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PLASTIC COMPOSITION

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This invention relates to an electrical insulating composition, more particularly a moldabe composition which has a low loss factor and withstands distortion under load at elevated temperatures. This composition is particularly useful at radio frequencies.

Of the plastic compositions known to the prior art, polystyrene has been most satisfactory for use at radio frequencies due to its good dielectric features and low loss factor. For this reason, polystyrene moldings have been employed for this type of service to a greater extent than other known plastics.

Polystyrene has certain disadvantageous characteristics which render a more extensive application for electrical insulation, at any frequency, undesirable. These characteristics, which are particularly undesirable, are its inflammability and rapid decrease of strength with temperature especially above 60° C. Commercial requirements for electrical insulation would be more satisfactorily met by an insulating material that does not need to be as closely guarded as polystyrene against elevated temperatures, fire hazards, usual operating stresses and accidental impacts. For these reasons, polystyrene has not been accepted in the industry to the extent which would be justified on the basis of its good electrical insulation properties.

An object of this invention is to provide an electrically insulating member having a low loss factor at high frequencies.

Another object of this invention is to provide a moldable composition which has good dielectric characteristics and fire resistance for producing members which will have greater resistance to distortion at elevated temperatures than polystyrene.

A further object of this invention is to provide a fire resisting, machinable, electrically insulating member for use at temperatures above room temperatures.

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

It is known to add modifying substances to polystryrene in order to improve some one property of the polystryrene. Thus plasticizing agents and stabilizers have been incorporated into polystryrene in order to improve the moldability and the stability of the material. Nearly all of the plasticizing or other additions to polystryrene have resulted in a serious deterioration of the dielectric properties of polystryrene alone. The power factor of polystyrene ordinarily does not exceed 0.04% at 1,000,000 cycles. The dielectric constant is remarkably uniform within a range of 2.6 to 2.8 throughout the range from 60 cycles to 1,000,000 cycles. Thus the loss factor of polystryrene alone does not exceed 0.12%.

The term "loss factor" as applied to a given material in the specification and claims is the product of the dielectric constant and the power factor, in percent, of the material.

Accordingly, the material is especially useful as an insulator at high frequencies where normal materials have loss factors considerably above this valve. The addition of slight amounts of materials intended to modify one or more properties of polystyrene is almost invariably followed by a disproportionate increase in the loss factor, for example, to 3% and higher. A customary requirement for insulating materials employed for radio panels, conductor and coil supports, etc., in radio transmitters and receivers and for other electrical insulation to be used at high frequencies is a loss factor of 1% or less both before and after immersion in water for 96 hours.

In radio transmitters wherein relatively large quantities of energy within confined spaces are involved, the ambient temperatures may rise well above 60° C. In some cases, it is necessary to employ fans and similar devices in order to dissipate the heat produced by the apparatus. Even in such cases the temperature cannot be kept much below 60° C. When it is appreciated that polystyrene is ordinarily incapable of sustaining more than its own weight at 80° C., the use of polystyrene within such apparatus is extremely hazardous. The development of a localized high temperature zone or the failure of a fan may result in excessive sagging or in the complete failure of polystyrene insulating supports. Furthermore, polystryrene is extremely inflammable and may catch fire from an arc or localized overheating. This renders the use of the material quite hazardous in such installations.

According to this invention, polystyrene is modified by the addition of certain halogenated hydrocarbons and resins having high softening and melting points in order to both reduce the distortion under load at elevated temperatures and increase the fire resistance of the material without materially increasing the loss factor. In particular, an insulating composition has been prepared that has a loss factor as low as 0.3% and which will not continue to support combustion after a flame has been applied to the composition and removed. The composition is able to support a considerable load at temperatures of 105° C. and in some cases support more than its own weight at 150° C. without harmful distortion. A composition having these characteristics constitutes an exceedingly important advance in the electrical insulator art, notably for use at high frequencies.

