven off from each melt. Since different lots of gilsonite vary somewhat, this process provides a means of avoiding wide variations in the finished product.

During the heating step, any ingredients in the original gilsonite which have melting points higher than 625° F. remain unmelted and settle to the bottom of the kettle. In drawing off the successive batches of gilsonite derivative, care is taken to leave undisturbed the material found in the lowermost several inches in the bottom of the kettle, since the insoluble and unmelted materials will collect in that layer. After the operation has continued for some period of time, all the material except that present in about the last five or six inches in the bottom of the kettle is withdrawn and the material left in the kettle is then discarded. A fresh batch of gilsonite is then placed in the kettle, and the operations described hereinabove are resumed. By following this procedure, the treated gilsonite is freed from the deleterious extraneous matter consisting principally of insoluble nonmineral matter and mineral matter.

It has been found that by heating gilsonite to a temperature of about 625° F. and controlling the heating step so that the gilsonite is brought to this temperature over a period of about 70 minutes, all the material that would volatilize from the gilsonite during the usual vulcanization processes is distilled therefrom. It appears that methane is the principal constituent of the volatile materials involved by such distillation. Analyses of the material before and after such treatment indicate that the amount of volatile materials driven off is at least about 2% but does not exceed about 5% of the weight of the original material. Preferably the amount of the volatile materials removed is from about 2.75% to about 3.25% of the original material, and the optimum amount to be driven off appears to be about 3% or just slightly thereover.

The product resulting from this selective distillation is, in effect, a derivative of gilsonite, since an examination of the material thus produced reveals that it differs materially from the original gilsonite in several respects. These differences are shown in the following table which outlines the results of tests made on a sample of gilsonite derivative thus prepared:

	Natural gilsonite	Gilsonite derivative
Specific Gravity	1.03	1.038
Softening Point (R & B Method) ° F.	272	256
Comparative physical characteristics:		
Slight softening ° C.	100	98
Distinct softening ° C.	103	101
Starts to lose form ° C.	109	103
Distinct slump ° C.	117	107
Loses shape entirely ° C.	121	113

It is apparent from this table that the softening point of the gilsonite derivative is 16° F. below that of the untreated material. By following the processes described hereinabove, gilsonite derivatives may be produced that have softening points of from about 15° F. to about 20° F. lower than that of gilsonite as it occurs in nature.

Since the gilsonite derivatives employed in making electrical insulating compounds embodying the invention contain practically no material that volatilizes at temperatures normally employed in vulcanizing insulating compounds, substantially no volatile material is released by the gilsonite derivative when insulating compounds containing them are vulcanized. Consequently, the resulting vulcanized compounds are free of the porosity and blistering which occur when natural gilsonite is employed.

Some of the undesirable characteristics of naturally occurring gilsonite are overcome by treating the gilsonite as described hereinabove to remove the inert extraneous matter and to drive off those portions of the gilsonite that would volatilize under the conditions present in vulcanization processes. However, even though the softening points of the gilsonite derivatives resulting from such treating are materially lower than that of the original gilsonite, such a derivative still has a softening point too high to permit it to be incorporated readily in vulcanizable insulating compounds, particularly those compounds containing Buna S as the vulcanizable constituent.

This difficulty is overcome by incorporating in gilsonite derivatives produced by the above-described treatment microcrystalline waxes and paraffin in such proportions that the resulting products have softening points not exceeding about 240° F., and preferably in the vicinity of about 205° F.±10° F., with the compounds having at the same time the least possible diminution in their hardness at temperatures below about 160° F. In making these bituminous compositions, satisfactory results have been obtained where the amount of gilsonite derivative used varies from about 80% to about 90% of the total composition, while the paraffin may vary from about 3% to about 15%, and the microcrystalline waxes may vary from about 2% to about 10%. The best results are obtained when the amount of microcrystalline waxes plus paraffin is from about 10% to about 20% of the total blended composition, and when the amount of microcrystalline waxes employed is from about ¼ to about ¾ of the paraffin used. A preferred composition is one in which the range of microcrystalline waxes plus paraffin is from about 11% to about 17% of the total blended bituminous composition, and the balance is a gilsonite derivate produced as described hereinabove.

