Feb. 20, 1951 S. GILMAN ET AL 2,542,808

ELECTRIC RESISTOR

Filed Dec. 12, 1945

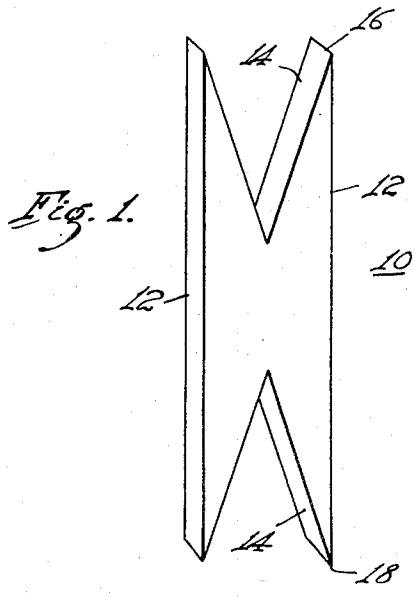


Fig. 1.

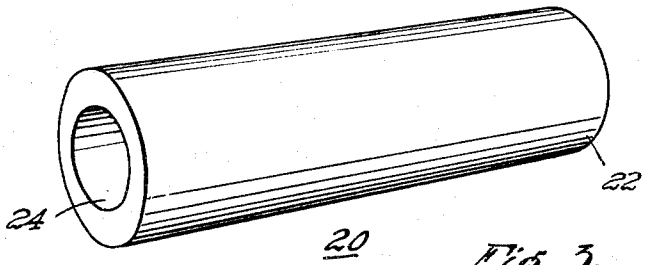


Fig. 3.

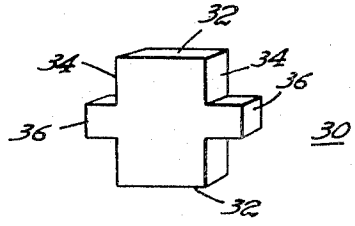


Fig. 2.

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UNITED STATES PATENT OFFICE

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ELECTRIC RESISTOR

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5 Claims. (Cl. 201—63)

1

This invention relates to molded members and, in particular, to attenuators and the like suitable for use in ultra-high frequency circuits.

Heretofore, attenuators and similar structures for ultra-high frequency circuits have been prepared from certain resinous dielectric materials inherently having high losses at ultra-high frequencies, such, for example, as rubber, or phenolic resins. Resistor cards prepared from a thin coating of a carbonaceous material on an insulating sheet also have been made use of. However the resistance cards are subject to wide fluctuations in resistivity even in various sections of the same card. The resinous dielectric materials vary considerably amongst themselves as to the losses produced due to the physical non-uniformity thereof. All of these expedients are limited in attenuation to very small values, usually less than 10 decibels for members six inches in length. Larger attenuations have been only secured by using extremely long pieces of either resistor cards or lossy dielectric material.

Furthermore, changes in atmospheric humidity and the relatively high degree of moisture absorption of these prior art attenuators cause relatively great changes in the attenuation with variations in the ambient atmosphere. Constancy of the ultra-high frequency circuits has been, therefore, difficult to obtain by their use.

The object of this invention is to provide for a molded member capable of use as an attenuator wherein the attenuation may be predetermined within a wide range of values for given physical dimensions.

A further object of the invention is to provide a molded member suitable for use as an attenuator, which member is so relatively impervious to moisture that its properties do not vary appreciably under normal conditions of use.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawing, in which;

Figure 1 is a perspective view of an attenuator constructed according to this invention;

Fig. 2 is a perspective view of another modification of an attenuator; and

Fig. 3 is a perspective view of a shielding member likewise constructed in accordance with the invention.