It has been found that certain halogenated

hydrocarbons having good electrically insulating properties may be incorporated into polystyrene in order to impart fire resistance thereto without causing any substantial increase in dielectric loss. The halogenated compounds which have been found to possess these characteristics are the symmetrically chlorinated aryl components having low or substantially zero dipole moment. Examples of such chlorinated compounds are decachlorobiphenyl, hexachlorobiphenyl, octochloronaphthalene, chlorinated terphenyl and hexachlorobenzene. In addition, compounds containing oxygen and nitrogen in the molecule which are symmetrically chlorinated may also be employed for this purpose, symmetrically chlorinated carbazole is one example of suitable materials of this latter type. The aryl compounds may be completely chlorinated providing a symmetrically balanced molecule having low dipole moment is produced. Also aryl compounds in which the halogen has been introduced into the molecule without complete halogenation to produce an essentially symmetrical molecule having a low dipole moment is equally usable in this application. Halogenated compounds of high melting point may in some cases be used even though they are not symmetrically substituted provided that the final composition is hard at the maximum temperature of use and the polar molecules are not free to rotate.

It is particularly desirable that the symmetrically halogenated aryl compound have a higher melting point than that of polystyrene, that is, above 150° C. Otherwise the introduction of a low melting point material into polystyrene would tend to further reduce its softening temperature and render it even less desirable for use at elevated temperatures.

In preparing the combination of symmetrically halogenated electrically insulating aryl compounds with polystyrene, it is possible to use non-compatible halogenated aryl compounds as well as the compatible compounds. The aryl compounds with the lower chlorine content, particularly the resinous chlorination products of aryl hydrocarbons are nearly always compatible with polystyrene and may be used to produce a composite material. Substantially incompatible materials such as octachloronaphthalene and decachlorobiphenyl produce particularly good results when incorporated into polystyrene due to their very high melting and softening temperatures. These symmetrically chlorinated halogen compounds greatly increase the fire resistance of the polystyrene when incorporated in amounts exceeding 20% of the total. Up to 60% has been added without causing any serious increase in the loss factor while imparting a high degree of fire resistance. Within this range of proportions, the resulting composite mixture may be exposed to an open flame without the material tending to support combustion. Upon removal of the flame, the material ceases to burn. Therefore, the combination would be highly useful in places where ordinary polystyrene would constitute a fire hazard.

In order to increase the strength and resistance to distortion of the composite material produced herein at temperatures above that at which polystyrene alone can be used, it has been discovered that a copolymer of maleic anhydride and styrene may be added over a wide range of proportions to effect a remarkable improvement in the thermal distortion characteristics thereof.

The copolymer which is produced by reacting substantially equimolecular proportions of maleic anhydride and styrene results in the most desirable thermal distortion characteristics when added to polystyrene. One method of preparing the copolymerized resin is to react substantially one part by weight of styrene with one part by weight of maleic anhydride in two parts by weight of acetone plus a small quantity of benzoyl peroxide as catalyst in an autoclave at 85° C. After several hours reaction, the result is a clear syrup. In order to separate the resin from the solvent acetone, the syrup is diluted with a large amount of acetone and poured into an ethyl alcohol-water medium. Upon stirring vigorously, the resin forms into flakes and comes down as a curdy precipitate. The precipitate may be filtered from the liquid, washed and dried.

The proportion of maleic anhydride to styrene may be varied from this equal molecular ratio up to a 1 to 8 ratio. As the amount of styrene in the resin is increased it has a lower softening temperature. While good results may be obtained with the larger proportions of styrene in the copolymer, the best temperature-distortion characteristics in the composite material are produced when the maleic anhydride-styrene ratio does not exceed 1 to 4.

The properties of the copolymers change with increasing amounts of styrene. For example, while the equimolecular resin is soluble in acetone alone, the other copolymers are soluble in acetone-toluene mixtures, preferably with increasing amounts of toluene as the amount of styrene increases.

The resinous 1 to 1 ratio copolymer has a viscosity of 10,000 centipoises when dissolved in acetone to form a 40% solution by weight. By varying the proportions of ingredients, the temperature and amount of catalyst, the resulting resin may be more highly polymerized. For example, a viscosity of 75,600 centipoises was secured by such changes in reaction. A type of resin may thus be produced most suitable for any specific application.

The flocculent, curdy copolymer of maleic anhydride and styrene is preferably dried at temperatures of 150° C. before adding to the polystyrene and symmetrically chlorinated aryl compound. The presence of small quantities of water in the resin will result in relatively large increases in the loss factor of the final composition. From 5% to 40% of the copolymer of maleic anhydride and styrene may be added to polystyrene and substantially symmetrically halogenated aryl compound to impart notable resistance to distortion at elevated temperatures.