Instead of using derivatives of gilsonite, derivatives or other hard, natural asphaltic materials, the original softening points of which do not materially exceed about 475° F., may be used. Thus, for example, a derivative of glance pitch may be substituted in whole or in part for gilsonite in such compositions.

Obviously, it is not necessary to add the waxy materials to the gilsonite derivative immediately after such derivative is withdrawn from the vessel in which it is formed. If desired, after the gilsonite has been heated under the conditions necessary to remove therefrom a predetermined amount of volatile material, it may be allowed to solidify and later on may be remelted and

blended with the waxy materials substantially as described hereinabove. In reheating the gilsonite derivative, the same care should be taken to avoid charring or burning it that was exercised in heating the gilsonite originally.

All or a part of the paraffin employed in such compositions may be replaced by microcrystalline waxes. The microcrystalline waxes employed in these compositions are waxes derived from petroleum, which are in the form of minute but clearly defined crystals. The microcrystalline waxes that have been found to be most satisfactory are commercially available blends of microcrystalline waxes that may contain small amounts of paraffin, and have melting points of from about 150° F. to about 165° F. Obviously, other similar microcrystalline waxes may be employed, if desired.

When it is desirable to lower the softening points of the bituminous compositions, some of these microcrystalline waxes may be replaced by microcrystalline waxes having lower melting points or the amounts of either or both of the microcrystalline waxes and paraffin may be increased. Conversely, when it is desired to raise the softening points of the bituminous compositions, microcrystalline waxes having higher melting points may be substituted in whole or in part for the lower melting microcrystalline waxes and paraffin or the amount of waxy materials may be reduced. Apparently, the maximum softening point that will permit ready incorporation of such compositions in insulating compounds is about 240° F.

These bituminous compositions may be mixed with the other compounding ingredients normally used in high quality, low capacity insulating compounds with the aid of the usual equipment employed to mix insulating compounds. Bituminous compositions having relatively high softening points may be incorporated with the other ingredients in a Bambury mixer, while those having lower melting points may be incorporated with the other ingredients on mixing rolls.

Specific examples have been given of Buna S compounds containing blended bituminous compositions which include gilsonite derivatives because the supply of Buna S is plentiful at present, and also because such examples are indicative of the ease with which these blended bituminous compositions may be incorporated in Buna S compounds. It is particularly difficult to incorporate the usual bituminous materials in insulating compounds in which Buna S is the vulcanizable constituent. However, it is obvious that insulating compounds having excellent mechanical and electrical properties may be prepared by incorporating such blended bituminous compositions in insulating compounds in which rubber is the vulcanizable material, or in which the vulcanizable constituent is another synthetic rubber-like material, such, for example, as neoprene or Buna N.

Buna S is a copolymer of butadiene and styrene, and the GR-S used in the above-described insulating compounds was the type of Buna S manufactured in plants sponsored or owned by the United States Government. Neoprene is polymerized chloroprene, and Buna N is a copolymer of butadiene and acrylonitrile. The GR-S employed corresponded to that specified on pages 2 and 3 of "Specifications for Government Synthetic Rubbers," effective January 1, 1946, issued by the Reconstruction Finance Corporation, Office of Rubber Reserve. The neoprene and Buna N made in government plants are designated GR-M and GR-A, respectively, and the specifications therefor also are given in this publication.

It has been found that satisfactory results may be obtained when the bituminous composition employed in the usual insulating compounds constitutes from about 10% to about 30% of the total composition or, based on the vulcanizable material content of the composition, when the quantity of bituminous composition used is from about ⅓ to ⅔ of the quantity of vulcanizable material employed in the compound. Since the amount of the bituminous compositions employed in an insulating compound embodying the invention constitutes from about ⅓ to ⅔ of the amount of the vulcanizable material present in the insulating compound, and the bituminous composition consists of from about 80% to about 90% of the above-described gilsonite derivative, from about 3% to about 15% of paraffin, and from about 2% to about 10% of microcrystalline waxes, it follows that the amount of gilsonite derivative present in such an insulating compound is from about 26% to about 60% of the amount of the vulcanizable material present therein, the amount of paraffin is from about 1% to about 10% of the amount of the vulcanizable material, and the amount of microcrystalline waxes is from about ⅔% to about 7% of the amount of the vulcanizable material.

