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W. A. YAGER

2,319,838

DIELECTRIC MATERIALS

Filed Dec. 6, 1938

FIG. 1

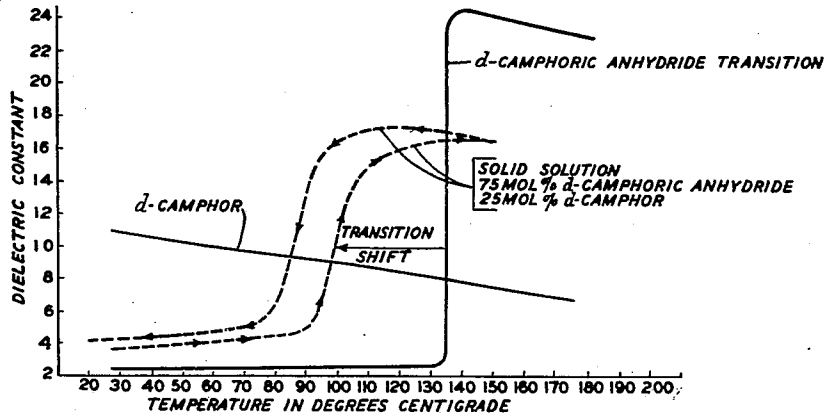


FIG. 2

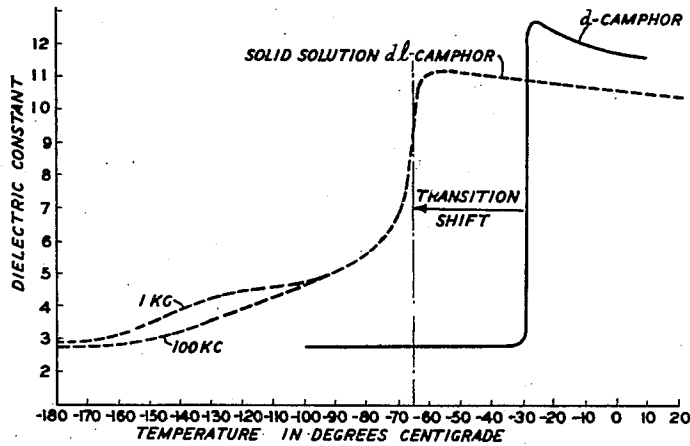
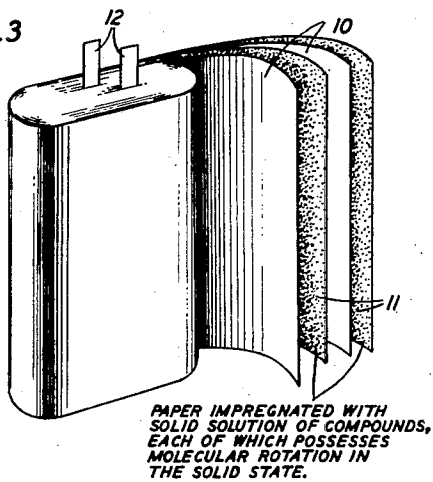
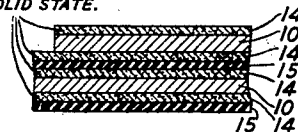


FIG. 3



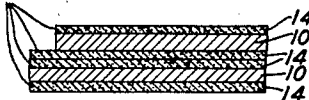
SOLID SOLUTION OF COMPOUNDS,
EACH OF WHICH POSSESSES
MOLECULAR ROTATION IN
THE SOLID STATE.

FIG. 4



SOLID SOLUTION OF COMPOUNDS,
EACH OF WHICH POSSESSES
MOLECULAR ROTATION IN
THE SOLID STATE.

FIG. 5



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DIELECTRIC MATERIAL

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Application December 6, 1938, Serial No. 244,168

9 Claims. (Cl. 106—287)

This invention relates to dielectric materials and more particularly to the use of these materials in electrical apparatus.