A convenient way of preparing a composition suitable for molding is to combine the required weight of dried resinous copolymer and symmetrically halogenated aryl compound and powdered polystyrene along with 0.3% to 0.5% calcium stearate as an internal lubricant and ball mill the mixture to cause thorough comingling of the three ingredients. A few hours ball milling is generally sufficient to cause pulverizing and a thorough admixture of the ingredients. Suitable dyes may be incorporated for coloring purposes. The composition thus produced is suitable for molding into any desired shape of insulating member by customary molding procedure. The powder may be measured out into a mold having predetermined form. It has been found that molding temperatures of above 180° C. produce the best physical structure. The ten-

sile strength, for example, is greatly increased by increasing the molding temperature from 160° C. to 200° C. The mold pressures may be from 1 to 2 tons per square inch with satisfactory results. The temperature and pressure in the mold will cause the material to flow and produce an article having uniform color. This composition has extremely low distortion or warpage from the shape of the mold.

In order to indicate the superior results produced from this composition, the following mixture was prepared and molded into various shapes. 25 parts of maleic anhydridestyrene copolymer, 35 parts of polystyrene, 40 parts of decachlorobiphenyl, and 0.5 part calcium stearate were ground in a ball mill until intimately comingled. The mixture was then molded at a pressure of two tons per square inch and at a temperature of 180° C. The dielectric constant of the molded product was 2.7. The power factor was 0.19% and the loss factor was 0.51%. This sample was immersed in water for 96 hours and when tested after removal, the dielectric constant was 2.7, the power factor was 0.24% and the loss factor was 0.65%. It will be noted that this particular composition is well under the desirable upper limit of 1% loss factor. By modifying the proportions of copolymer and the symmetrically halogenated aryl compound, the loss factor can be reduced to less than half of this particular value.

In order to show the resistance to distortion under load at elevated temperatures a strip of this same composition having the dimensions of 5 inches by ½ inch by ¼ inch was supported at both ends on blocks with a 3 inch unsupported center span. This strip was then heated to 105° C. for three days with a 325 gram weight placed on the unsupported span. The strip had a barely noticeable deflection under this load. Polystyrene alone molded into a similar strip failed completely in a similar test. The strip flowed off the supports and softened sufficiently to show the markings of the oven surface onto which it had flowed. Similarly, a two component material comprising only polystyrene and symmetrically halogenated biphenyl also was bent into the shape of a U until it had rested on the oven shelf. At 150° C. polystyrene flows sufficiently to take the shape of the containing vessel while the three component material is self-sustaining and may even carry an appreciable load for twenty hours or more.

The following additional thermal distortion tests of a more severe loading type were run at 96° C. In each case a test bar 5 inches by ½ inch by ¼ inch was supported at both ends and a one-pound weight was suspended from a fine wire looped around the center of the bar. The length of the unsupported span was 4 inches and the thickness was ¼ inch. The length of time required for the bar to sag one inch was taken as the point of failure.

Composition	Time required to fail
	Hours
65% polystyrene 35% decachlorobiphenyl	⅛
45% polystyrene 40% decachlorobiphenyl 15% styrene-maleic anhydride copolymer	23
35% polystyrene 40% decachlorobiphenyl 25% styrene-maleic anhydride copolymer	53

The more of the maleic anhydride and styrene copolymer that is added to the composition the greater is the stability to distortion under load at elevated temperatures. There is, however, a correspondingly small increase in loss factor. For some purposes where the loss factor is not as critical as in the radio standard herein set forth, this increase in thermal strength characteristics may more than compensate for the slight increase in loss factor. Thus the composition may include up to 50% of the copolymer.

In order to increase the fireproof characteristics of the material, the proportion of symmetrically chlorinated aryl compound may be varied from 20% to 60% of the total. In cases where the greater amounts of halogenated aryl is employed, the fire resistance is greatly increased.

The material is very readily machined. It may be sawed, drilled or turned on a lathe with good machined surfaces resulting. In some forms, polystyrene alone could not be subjected to similar machining operations without resulting in chipped corners and rough machined surfaces due to its relative brittleness.

In some instances the fire resistance conferred by the halogenated compund may not be required. Therefore the halogenated aryl compound may be omitted from the composition. A two component moldable material comprising from 5% to 40% of the copolymer of maleic anhydride and styrene, balance polystyrene, may be prepared. This composition will have improved strength as compared to one having the halogenated aryl compound.