All values of softening points referred to herein and in the annexed claims are those obtained by using the standard method of determining softening points known alternatively as the "ring and ball" (R. & B.) method and the "ball and ring" (B. & R.) method.

It is obvious from the foregoing description that this invention provides electrical insulating compounds of improved quality. Such compounds are characterized by their resistance to deterioration due to exposure to ozone and sunlight, and by their low dielectric constants. These compounds possess mechanical and electrical characteristics that are far superior to those exhibited by similar insulating compounds in which such bituminous compositions are not present and are especially suited for use in insulating conductors used in communication systems.

It appears that some cracking of the constituents of the gilsonite occurs when it is heated as described, and the volatile matter driven therefrom apparently includes some products that result from destructive distillation of the gilsonite. Hence, it is to be understood that the terms "volatile matter," "volatile materials," and "volatile constituents," or words of similar import, as used herein and in the annexed claims, are intended to embrace any volatile materials that may be present in the gilsonite originally and any volatile materials produced by cracking or destructive distillation of the gilsonite.

This application is a continuation-in-part of my aforementioned copending application Serial No. 571,541, filed January 5, 1945.

What is claimed is:

1. An electrical insulating compound, which comprises rubber, and a quantity of a blended bituminous composition equivalent to from about ⅓ to about ⅔ of the weight of the rubber in the compound, said bituminous composition consisting of at least 80% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% by weight of volatile matter orig-

inally present therein and in which the balance is microcrystalline waxes and paraffin in such proportions as to cause the resulting bituminous composition to have a softening point below about 240° F. and to be readily dispersible in the compound.

2. An electrical insulating compound, which comprises a rubber-like butadiene-styrene copolymer, and a quantity of a blended bituminous composition equivalent to from about ⅓ to about ⅔ of the weight of the copolymer in the compound, said bituminous composition consisting of at least 80% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% by weight of volatile matter originally present therein and in which the balance is microcrystalline waxes and paraffin in such proportions as to cause the resulting bituminous composition to have a softening point below about 240° F. and to be readily dispersible in the compound.

3. An electrical insulating compound, which comprises a mixture of rubber and a rubber-like, butadiene-styrene copolymer, and a quantity of a blended bituminous composition equivalent to from about ⅓ to about ⅔ of the weight of the vulcanizable material in the compound, said bituminous composition consisting of at least 80% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% by weight of volatile matter originally present therein and in which the balance is microcrystalline waxes and paraffin in such proportions as to cause the resulting bituminous composition to have a softening point below about 240° F. and to be readily dispersible in the compound.

4. An electrical insulating compound resulting from the vulcanization of a vulcanizable insulating compound comprising from about 30% to about 55% of a rubber-like, butadiene-styrene copolymer, and from about 10% to about 30% of a blended bituminous composition consisting of from about 80% to about 90% of a gilsonite derivative uniformly blended with from about 3% to about 15% of paraffin and from about 2% to about 10% of microcrystalline waxes having melting points of from about 150° F. to about 165° F., said gilsonite derivative being the product obtained by removing from gilsonite at least about 2% but not exceeding about 5% of volatile matter.

5. An electrical insulating compound, which comprises from about 30% to about 55% of a vulcanizable material of the group consisting of natural rubber, rubber-like butadiene copolymers with other monomers copolymerizable therewith, mixtures of natural rubber and such rubber-like copolymers, and rubber-like polyhaloprenes, and from about 10% to about 30% of a bituminous composition consisting of from about 80% to about 90% of a gilsonite derivative, from about 3% to about 15% of paraffin and from about 2% to about 10% of microcrystalline waxes, said gilsonite derivative being the product obtained by distilling from gilsonite sufficient volatile matter to cause it to have a softening point from about 15° F. to about 20° F. lower than that of the original gilsonite.