In telephone exchanges, particularly in urban centers, space is at a premium and any substantial reduction in the size of apparatus is of paramount importance. Then, too, in mobile bodies, such as airplanes, weight and space are factors which dictate reduction of communication apparatus employed therein to the minimum in size necessary for successful operation. In both telephone and communication systems condensers are used in relatively great numbers and any reduction in their size without appreciable diminution in their functional characteristics results in material economies.

An object of this invention is to reduce substantially the size of apparatus employed in electrical systems.

Another object is to utilize in electrical apparatus materials having high dielectric constants and desirable physical and electrical properties.

In accordance with this invention solid solutions of a plurality of dielectric materials, each of which possesses sufficient geometric symmetry about its center of gravity to permit molecular rotation, are employed. These solid solutions when utilized alone or in conjunction with other dielectrics, such as paper, provide high capacity in electrical apparatus and at the same time have physical properties such as melting point, compressibility, viscosity and penetrability which render them admirably adapted for use in electrical apparatus.

In a copending application of Biggs, Morgan and White, Serial No. 244,171, filed December 6, 1939, and assigned to the same assignee, there are described materials having high dielectric constants in the solid state. These materials comprise the class which consists of hexasubstituted benzenes, the substituents consisting of methyl and polar groups, at least one of the substituents being a methyl group and one a polar group, pentasubstituted benzenes, the substituents consisting of methyl and polar groups, at least two of the substituents being methyl groups and at least one a polar group, pentasubstituted benzenes, the substituents consisting of methyl and polar groups, at least one of the substituents being a methyl group and at least two other substituents being two different polar groups, and pentasubstituted benzenes, the substituents consisting of methyl and polar groups, at least one of the substituents being a methyl group and at least one of the polar substituents being a mem-

ber of the class which consists of amino, bromo, fluoro, iodo, hydroxy and nitro, the molecule of each compound having sufficient geometric symmetry in one plane about the molecular center of gravity to permit molecular rotation or having a finite dipole moment or having a dielectric constant in the solid state equal to or greater than that in the liquid state, or having a dielectric constant higher than the square of its optical refractive index.

In U. S. Patent 2,126,363, granted to A. H. White and W. A. Yager on August 9, 1938, the polar derivatives of polymethylene cyclic hydrocarbons are proposed for use in electrical apparatus. These polar derivatives of polymethylene cyclic hydrocarbons also have sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation. Some of the compounds in the above-noted application to Biggs, Morgan and White manifest a transition in dielectric properties in the solid state from a state of high dielectric constant to a state of lower dielectric constant with decreasing temperatures and from a state of low dielectric constant to a state of high dielectric constant with increasing temperatures, while others exhibit anomalous dispersion. All of the polar derivatives of polymethylene cyclic hydrocarbons which possess molecular rotation in the solid state to which the above-noted U. S. patent to White and Yager relates, manifest the transition phenomenon. When two or more dielectrics, each of which has a characteristic temperature at which anomalous dispersion or a transition occurs, form a solid solution, the temperature of anomalous dispersion or transition of at least one of the components is substantially reduced.

It is well known that in solid solutions of two or more metals the formation of the solid solution often causes the spreading of the lattice parameters. If an analogous spreading of lattice parameters occurs in solid solutions of organic compounds, a reduction in the magnitude of the potential barriers opposing rotation of the molecules might be expected. Whether or not a molecule rotates in its crystal lattice depends upon whether its kinetic energy is sufficient to overcome the potential barrier opposing rotation. In general, the greater the geometric symmetry of a molecule and the lower the potential barrier tending to fix its orientation in the crystal the more likely it is to rotate in the crystal lattice. The reason that the majority of organic molecules do not rotate in the crystal lattice is that the potential barriers are so great that the ma-

