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2,921,869

COATED POLYMERIC THERMOPLASTIC DIELECTRIC FILM

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This invention relates to a process of improving the dielectric life of polymeric thermoplastic materials useful as electrical insulation and to the product of such process and, more particularly, to a coated polyethylene terephthalate film having an improved dielectric life.

Polyethylene terephthalate film, particularly oriented film (film which has been stretched and/or rolled in two directions and heat-set at elevated temperatures within the range from 150°–250° C.) has been found to possess a unique combination of electrical, physical and chemical properties which make it outstanding for use as a dielectric. That is particularly true of polyethylene terephthalate film which has been stretched and/or rolled to substantially the same degree in both directions, e.g., 3X, where X equals the original dimension of the film, to obtain a substantially "balanced" film, which means that the physical properties of the film, as measured in both directions, are substantially the same. The oriented, heat-set, polyethylene terephthalate film is outstanding as a dielectric because it retains a considerable percentage of its electrical properties, strength, and durability at elevated operating temperatures. Consequently, the film is particularly useful as a dielectric in capacitors, motors, generators, transformers, etc., at not only moderate operating temperatures, but also at ambient temperatures approaching 150°–175° C.

In extending the usefulness of polyethylene terephthalate and like thermoplastic polymer film dielectric to a wider variety of electrical end uses, it became apparent that the dielectric life of the film required improvement, particularly for use in equipment subjected to high voltage stresses. As employed herein, the term "dielectric life" of the polymeric thermoplastic film applies to the actual time that a particular film may be subjected to a particular voltage stress under conditions of corona discharge before actual physical breakdown, i.e., rupture, of the film dielectric.

It is the action upon the polymeric film dielectric of corona discharge (in air or other gaseous medium) which causes actual physical breakdown of the film under conditions of a particular voltage stress (a potential difference large enough to produce a visible discharge but not large enough to produce instantaneous breakdown). Obviously, the lower the voltage stress, the longer the dielectric life of the film. "Corona discharge" is defined as the discharge of electricity which appears upon the surface of a conductor when the potential gradient exceeds a certain value. For example, when a continuous potential applied to a pair of narrow wires is slowly increased, the voltage will be reached at which a hissing noise is heard, and a pale violet light is visible (in the dark) around the wires. This voltage is defined as the "critical visual corona point." Corona is due to ionization of the air or surrounding gases (it does not occur in a vacuum). That is, the air in the ionized region is conducting, and this results in increasing the effective diameter of the conductor. For example, even though a film dielectric is wound tightly around a wire, air is

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not entirely excluded from the space between the conductor and the film dielectric; and it is the air or other gaseous medium which is ionized. The corona envelopes a conductor as a concentric cylinder, and the outside diameter becomes such that the gradient at that point decreases to the rupturing point of the air. Beyond this point, the corona cannot increase for the constant applied voltage because the gradient decreases with increasing radial distance from the wire. The glow or breakdown of the surrounding air starts first at the point of maximum gradient or at the conductor surface. It is the bombardment of the dielectric film with ions or electrons that actually results initially in roughening or pitting the surface of the film. As the bombardment continues, the film eventually ruptures; hence, this causes short circuits owing to the physical failure.

An object of the present invention is to provide a polymeric thermoplastic dielectric film having increased dielectric life. A further object is to provide a polyethylene terephthalate film dielectric having increased dielectric life. A further object is to provide a process of improving the dielectric life of polymeric thermoplastic dielectric compositions, particularly polyethylene terephthalate film. A still further object is to provide a novel coating composition useful for improving the dielectric life of polymeric thermoplastic dielectric film. Other objects will be apparent from the following description of the invention.

These objects are realized in accordance with the present invention which, briefly stated, comprises providing a dielectric base film of thermoplastic polymeric material, e.g., polyethylene terephthalate, with a relatively thin, adherent, continuous coating consisting essentially of a homogeneous mixture of from 95% to 40% by weight of (A) a cured resinous compound selected from the group consisting of (1) phenol formaldehyde resins, (2) alkyd resins resulting from the inter-reaction of a polybasic carboxylic acid and a polyhydric alcohol, (3) long chain fatty acid-modified alkyd resins, and (4) the condensation product of epichlorohydrin and bis p,p'-hydroxyphenyldimethylmethane, and from 5% to 40% by weight of (B) finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 microns and 5 microns.