6. An electrical insulating compound resulting from the vulcanization of a vulcanizable mixture comprising from about 30% to about 55% of a rubber-like, butadiene-styrene copolymer, and from about 10% to about 30% of a blended bituminous composition consisting of about 86.5% of gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile matter, about 5.5% of microcrystalline waxes and about 8% of paraffin.

7. An electrical insulating compound resulting from the vulcanization of a mixture containing approximately 41% of rubber-like, butadiene-styrene copolymer, 2% of zinc oxide, 28% of whiting, 1.6% of vulcanizing agents, and 22% of a blended bituminous composition consisting of about 86.5% of gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile matter, about 5.5% of microcrystalline waxes and about 8% of paraffin.

8. An electrical insulating compound resulting from the vulcanization of a vulcanizable mixture containing approximately 36% of rubber-like, butadiene-styrene copolymer, 10.5% of carbon black, 35% of zinc oxide, 1.4% of sulphur, and 10.5% of a blended bituminous composition consisting of about 86.5% of gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile matter, about 5.5% of microcrystalline waxes and about 8% of paraffin.

9. An electrical insulating compound resulting from the vulcanization of a vulcanizable mixture containing approximately 44% of rubber-like, butadiene-styrene copolymer, 22% of carbon black, 9% of aluminum hydrate, 2% of zinc oxide, 1.75% of sulphur, and 13% of a blended bituminous composition consisting of about 86.5% of gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile matter, about 5.5% of microcrystalline waxes and about 8% of paraffin.

10. An electrical insulating compound, which comprises from 30% to 55% of a rubber-like, butadiene-styrene copolymer, and from 10% to 30% of a blended bituminous composition consisting of from 80% to 90% of a gilsonite derivative obtained by distilling from gilsonite originally having a softening point of about 270° F. sufficient volatile matter to cause it to have a softening point of from about 250° F. to about 260° F., from 3% to 15% of paraffin, and from 2% to 10% of microcrystalline waxes having melting points of from 150° F. to 160° F.

11. A bituminous composition for incorporation in vulcanizable compounds, which consists of at least 80% but not exceeding about 90% of a gilsonite derivative, and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin in such proportion as to cause the resulting composition to have a softening point below about 240° F. and to be readily dispersible in vulcanizable insulating compounds, said gilsonite derivative being natural gilsonite from which has been distilled substantially all material that volatilizes at a temperature of about 450° F., whereby when a vulcanizable compound containing such a bituminous composition is vulcanized the resulting compound is substantially free of porosity caused by the evolution of volatile material from the gilsonite derivative.

12. A bituminous composition for incorporation in vulcanizable compounds, which consists of at least 80% of a derivative of glance pitch, and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin, said derivative being the product obtained by distilling at least about 2% but not exceeding 5% by weight of gaseous matter from glance pitch and the waxy material being present in such proportion as to cause the resulting composition to have a softening point not exceeding about 240° F. and to be

readily dispersible in vulcanizable insulating compounds.

13. A bituminous composition for incorporation in insulating compounds, which consists of from about 80% to about 90% of a gilsonite derivative, from about 3% to about 15% of paraffin, and from about 2% to about 10% of microcrystalline waxes, said gilsonite derivative being the product obtained by removing from gilsonite a predetermined quantity of volatile constituents constituting at least about 2% but not exceeding about 5% by weight of the original gilsonite.

14. A bituminous composition for incorporation in insulating compounds, which consists of from about 80% to about 90% of a gilsonite derivative, and from about 10% to about 20% of microcrystalline waxes and paraffin, the gilsonite derivative employed being the product obtained by removing at least about 2% but not over about 5% by weight of volatile constituents from gilsonite and the amount of microcrystalline waxes used being from about ¼ to about ¾ of the amount of paraffin used.