We have discovered that attenuators having new and unusual properties may be prepared by combining predetermined proportions of finely divided graphite or other energy absorbing solid with a completely polymerizable fluid resin composition composed of (A) 5 to 95 parts by weight of a liquid monomer having the group

$$H_2C=C<$$

2

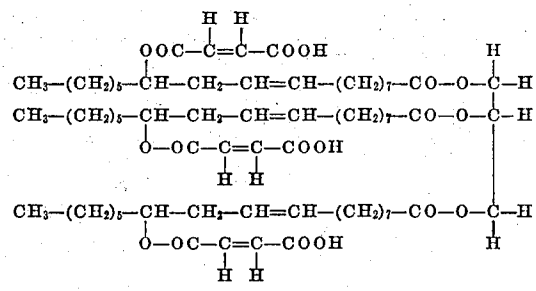
and of (B) from 95 to 5 parts by weight of the reaction product of an ethylene alpha-beta dicarboxylic acid or anhydride thereof with castor oil alone or combined with another vegetable oil and polymerizing the resin composition to a thermoset state. The resin composition carrying a predetermined amount of graphite dispersed therein is completely polymerizable and may be cast or otherwise molded into any predetermined shape wherein the components (A) and (B) copolymerize completely without the necessity of evaporating volatile components. This provides that the members so prepared are homogeneous and free from voids, pores or other flaws. For the purpose of this invention this homogeneity and freedom from voids is critical. The thermoset resinous material has outstanding moisture resistance. This latter property is important since it assures constancy of attenuation. By varying the proportions of the liquid monomer to the reaction product, the members prepared may be either soft and rubbery or may be quite hard whereby they are readily machinable in conventional metal working machines. In all cases, the final product is a thermoset resin which does not fuse or liquefy even at high temperatures short of carbonization.

The reaction product (B) employed in producing the fluid resin composition may be prepared by reacting castor oil alone or castor oil combined with another vegetable oil. Drying oils such as linseed oil, tung oil, hempseed oil, poppy seed oil, sunflower oil, walnut oil, and oiticica oil; semidrying oils such, for example, as corn oil, cottonseed oil, pumpkin seed oil, sesame oil and soybean oil; and nondrying oils such as peanut oil and olive oil may be admixed with the castor oil. If soft and flexible resinous products are desired, a nondrying oil such as peanut oil is admixed as the major ingredient with the castor oil in minor proportion. In any event, a substantial proportion of the mixture of oils should be castor oil. As the lower limit, about 25% of the total amount of the oils should be castor oil.

Examples of suitable ethylene alpha-beta dicarboxylic acids and anhydrides thereof to be reacted with the castor oil are maleic acid and maleic anhydride. Citraconic anhydride, chlormaleic anhydride and their acids are other examples of suitable compounds for reaction with the oils. The reaction with the oil is most conveniently carried out by employing the anhydrides, though by use of somewhat higher temperatures during the reaction, and in some cases the addition of a suitable catalyst, the corresponding acids may be employed.

It is desirable to react the castor oil, with or without another vegetable oil, and the ethylene alpha-beta dicarboxylic acid or anhydride to

produce the half ester of the castor oil. For example, when castor oil is reacted with maleic anhydride, castor oil maleate is formed. One, two or three molecules of maleic anhydride can be reacted with each molecule of castor oil since the castor oil contains three ricinoleic acid radicals, each of which has a hydroxy group at which the esterification of the acid anhydride may occur. The full half ester composed of three molecules of maleic anhydride per castor oil molecule is quite desirable for some forms of the invention since the maximum degree of cross-linkage will be obtained in the final resinous product. The full half ester produced by reacting three mols of maleic anhydride with one mol of castor oil is believed to have the following composition:



The monomaleate half ester of castor oil and the dimaleate of castor oil may also be used in carrying out the invention just as successfully as the full half ester. In general, from three to ten parts, by weight, of maleic anhydride for every thirty parts, by weight, of castor oil will produce a reaction product having satisfactory characteristics.

The nonhydroxylated oil component of the oil mixture probably reacts with an unsaturated dibasic anhydride, such as maleic anhydride, by ester interchange and the Diels-Adler addition reaction, depending on the molar proportions of the ethylene alpha-beta dicarboxylic acid as well as the conditions of the reaction. The reaction product secured will vary to some extent on these conditions of reaction. However, at least one mol of the ethylene alpha-beta dicarboxylic acid, such as maleic anhydride, should be present for each mol of the vegetable oil in the mixture.