In order to increase some of the physical characteristics of the three component composition herein disclosed, it is feasible to add inorganic materials which have loss characteristics not widely differing from that of polystyrene. For example, crushed quartz or glass may be incorporated in the composition as a filler in order to produce some advantageous physical characteristics. A preferred filler, however, is fiber glass which consists of strands of fineness of an average of 0.00025 inch. This fiber glass material may be incorporated into the loose mixture in the form of loose fibers several inches in length or less depending upon the size of the piece to be molded. The fiber glass may also be employed in the form of cloth. In this latter case alternate layers of ball milled composition and cloth may be placed within the mold and the whole consolidated under pressure and temperature. Thus in a quarter inch thick panel, 2, 4 or more layers of cloth may be incorporated in order to give improved strength and shock resistance to the panel. Such panels may be hammered until the resin cracks without the panel falling apart or shattering. When used as a support for electrical coils and the like, a support incorporating fiber glass cloth filler will be effective even under extreme heat conditions.

Thus it will be seen that a low loss, flameproof, moldable plastic composition is secured in the instant invention, this composition producing electrically insulating members that are superior to polystyrene alone in physical characteristics and well within commercial limits relative to loss factor.

Other modifications will suggest themselves to those skilled in the art from our disclosure herein set forth, and, therefore, the invention is to be limited only by our claims.

We claim as our invention:

1. A moldable, fire-resisting composition suit-

able for an insulating member, comprising, in combination, 35% and higher amounts of polystyrene, a substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C. in amount sufficient to provide for fire resistance, and the resinous reaction product of one mol of maleic anhydride and from one to eight mols of styrene in amount sufficient to impart improved thermal strength characteristics to the polystyrene.

2. A moldable, fire resisting composition suitable for electrically insulating members, comprising, in combination, 25% to 60% of substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C., 5% to 40% of the resinous reaction product of one mol of maleic anhydride and from one to eight mols of styrene, the balance polystyrene in an amount of at least 35%, the composition being characterized in that the molded members have a low loss factor at 300 kilocycles, improved resistance to distortion under load at elevated temperatures over polystyrene alone and good machinability.

3. An electrically insulating member having a loss factor of less than 1% at 300 kilocycles composed of a mixture of 25% to 60% of substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C., 5% to 40% of the resinous reaction product of one mol of maleic anhydride and from one to eight mols of styrene and the the balance of the mixture being polystyrene in an amount of at least 35%, the mixture consolidated under pressure and temperature into predetermined shape, the member having a fire resistance, machinability and improved resistance to distortion under load at elevated temperatures over polystyrene alone.

4. An electrically insulating member having a loss factor of less than 1% at 300 kilocycles composed of a mixture of 25% to 60% of substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C., 5% to 40% of the resinous reaction product of one mol of maleic anhydride and from one to eight mols of styrene and the balance of the mixture being polystyrene in an amount of at least 35%, the mixture consolidated under pressure and temperature into predetermined shape and glass fibers being distributed in the consolidated member, the member having fire resistance, machinability and improved resistance to distortion under load at elevated temperatures over polystyrene alone.

5. An electrically insulating member having a loss factor of less than 1% at 300 kilocycles composed of a mixture of 25% to 60% of substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C., 5% to 40% of the resinous reaction product of one part by weight of maleic anhydride and from one to eight parts by weight of styrene and the balance of the mixture being polystyrene in an amount of at least 35%, the mixture consolidated under pressure and temperature into predetermined shape, and fabric of fine glass fibers being disposed in the consolidated member, the member having fire resistance, machinability and improved strength characteristics at elevated temperatures over polystyrene alone.

6. An electrically insulating member having a loss factor of less than 1% at 300 kilocycles composed of a mixture of 25% to 60% of substantially symmetrically halogenated aryl compound having good electrically insulating properties and melting above 150° C., 5% to 40% of the resinous reaction product of one mol of maleic anhydride and from one to eight mols of styrene and the balance of the mixture being polystyrene in an amount of at least 35%, the mixture consolidated under pressure and at a temperature of above 180° C. into predetermined shape, the member having fire resistance, machinability and improved thermal strength characteristics over polystyrene alone.

7. A molded electrically insulating member comprising, in combination, 5% to 40% of the resinous reaction product of substantially molecular quantities of maleic anhydride and styrene and 60% to 95% of polystyrene, the whole being commingled and dried prior to molding into predetermined shape, to provide for increased strength at elevated temperatures and higher flow temperatures as compared to polystyrene alone.

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