The present invention will be further described specifically with respect to improving the dielectric life of polyethylene terephthalate film but it should be understood that the invention is applicable as well to enhancing the dielectric life of other types of unplasticized polymeric thermoplastic films useful as dielectrics, such as films of polyethylene, polytetrafluoroethylene, polystyrene, polyamides, etc.

Any phenol-formaldehyde resin is operable in this invention. It has been found that both heat-reactive and non-heat-reactive resins (i.e., thermosetting resins and non-thermo-setting resins) and both oil-reactive and non-oil-reactive resins are operative. The term "phenol" includes beside phenol itself, phenol derivatives such as cresol, paraphenylphenol, xylenol, ethyl phenols, salicylic acid, and resorcinol and chlorinated phenols. The oil-reactive phenols may be modified by the addition of up to 80% by weight of a drying or semi-drying oil. Preferably, the oil is added to a solution of the resin in a volatile organic solvent, e.g., toluene, xylene, mineral spirits, etc.

The alkyd resins utilized in the coating compositions characterizing the present invention may be prepared in known manner by inter-reacting a polycarboxylic acid or the anhydride thereof, having from 2 to 3 carboxyl radicals per molecule with a polyhydric alcohol having 3 to 4 hydroxyl radicals per molecule. A preferred

composition is the alkyd resin formed by the inter-reaction of phthalic anhydride and glycerine.

These alkyd resins may be modified by the addition of from 15% to 80% of a higher fatty acid, i.e., a fatty acid having at least 8 carbon atoms. The fatty acids are preferably selected from the group comprising unsaturated dry oil type fatty acids, e.g., coconut oil acid, and saturated non-drying monocarboxylic fatty acids, e.g., 2-ethyl hexoic acid.

The epoxide resins employed in this invention are formed by the condensation of epichlorohydrin and bis-p,p'-hydroxy-phenyldimethylmethane in the presence of sodium hydroxide. During the condensation HCl or NaCl is split out to form polyethers which have epoxy groups on the end of the chain. The degree of polymerization is expressed in terms of epoxy equivalents. The term "epoxy equivalent" is defined as the weight of the resin in grams which contains 1 gram equivalent weight of the epoxy groups. The resins of the above type are available commercially. One brand of such resins is sold by the Shell Chemical Corporation under the name "Epon."

Types of finely divided particles which are to be blended with the blend of alkyd or phenolic resins are selected from the following compounds: (1) amorphous silica, and (2) estersils as defined in U.S. Patent 2,657,149. The essential requirement is that whenever any of the above compounds are blended with the alkyd, phenolic, or epoxy resins characteristic of the coating compositions of the present invention, the compound must be in finely divided form such that the ultimate particles, either in the form of super-colloidal aggregates or individual particles, have an average greatest dimension ranging between 5 millimicrons and 5 microns, and preferably below 50 millimicrons. Some types of the above compounds may not be commercially available in finely divided form wherein the average particle size is 5 microns or less. In such cases, it is necessary to process the particles by ball-milling or other techniques to produce the size of the average particle.

The commercially available types of amorphous silicas may be satisfactorily employed in the present invention. These silicas may be arbitrarily divided into four classifications, namely: aerogel, precipitated, vapor phase, and diatomaceous types. "Santocel" CS, manufactured by the Monsanto Chemical Company is an example of the aerogel type. This is slightly acidic and contains a small amount of alcohol, water and sodium sulfate as the chief impurities. The particle diameter is approximately 30 millimicrons, with a surface area of approximately 100-150 m.²/gm. (square meters per gram). The precipitated silicas may be represented by "Hi-Sil" X-303 or "Hi-Sil" XW, manufactured by the Columbia-Southern Chemical Corporation. This material has an average particle diameter of 20-25 millimicrons and a surface area within the range of 140-160 m.²/gm. A typical representative of the vapor phase type of silica is "Aerosil," manufactured by Godfrey L. Cabot, Inc. This material has an average particle diameter approximately 14-20 millimicrons and a surface area of 175-200 m.²/gm. The diatomaceous types of silicas may be further divided into two groups which are important in compounding the present coating compositions. These are the heat-calcined, and flux-calcined materials. Both are relatively free from organic contaminants. Particle sizes are much larger than those of the silicas mentioned above, ranging from 1-6 microns. The surface areas are larger than would be calculated from particle diameter owing to high internal area in this form of silica. In the heat-calcined group are such products as "Celite" 270, manufactured by Johns-Manville Corporation and "Dicalite" PS, manufactured by Great Lakes Carbon Corporation. In the flux-calcined group are "Dicalite" White and "Celite" Superfloss.