15. A bituminous composition readily dispersible in vulcanizable compounds, which consists of from about 83% to about 87% of a gilsonite derivative obtained by heating gilsonite at a temperature sufficiently high and for a period sufficiently long to lower the softening point thereof by about 15° F., and in which the balance is microcrystalline waxes plus paraffin in the ratio of from about 1 to 3 parts of microcrystalline waxes for each 4 parts of paraffin.

16. A bituminous composition for incorporation in vulcanizable insulating compounds, which consists of from about 80% to about 90% of a gilsonite derivative uniformly blended with material from the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin in sufficient quantities to cause the resulting composition to have a softening point in the vicinity of 205° F. and to be readily dispersible in vulcanizable insulating compounds, said gilsonite derivative being the product obtained by removing at least 2% but not exceeding 5% by weight of volatile constituents from gilsonite.

17. A bituminous composition for incorporation in insulating compounds, which consists of from about 80% to about 90% of a gilsonite derivative obtained by removing from gilsonite originally having a softening point of about 270° F. sufficient volatile material to cause the resulting product to have a softening point of from about 250° F. to about 260° F., and from about 10% to about 20% of microcrystalline waxes and paraffin, the amount of microcrystalline waxes present being from about ¼ to about ¾ of the amount of paraffin.

18. A bituminous composition for incorporation in insulating compounds, which consists of about 80% to about 90% of a gilsonite derivative uniformly blended with from about 3% to about 15% of paraffin and from about 2% to about 10% of microcrystalline waxes, said gilsonite derivative being the product obtained by removing about 3% by weight of the volatile constituents from gilsonite and the paraffin and microcrystalline waxes being present in such proportion as to cause the resulting composition to have a softening point of about 205° F.

19. A bituminous composition for incorporation in vulcanizable insulating compounds, which consists of about 86.45% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile material, uniformly blended with about 8.0% of paraffin, and about 5.55% of microcrystalline waxes.

20. A bituminous composition for incorporation in vulcanizable insulating compounds, which consists of about 83.80% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile material, uniformly blended with about 10.65% of paraffin, and about 5.55% of microcrystalline waxes.

21. A bituminous composition for incorporation in vulcanizable insulating compounds, which consists of about 85.3% of a gilsonite derivative obtained by distilling from gilsonite from about 2% to about 5% of volatile material, uniformly blended with about 11.0% of paraffin, and about 3.7% of microcrystalline waxes.

22. A bituminous composition for incorporation in vulcanizable insulating compounds, which consists approximately of 86.45% of a gilsonite derivative obtained by distilling from gilsonite originally having a softening point of about 272° F. volatile material to cause the resulting product to have a softening point of about 256° F., 8.0% of paraffin, and 5.55% of microcrystalline waxes.

23. A bituminous composition for incorporation in rubber and rubber-like insulating compounds, which consists of from 83% to 89% of a gilsonite derivative, and from 17% to 11% of paraffin plus microcrystalline waxes having melting points of from about 150° F. to about 165° F., the gilsonite derivative employed being natural gilsonite freed of a quantity of volatile material equal to from 2% to 5% of its original weight and the amount of microcrystalline waxes present in the composition being from about ¼ to about ¾ of the amount of paraffin present therein.

24. A bituminous composition for incorporation in insulating compounds, which consists of at least 80% of a gilsonite derivative, and in which the balance is microcrystalline waxes and paraffin in such proportions that the amount of microcrystalline waxes present is from about ¼ to about ¾ of the amount of paraffin and the resulting composition is readily dispersible in vulcanizable rubber and rubber-like insulating compounds, said gilsonite derivative being the product obtained by heating gilsonite at a temperature of from about 425° F. to about 640° F. for a period sufficiently long to drive off about 3% by weight of volatile material therefrom.