The reaction products of the castor oil, with or without other vegetable oils, with the ethylene alpha-beta dicarboxylic acids or anhydrides are generally syrupy or soft gummy substances. They may be dissolved in liquid monomers having the group $H_2C{-}C<$ in the proportions of from 10 parts to 95 parts by weight of liquid monomers and 90 parts to 5 parts by weight of the reaction product.

In forming a liquid composition, various liquid monomers having the group $H_2C{=}C<$ have been found satisfactory as solvents and co-reactants for the reaction product of the maleic anhydride and mixed acid esters. Monostyrene is one highly effective copolymerizable solvent. Nuclearly chlorinated and monoalkyl nuclear substituted styrenes are similarly effective for the practice of the invention; paramethyl styrene and parachlor styrene being typical examples. Other monomers having the group $H_2C{=}C<$ such, for example, as alpha-methyl styrene, alpha methyl para methyl styrene, vinyl acetate and other vinyl esters, methyl vinyl ketone, acrylic nitrile, methyl methacrylate and allyl esters, such as diallyl phthalate have been used to dissolve and to copolymerize with the ester reaction product with successful results.

The use of higher proportions of the liquid monomer (A), such as styrene, to the reaction product (B) results in a harder final resin product. The 90% and higher styrene copolymers are quite hard, whereas the copolymers having 75% and less styrene are more flexible and elastic. For service involving shock and stresses, the use of the copolymer having 25% or more of the reaction product (B) of the mixture of fatty acid esters and dibasic acid is, therefore, suggested.

In order to prevent spontaneous polymerization and undue thickening of the solution in the liquid vinyl monomer, it is desirable to incorporate a small quantity of inhibitor in the solution. The addition of $\frac{1}{10}$ of 1% or less of hydroquinone has been satisfactory in preventing undue thickening due to such spontaneous polymerization. Particularly with the solution having higher proportion of monostyrene the addition of an inhibitor may be indicated. When a catalyst, such for example as a peroxide or an ozonide is being added, sufficient should be employed to compensate for the inhibitor present.

Typical examples of the practice of the invention are embodied in the following:

Example No. I

A reaction product (B) composed of:

100 parts by weight of castor oil
30 parts by weight of maleic anhydride

was prepared by heating the mixture at 120° C. for several hours to produce a castor oil maleate of a molasses-like consistency. About 15 parts by weight of the cooled castor oil maleate was dissolved in 85 parts by weight of monomeric styrene plus 0.02% of hydroquinone to inhibit premature polymerization. A resinous solution of the consistency of thin oil was so produced. With 1% benzoyl peroxide, sections having a thickness of half an inch were cast and upon heating for four hours at 135° C. formed excellent thermoset members.

In order to enhance the thixotropic properties of the solution of Example I, 65 parts by weight of the solution was admixed in an evacuated flask with 35 parts by weight of 325 mesh mica and 1% of benzoyl peroxide catalyst based on the weight of the resinous components. A thick, golden-brown resinous material was produced by the process. When heated at 125° C. for several hours, the material with the mica thermoset into a solid void-free body.

The castor oil-maleate-styrene thermoset resin has an exceptionally flat hardness-temperature curve. Durometer measurements of one sample at 28° C. gave values of 80 while at 100° C. the value was 70. This relatively small change in hardness over this range is a particularly valuable feature.

Oils and many other petroleum products exert no solvent effect on this family of thermoset resins.

Example No. II

A reaction product composed of:

61 parts by weight of linseed oil
15.8 parts by weight of castor oil
23.2 parts by weight maleic anhydride

was produced by heating the mixture for eight hours at 175° C. to 200° C. 75 parts of this resin were dissolved in 25 parts of monomeric styrene and 0.03% hydroquinone inhibitor and 1% by weight of benzoyl peroxide catalyst was added. Graphite of 325 mesh fineness was added and

cast members were readily obtained by heating at temperatures of from 65° C. to 150° C.