The estersils useful for purposes of this invention are

described in U.S. Patent 2,657,149 to Ralph K. Her. In brief, the estersils are esterified super-colloidal substrates, that is, a substrate in the form of particles coated with —OR groups, the substrates having a surface of silica and having a specific surface area of at least 1 m.²/gm., the coating of —OR groups being chemically bound to said silica, and R being a hydrocarbon radical of at least 2 carbon atoms wherein the carbon atom attached to oxygen is also attached to hydrogen. In general, the estersils have a specific area of at least 1 m.²/gm., usually within the range of 1-900 m.²/gm.

The coating compositions may conveniently be prepared by first dissolving the resin component in a suitable volatile organic solvent such as toluene, xylene or mineral spirits, and ball-milling the resulting solution admixed with the finely divided particles of silica or estersil to form a homogeneous blend. The composition should contain from 10 to 60%, and preferably from 20 to 40%, by weight of total solids.

The coating composition may be applied to one or both surfaces, preferably both surfaces, of the base film by any desired expedient; and the coated film may thereafter be dried at room temperature or moderately elevated temperatures to remove solvent. Curing of the resin/particle blend to harden the resin should be carried out at elevated temperatures, e.g., 100°-175° C., for durations from 10 minutes to 60 minutes. In some instances, air-drying at room temperature, is sufficient to effect hardening of the coating.

It may be necessary, depending upon the end use for the coated dielectric films of the present invention, to apply a subcoating to the base dielectric film, e.g., oriented, heat-set, polyethylene terephthalate film, to improve adhesion between the base film and the resin/particle coating. When applying the subject coating compositions to polyethylene terephthalate film, for example, it is preferred to apply a subcoating which is chemically similar to the base film. Any suitable subcoatings may be employed provided that they improve the adhesion between the base film and the present coating and do not adversely affect the original combination of physical, electrical and chemical properties of the base film. Preferred subcoatings for polyethylene terephthalate film include copolyesters derived by reacting glycol, terephthalic acid, or low alkyl ester thereof with a second acid or alkyl ester thereof from the group consisting of sebacic acid, isophthalic acid and hexahydroterephthalic acid. Normally, in preparing suitable subcoatings, it is preferred that the subcoating composition contain at least 50% of the terephthalic acid component, based upon the weight of the acid components. The subcoating compositions may be applied to the base dielectric film from solvent solutions or homogeneous thin films of the copolyester compositions may be first applied to the dielectric base film by lamination under heat and moderate pressure.

The following examples of preferred embodiments further illustrate the principles and practice of the invention. Parts are by weight.

EXAMPLE 1

The following formulation:

	Parts
"Super-Beckacite" 1003 (Thermosetting varnish oil reactive-soluble, phenol formaldehyde resin—Reichold Chemical Company) -----	75
Estersil (as described in U.S. Patent 2,657,149) ----	20
Toluene -----	173

was mixed (35.5% solids) and placed in a ball-mill apparatus. The contents were agitated for 116 hours. Polyethylene terephthalate (0.5 mil in thickness) was coated with this composition and air-dried at room temperature. The film was then cured in an oven at 150° C. for 10 minutes.

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EXAMPLE 2

The following formulation:

	Parts
"Glyptal" 2502 resin (60% solvent solution-glyceryl phthalate having high hydroxy content—General Electric Company) -----	110.6
Estersil (17% toluene dispersion as described in U.S. Patent 2,657,149) -----	100.2
Toluene -----	26.0

was mixed (35.3% solids) and agitated in a ball-mill apparatus for 72 hours. Polyethylene terephthalate film (0.5 mil in thickness) was coated with this mixture and air-dried at room temperature. The coated film was cured in an oven at 150° C. for 10 minutes.