terial melts before the molecules acquire sufficient kinetic energy to overcome them. Consequently, if these potential barriers could be sufficiently reduced in some manner, it should be possible for the molecules to rotate in the lattice below the melting point. If the reduction in the potential barriers resulting from the formation of a solid solution is sufficiently great, molecular rotation might well occur in the crystal lattice of the solid solution, even if it cannot occur in the lattice of the components. It has been found that when two or more components, each of which has sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation, form a solid solution, the molecules of at least one of the components are able to rotate more freely in the crystal lattice of the solid solution than in the crystal lattices of the pure components. As a consequence, the temperature of anomalous dispersion or of transition of these molecules is shifted to lower temperature. For example, a solid solution of equal parts of d-camphor and l-camphor has a transition point at about -65°C . with ascending temperatures, whereas the transition temperature of both d-camphor and l-camphor is essentially the same, or -29°C . The importance of the ability to shift a dielectric transition or region of anomalous dispersion to lower temperature is obvious. For example, the transition of 4, 5, 6-trichloro-ortho-xylene occurs at $+20^{\circ}\text{C}$. so that the change in dielectric constant occurs within the normal operating temperature range of many electrical devices, such as condensers. This compound is, therefore, unsatisfactory for many commercial applications. A solid solution containing as little as 13 mol per cent of tetrachloro ortho-xylene or dichloroprehnitene has a transition temperature of -15°C . This solid solution would accordingly be entirely satisfactory for use in condensers.

Another advantage of the use of solid solutions in accordance with this invention is the flexibility of the melting ranges obtainable. By varying the composition of the components, any temperature of initial crystallization between the melting points of two constituents may be obtained. Consequently, if the dielectric properties of a compound having sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation are particularly good, but its melting point is too low or too high for use in electrical apparatus, the desired melting point can be obtained by the formation of a solid solution with another compound which has sufficient geometric symmetry to permit molecular rotation and which has a higher or lower melting point, as the case may be. A decrease in the melting point of a dielectric might be desired to facilitate the manufacture of electrical devices, such as condensers. For example, the paper employed in the coil type of condensers is severely damaged and decomposes above a temperature of 160°C . Accordingly, a dielectric having a melting point above this temperature could not be employed as an impregnating medium.

A more comprehensive understanding of this invention is obtained by reference to the accompanying drawing, in which

Figs. 1 and 2 show the changes in dielectric properties of solid solutions of two compounds, each of which has sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation;

Fig. 3 is a perspective view of an embodiment of this invention;

Fig. 4 is a cross-section of a capacitance constructed in accordance with this invention; and

Fig. 5 is an alternative form of the invention shown in Fig. 4.

In Fig. 1 the dielectric behavior of d-camphoric anhydride, d-camphor and a solid solution containing 25 mol per cent of d-camphor and 75 mol per cent of d-camphoric anhydride is shown. It is observed that the dielectric transition of d-camphoric anhydride in the solid solution with d-camphor is shifted from 135°C . to 100°C . for ascending temperatures and to about 88°C . for descending temperatures. The dielectric transition of d- and l-camphor occurs at essentially the same temperature. Fig. 2 shows that the formation of a solid solution comprising equal parts of the d and l forms of camphor shifts the transition from about -29°C . to about -65°C . for ascending temperatures. In both of these examples the transition temperature of a compound which has sufficient geometric symmetry about its molecular center of gravity to permit molecular rotation is materially lowered by the formation of a solid solution with another compound having this characteristic. Further, the transition temperature of a solid solution is not the weighted mean of the transition temperatures of the components of the solid solution. Thus the transition temperature of d-camphor and l-camphor is approximately the same, or -29°C ., but the transition temperature of the solid solution of d-l-camphor is -65°C . Mixtures of various types of dielectric materials have been suggested in the past but it was not heretofore appreciated that by such mixtures any unexpected advantage would be derived therefrom as is obtained, for example, in the unforeseen lowering of the transition temperature of the mixtures just described.