Example No. III

A mixture of:

20 parts by weight of castor oil
60 parts of peanut oil
20 parts of linseed oil
30 parts of maleic anhydride

was heated at a temperature of 175° C., for eight hours to a thick syrupy state. The reaction product was dissolved in 30 parts by weight of monostyrene to 70 parts by weight of the linseed oil-castor oil-peanut oil maleate and 1% benzoyl peroxide was added. The presence of the peanut oil prevented undue oxidation of the surface as compared to that produced on the linseed oil-castor oil resin of Example No. II. The proportion of peanut oil may be increased or decreased to meet requirements.

For preparing an attenuator member the resin of Example I composed of 15 parts of castor oil maleate and 85 parts of monostyrene by weight and carrying 35% of mica dust was molded by casting into a mold. The resinous material was polymerized by heat treating at a temperature of 135° C. for several hours, and then machined into the shape of member 10 shown in Fig. 1 of the drawing. The dimension between the faces 12 was approximately one inch. The attenuation of the member was 1.25 decibels at 100 megacycles.

The resin of Example I, but containing 35% castor oil maleate and 65% monostyrene, was placed in a flask and 25% by weight of finely divided graphite was added thereto and admixed while under a vacuum. The thoroughly mixed resin and graphite composition was then cast in a mold and after polymerization was machined to the shape of member 10 of Fig. 1 of the drawing with six inches between the tips 16—18. The attention was 31.6 db.; the dielectric constant at 215 megacycles was 18.8. When this last mentioned resin was admixed with 43.2% graphite in an evacuated flask and then molded and machined into a thermoset member, the attenuation for a member having four inches between tips 16—18 was greater than 80 decibels. A spectrum analyzer showed an attenuation of approximately 90 decibels. The dielectric constant at 195 megacycles was 30.2.

The resin of Example I was combined with various amounts of finely divided graphite with the following results when tested with the same ultra-high frequency wave band:

Example No. V

Graphite	Attenuation (db)
Per cent	
5	3.5
10	7.2
20	26
30	55

An unexpected property of the molded members of this invention is that the dielectric constant increases with increase in the proportion of graphite. In effect, this increases the length of the attenuator. Furthermore, the attenuators have the property of attenuating higher harmonics much more than the fundamental, because the attenuating material occupies more wave lengths, whereas the resistor cards as employed heretofore have the reverse property.

While graphite of a fineness of 200 mesh and finer embodied in the thermoset resin herein described has produced excellent results, other energy absorbing conducting powders may be added to replace a part or all of the graphite. Lampblack, wood chars and similar carbon materials may be incorporated in the resinous composition. Titanium dioxide has been combined with the graphite in preparing attenuators which gave excellent results in service. Finely divided iron, manganin and similar metals may be incorporated in the resin composition.

Referring to Fig. 1 of the drawing, there is illustrated a typical attenuator member 10 having two parallel faces 12 whose distance depends on the wave guide height—one inch being a common dimension. The thickness of the member may be of the order of ½ inch. The body of the member 10 slopes inwardly toward the center along sides 14 to a narrow central portion. The distance between the tips 16—18 determines the effectiveness of the attenuator.

Figure 2 of the drawing illustrates a different form of attenuator 30 which has given good results. The attenuator 30 has a dimension of about one inch between sides 32—32, though this distance may vary in accordance with the wave guide width. The distance between faces 34—34 may be as little as ½ inch and as much as 4 inches and longer. The rectangular projections 36, disposed lengthwise of the wave guide, may be cubes with sides of ½ inch dimension.

The molded resin composition and graphite members of this invention may be employed for numerous other applications. Various shielding materials to prevent radio frequency power and noise leakages, coaxial line attenuators, shielding around joints in coaxial lines and wave guides may be produced from the compositions described herein. The fluid compositions may be molded in place for either wave guide or coaxial line attenuators.