EXAMPLE 3

The following formulation:

	Parts
"Glyptal" 2502 (60% solvent solution-glyceryl phthalate having high hydroxy content—General Electric Company) -----	110.6
Toluene -----	109
"Cab-O-Sil" (finely divided silica—Godfrey L. Cabot, Inc.) -----	27

was mixed (37.7% solids) and agitated in a ball-mill apparatus for 168 hours. This mixture was applied to 0.5 mil thick polyethylene terephthalate film and the film was air-dried at room temperature. The coated film was then cured in an oven at 150° C. for 10 minutes.

EXAMPLE 4

The following formulation:

	Parts
"Epon" (epoxide resin—Shell Chemical Company) -	40
Estersil (as described in U.S. Patent 2,657,149) ---	10
Toluene -----	100
Methyl ethyl ketone -----	100

was mixed (20% solids) and agitated in a ball-mill apparatus for 240 hours. Polyethylene terephthalate film (0.5 mil in thickness) was coated with this mixture and air-dried at room temperature. The coated film was cured in an oven at 150° C. for 10 minutes.

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was mixed (37.7%) and agitated in a ball-mill apparatus for 168 hours. This mixture was applied to 1.5 mil thick polyethylene film and the film was air-dried at room temperature. The coated film was then cured in an oven at 75° C. for 20 minutes.

Table I, below, records the corona life of the coatings described in Examples 1-5, inclusive. The fifth failure in 10 samples was taken as representative of possible corona life. Also listed are overall thickness (gauge) of the coated film and the temperature at which the corona life of the film was tested. All of the films listed under Examples 1-5, inclusive, were coated on both sides of the film. The coated films, as described in Table I, were subjected to the dielectric life test as described below.

Dielectric life test

The film sample to be tested was placed on a brass plate to which the high voltage was to be applied. A brass rod (6" long and 1/4" in diameter) was placed on top of the film sample and normal to the brass plate (the film sample was sandwiched between the brass plate and an end of the brass rod). The rod served as the ground electrode. The end of the rod touching the film sample was rounded off at a radius of curvature of 1/16". The pressure exerted on the film was due only to the gravitational forces on the rod. The entire test apparatus was set up in air. Sufficient voltage was applied to the plate to give a voltage stress of 1,000 volts per mil across the sample. Failure of the sample was indicated by a rapid increase in the flow of current between the brass plate and brass rod. At the moment current flowed, an arc was struck between the electrodes, the arc passing through the hole in the film caused by the failure. The abrupt increase in the flow of current was used to trip a relay giving a record of the failure. Ten samples were treated simultaneously. The time to the failure of the fifth sample was used as a measure of the dielectric life (under corona discharge conditions) of the material tested. As employed herein, "dielectric life" of a polymeric thermoplastic film applies to the actual time that a particular film may be subjected to a particular voltage stress under conditions of corona discharge before actual physical breakdown, i.e., rupture, of the film dielectric.

TABLE I

Dielectric life (corona resistance) of polyethylene terephthalate and polyethylene film coated with resin/finely divided particles composition at 23° C.

Example No.	Coating	Wt. Ratio of Components	Overall Gauge (Thickness) (Mils)	Ball Mill Time (Hours)	Dielectric Life at 1,000 Volts/Mil (Time to fifth failure of 10 samples) (Hours)
PART I—0.5 MIL POLYETHYLENE TEREPHTHALATE FILM					
Control	None		0.5		7.5
1	"Super-Beckacite" 1003/Estersil 2	80/20	0.84	168	36
2	"Glyptal" 2502 3/Estersil 2	80/20	1.04	72	162
3	"Glyptal" 2502 3/"Cab-O-Sil" 4	70/30	1.28	168	51
4	"Epon" 1009 5/Estersil 2	80/20	1.67	240	>94
PART II—1.5 MIL POLYETHYLENE FILM					
5	"Glyptal" 2502 3/"Cab-O-Sil" 4	70/30	2.14	168	>155
Control	No Coating		1.5		25

1 "Super-Beckacite" 1003—phenol-formaldehyde resin—Reichold Chemical Co.

2 Estersil—described in U.S. Patent 2,657,149.

3 "Glyptal" 2502—alkyd resin—General Electric Company.