The solid solutions of compounds, each of which possesses sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation may be employed in condensers, as shown in Figs. 3, 4 and 5. In Fig. 3 sheets of a porous dielectric 11, such as paper, are impregnated with a solid solution to which this invention relates. Interposed between the sheets of dielectric are metal foils 10. Both the dielectric and foils are wound in a well-known manner to form a condenser. Two metallic strips 12 are electrically connected to the electrodes 10 to form the terminals of the condenser. Alternatively, the solid solution may be a coating 14 or a metal foil 10, as shown in Figs. 4 and 5. A strip of another dielectric 15 may be positioned between the coatings 14 as shown in Fig. 4, and the coated foils piled alternately in a well-known manner to form a condenser. The solid solutions in accordance with this invention may also be employed in other electrical apparatus, such as wave guides, as shown in U. S. 2,129,711 granted to G. S. Southworth on September 13, 1938, where a relatively high capacitance is required.

Two or more compounds, each of which has sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation may be used to form a solid solution to lower the transition temperature or to obtain a dielectric having desirable electrical properties and a definite melting temperature. Compounds which have sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation are polar derivatives of polymethylene cyclic hydrocarbons which in the solid state un-

dergo a transition in dielectric properties at a particular temperature or range of temperatures, such as those disclosed in U. S. Patent 2,126,363 to White and Yager, or the penta or hexasubstituted benzenes disclosed in the above-noted copending application of Biggs-Morgan-White. Examples of polar derivatives of polymethylene cyclic hydrocarbons to which this invention relates are d-camphor, d-l-camphor, camphoric anhydride, borneol, isborneol, borneol chloride, cyclohexanol and chlorocyclohexane.

Examples of the penta and hexasubstituted benzene disclosed in the copending application of Biggs-Morgan-White are: pentamethyl chlorobenzene, dichloroprehnitenene, dichloroisodurene, trichlorohemimellitene, trichloropseudocumene, tetrachlorometaxylene, tetrachloro-ortho-xylene, pentachlorotoluene, pentamethyl fluorobenzene, tetrachloro-meta-fluorotoluene, dinitroprehnitenene, dinitroisodurene, 2,4,5-trichloro-meta-xylene, 4,5,6-trichloro-ortho-xylene, 2,4,6-trichloro-meta-fluorotoluene, 3-nitro-4,5-dichloro-ortho-xylene and 5-nitro-3,4-dichloro-ortho-xylene.

While the preferred embodiments of this invention have been illustrated and described, various modifications may be made therein without departing from the scope of the appended claims.

What is claimed is:

1. A dielectric element comprising a solid solution of polar compounds, each of which possesses molecular rotation in the solid state as evidenced by a dielectric constant considerably higher than the square of the optical refractive index of the substance.
2. A dielectric element comprising a plurality of polar compounds forming a solid solution, each of which compounds undergoes a transition in dielectric properties at a temperature below the melting point of these compounds.
3. A dielectric element comprising a plurality of polar compounds forming a solid solution, the dielectric constant of each of said compounds

being substantially higher than the square of its respective optical refractive index.

4. A dielectric material comprising a solid solution of d-camphor and d-camphoric anhydride.

5. A dielectric material comprising a solid solution of d-camphor and l-camphor.

6. A dielectric element comprising a solid solution of constituents comprising at least two organic compounds, each of which is made up of molecules having a finite dipole moment and having sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation in the solid state, each of which compounds in the pure solid state has by virtue of these characteristics a dielectric constant substantially equal to or higher than its dielectric constant in the liquid state and higher than the square of its optical refractive index.

7. A dielectric element comprising a solid solution of constituents comprising at least two carbocyclic polar compounds, each of which is made up of molecules having a finite dipole moment and having sufficient geometric symmetry about the molecular center of gravity to permit molecular rotation in the solid state, each of which compounds in the pure solid state has by virtue of these characteristics a dielectric constant substantially equal to or higher than its dielectric constant in the liquid state and higher than the square of its optical refractive index.

8. A dielectric element comprising a solid solution of at least two polar derivatives of polymethylene cyclic hydrocarbons, each having a dielectric constant in the solid state, above a dielectric transition point, substantially greater than the square of its optical refractive index for visible light.

9. In an electric condenser a dielectric comprising a plurality of polar organic compounds forming a solid solution, the dielectric constant of each of said compounds being higher than the square of its respective optical refractive index.

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