Referring to Fig. 3 of the drawing, there is illustrated the cylindrical shielding member 20 composed of a molded body 22 with an internal bore 24 to accommodate an electrical conductor. The member 20 may be prepared from any of the resinous compositions herein described with proportions of finely divided graphite, or other energy absorbing material.

Due to the unusual moisture resistance of the thermoset resinous compositions described herein, the attenuators and other ultra-high frequency members prepared therefrom will not be subject to any significant variation in properties due to variations of atmospheric humidity or even by contact with water. The attenuation will be relatively constant regardless of the age of the attenuator or the conditions of operation. These features are not obtainable with other resins available to the art and enable a unique product to be produced.

The resin compositions described herein, particularly those having over 75% of a monomer, such as monostyrene, have closely similar low loss values and, therefore, ordinary variations in the proportions of the resin components to one another do not cause any appreciable change in attenuation. The proportion of graphite or other conducting powder to the resin will be the critical determining factor of the characteristics of the attenuator. This feature enables the preparation of attenuators that are mechanically sim-

ila, but may have a value of attenuation selected from a wide range. A close control of the graphite or other conducting powder within the molded members will control the degree of attenuation within reasonably close limits.

Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above described disclosure shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. A member suitable for use as an attenuator in a circuit carrying an ultra-high frequency electrical current comprising, in combination, a molded member of a thickness of the order of half an inch composed of thermoset resin having highly electrically insulating properties, the resin derived by reacting from 5 to 95 parts by weight of a monomer having the group $H_2C{=}C<$ and from 95 to 5 parts by weight of the ester reaction product of castor oil and an acidic compound selected from the group consisting of ethylene alpha-beta dicarboxylic acids and their anhydrides, and from 2% to 50% of the weight of the member composed of finely divided electrically conducting material distributed throughout the resin.

2. A member suitable for use as an attenuator in a circuit carrying an ultra-high frequency electrical current comprising, in combination, a molded member of a thickness of the order of half an inch composed of thermoset resin having highly electrically insulating properties, the resin derived by reacting from 5 to 95 parts by weight of a monomer having the group $H_2C{=}C<$ and from 95 to 5 parts by weight of the reaction product of castor oil and another vegetable oil with an acidic compound selected from the group consisting of ethylene alpha-beta dicarboxylic acids and their anhydrides, and from 2% to 50% of the weight of the member composed of finely divided graphite distributed throughout the resin.

3. A member suitable for use as an attenuator in a circuit carrying an ultra-high frequency electrical current comprising, in connection, a molded member of a thickness of the order of half an inch composed of thermoset resin body derived by reacting from 5 to 95 parts by weight of a monomer having the group $H_2C{=}C<$ and from 95 to 5 parts by weight of the ester reaction product of castor oil and maleic anhydride, and from 2% to 50% of the weight of the member composed of finely divided graphite distributed throughout the resin.

4. A member suitable for use as an attenuator in a circuit carrying an ultra-high frequency electrical current comprising, in combination, a molded member of a thickness of at least ½ inch composed of thermoset resin body derived by reacting from 5 to 95 parts by weight of a monomer having the group $H_2C{=}C<$ and from 95 to 5 parts by weight of the ester reaction product of castor oil and an acidic compound selected from the group consisting of ethylene alpha-beta dicarboxylic acids and their anhydrides, finely divided graphite distributed in the resin, and a substantial amount of mica powder embodied in the resin.

5. A member suitable for use as an attenuator in a circuit carrying an ultra-high frequency electrical current comprising, in combination, a molded member of a thickness of the order of half an inch composed of thermoset resin body derived by reacting from 5 to 95 parts by weight of monostyrene and from 95 to 5 parts by weight of the ester reaction product of castor oil and an acidic compound selected from the group consisting of ethylene alpha-beta dicarboxylic acids and their anhydrides, and from 2% to 50% of the weight of the member of finely divided graphite distributed in the resin.

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