4 "Cab-O-Sil"—finely divided silica—G. L. Cabot, Inc.

5 "Epon"—epoxide resin—Shell Chemical Company.

EXAMPLE 5

The following formulation:

	Parts
"Glyptal" 2502 (60% solvent solution-glyceryl phthalate having high hydroxy content—General Electric Company) -----	110.6
Toluene -----	109
"Cab-O-Sil" (finely divided silica—Godfrey L. Cabot, Inc.) -----	27

As can be seen from the table above, the use of coatings composed of phenol-formaldehyde, alkyd and epoxide resins in combination with a finely divided silica filler, has substantially increased the corona life at 1,000 volts/mil. These coatings extend the usefulness of polyethylene terephthalate, polyethylene and high-density polyethylene and like thermoplastic film dielectric to a variety of end uses, particularly useful in equipment subjected to high voltage stresses.

I claim:

1. An electrical insulating material comprising a polymeric thermoplastic dielectric base film having an adherent continuous coating consisting essentially of from 95% to 40% by weight of (A) a cured resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, (2), alkyd resins resulting from the inter-reaction of a polybasic carboxylic acid and a polyhydric alcohol (3) long chain fatty acid-modified alkyd resins, and (4) the condensation product of epichlorohydrin and bis p,p'-hydroxyphenyldimethylmethane and from 5% to 60% by weight of (B) finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 millimicrons and 5 microns.

2. The product of claim 1 wherein the base film is polyethylene terephthalate film.

3. The product of claim 1 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

4. An electrical insulating material comprising polyethylene terephthalate base film having an adherent, continuous coating consisting essentially of from 95% to 40% by weight of a cured, phenol-formaldehyde resin and from 5% to 60% by weight of finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 millimicrons and 5 microns.

5. The product of claim 4 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

6. An electrical insulating material comprising polyethylene terephthalate base film having an adherent, continuous coating consisting essentially of from 95% to 40% by weight of a cured alkyd resin resulting from the inter-reaction of a polybasic carboxylic acid and a polyhydric alcohol and from 5% to 60% by weight of finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 millimicrons and 5 microns.

7. The product of claim 6 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

8. An electrical insulating material comprising polyethylene terephthalate base film having an adherent, continuous coating consisting essentially of from 95% to 40% by weight of a cured higher fatty acid-modified alkyd resin of a polybasic carboxylic acid and a polyhydric alcohol, and from 5% to 60% by weight of finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 millimicrons and 5 microns.

9. The product of claim 8 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

10. An electrical insulating material comprising polyethylene terephthalate base film having an adherent, continuous coating consisting essentially of from 95% to 40% by weight of the cured condensation product of epichlorohydrin and bis p,p'-hydroxyphenyldimethylmethane, and from 5% to 60% by weight of finely divided particles from the group consisting of amorphous silica and estersils, said particles having an ultimate average particle size between 5 millimicrons and 5 microns.

11. The product of claim 10 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

12. A process for coating non-fibrous polyethylene terephthalate film which comprises applying to said film a dispersion in a solvent of 10-60% solids, said solids consisting essentially of from 95% to 40% by weight of (A) a cured resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, (2) alkyd resins resulting from the inter-reaction of a polybasic carboxylic acid and a polyhydric alcohol, (3) long chain fatty acid-modified alkyd resins, and (4) the condensation product of epichlorohydrin and bis p,p'-hydroxyphenyldimethylmethane and from 5% to 60% by weight of (B) finely divided particles from the group consisting of amorphous silica and estersils, said particle size between 5 millimicrons and 5 microns; driving off said solvent to dry the coated film; and curing the coated film.

13. A process as in claim 12 wherein the base film is balanced, heat-set, polyethylene terephthalate film.

14. A process as in claim 12 wherein said cured resinous compound is a phenol-formaldehyde resin.

15. A process as in claim 12 wherein said cured resinous compound is an alkyd resin resulting from the inter-reaction of a polybasic carboxylic acid and a polyhydric alcohol.

16. A process as in claim 12 wherein said cured resinous compound is a long chain fatty acid-modified alkyd resin.

17. A process as in claim 12 wherein said cured resinous compound is a condensation product of epichlorohydrin and bis p,p'-hydroxyphenyldimethylmethane.

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