25. An electrical insulating compound having a high resistance to deterioration by ozone and sunlight, which comprises a vulcanizable material of the group consisting of natural rubber, rubber-like butadiene copolymers with other monomers copolymerizable therewith, mixtures of natural rubber and such rubber-like copolymers, and rubber-like polyhaloprenes, and a quantity of a blended bituminous composition equivalent to from about ⅓ to about ⅔ of the weight of the vulcanizable material in the compound, said bituminous composition consisting of at least 80% of a derivative of a natural, hard asphaltic material originally having a softening point not materially exceeding about 475° F., and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin, the waxy material being present in sufficient quantity to cause the resulting composition to have a softening point below about 240° F. and to be readily dispersible in vulcanizable insulating compounds, said derivative being such an asphaltic material from which has been removed a quantity of gaseous matter equal to

at least 2% but not exceeding 5% of its original weight.

26. An electrical insulating compound resulting from the vulcanization of a vulcanizable mixture comprising from about 30% to about 55% of a rubber-like butadiene-styrene copolymer, and from about 10% to about 30% of a bituminous composition consisting of at least 80% but not exceeding about 90% of a gilsonite derivative, and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin in such proportion as to cause the resulting composition to have a softening point below about 240° F. and to be readily dispersible in vulcanizable insulating compounds, said gilsonite derivative being natural gilsonite from which has been distilled substantially all materials that volatilize at a temperature of about 450° F. whereby the insulating compound is substantially free of porosity caused by the evolution of volatile materials from the gilsonite derivative during vulcanization of the compound.

27. A vulcanizable electrical insulating compound having a high resistance to deterioration by ozone and sunlight, which comprises from about 30% to about 55% of a rubber-like, butadiene-styrene copolymer, a quantity of a gilsonite derivative equivalent to from about 26% to about 60% of the weight of said copolymer, a quantity of paraffin equivalent to from about 1% to about 10% of the weight of said copolymer, and a quantity of microcrystalline waxes equivalent to from about ⅔% to about 7% of the weight of said copolymer, said gilsonite derivative being the product obtained by distilling from gilsonite from about 2% to about 5% by weight of volatile material originally present therein.

28. An electrical insulating compound, which comprises a vulcanizable material of the group consisting of natural rubber, rubber-like butadiene copolymers with other monomers copolymerizable therewith, mixtures of natural rubber and such rubber-like copolymers, and rubber-like polyhaloprenes, and a quantity of a blended bituminous composition equivalent to from about ⅓ to about ⅔ of the weight of the vulcanizable material in the compound, said bituminous composition consisting of at least 80% of a gilsonite derivative obtained by removing from gilsonite at least about 2% but not exceeding 5% by weight of volatile matter originally present therein and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin in such proportions as to cause the resulting bituminous composition to have a softening point below about 240° F. and to be readily dispersible in the compound.

29. The method of making electrical insulating compounds, which comprises blending with from about 80 to about 90 parts of a gilsonite derivative from about 20 to about 10 parts of microcrystalline waxes and paraffin in such proportions as to cause the resulting blended bituminous composition to have a softening point materially below 240° F., said gilsonite derivative being the product obtained by distilling from gilsonite originally having a softening point of about 270° F. sufficient volatile matter to cause it to have a softening point of from about 250° F. to about 260° F., incorporating the blended bituminous composition uniformly in a vulcanizable electrical insulating compound in which the vulcanizable constituent is a rubber-like, butadiene-styrene copolymer, and vulcanizing the resulting compound, the bituminous composition comprising from about 10% to about 30% of the insulating compound and the copolymer comprising from about 30% to about 55% thereof.

30. A bituminous composition for incorporation in vulcanizable compounds, which consists of at least 80% of a derivative of a natural, hard asphaltic material originally having a softening point not materially exceeding about 475° F., and in which the balance is waxy material of the group consisting of microcrystalline waxes and microcrystalline waxes plus paraffin, the waxy material being present in sufficient quantity to cause the resulting composition to have a softening point below about 240° F. and to be readily dispersible in vulcanizable insulating compounds, said derivative being such an asphaltic material from which has been removed a quantity of gaseous matter equal to at least 2% but not exceeding 5% of its original weight.

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