

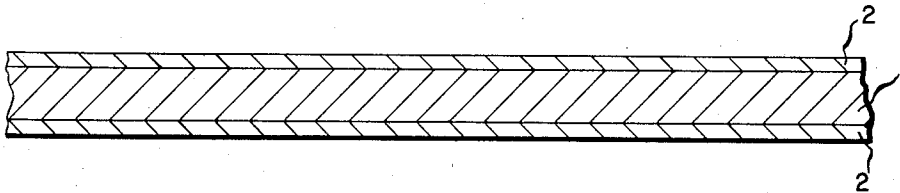
Jan. 20, 1959

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2,870,044

COATED POLYMERIC THERMOPLASTIC DIELECTRIC FILM

Filed March 27, 1956



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COATED POLYMERIC THERMOPLASTIC DIELECTRIC FILM

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Application March 27, 1956, Serial No. 574,082

6 Claims. (Cl. 117—138.8)

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. This 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 polymeric 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.

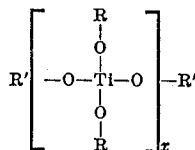
It is the action upon the polymeric film dielectric of corona discharge (in air or other gaseous medium) which causes actual physical breakdown of the film under conditions of a particular voltage stress (a potential difference large enough to produce a visible discharge but not large enough to produce 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 not entirely excluded from the space

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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, cured coating consisting essentially of from 80 to 20% by weight, based on the total weight of solids, of (A) a resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, and (2) alkyd resins prepared from the inter-reaction of a polybasic carboxylic acid, a polyhydric alcohol, and at least 35% by weight, based on the total weight of reactants, of at least one member of the group consisting of fatty acids containing at least 8 carbon atoms and fatty oils, said alkyd resin having an unreacted hydroxyl content of at least 3% based on the weight of the polyhydric alcohol, and from 20 to 80% of (B) a titanium organic compound having the formula:



where R is a member of the group consisting of alkyl radicals and acyl radicals of the formula R'C=O, where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10.

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.

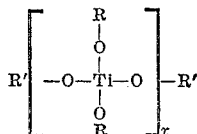
All phenol-formaldehyde resins, e. g., both heat-reactive and non-heat-reactive resins (i. e., thermosetting resins and non-thermosetting resins) and both oil-reactive and non-oil-reactive resins, are operative for purposes of this invention. The term "phenol" includes, besides phenol itself, phenol derivatives such as cresol, p-phenyl phenol, xlenol, ethyl phenols, salicylic acid, resorcinol, and chlorinated phenols. Probably, the phenolic resin should contain 50% or more of a drying oil, the latter

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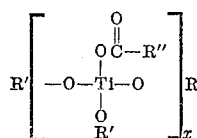
being effective to prevent crazing and to prolong the life of the coating against mechanical failure.

The alkyd resins used in the coating compositions of the present invention may be prepared in known manner by inter-reacting a polycarboxylic acid or the anhydride thereof, having from 2-3 carboxyl radicals per molecule, e. g., phthalic anhydride, with a polyhydric alcohol having from 3-4 hydroxyl radicals per molecule, e. g., glycerol, and at least 35%, and preferably 35-70%, by weight, based on the total weight of reactants, of at least one higher fatty acid, i. e., a fatty acid containing at least 8 carbons, e. g., unsaturated drying oil type fatty acids such as cottonseed oil acid, soya oil acid, or coconut oil acid, or saturated non-drying oil type monocarboxylic acids such as 2-ethylhexoic acid, nonanoic acid, or stearic acid, and/or a fatty oil, either drying or non-drying. A preferred composition as utilized in the process of the present invention is an alkyd resin prepared by reacting phthalic anhydride, glycerine, and an unsaturated drying oil type fatty acid such as soya oil acids.

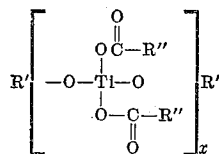
The titanium organic compounds utilized in the compounding of the coating compositions characteristic of the present invention may be classified under the general formula:



where R is a member of the group consisting of alkyl radicals and acyl radicals of the formula $\text{R}''\text{C}=\text{O}$, where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10. Of particular utility are the organic esters of orthotitanic acid (alkyl titanates) having the formula $\text{Ti}(\text{OR}')_4$ wherein R is an alkyl radical containing 1-8 carbon atoms, the products of partially hydrolyzed (condensed) alkyl titanates, and acyl alkyl polytitanates (titanium acylates or carboxylates) obtained by the acylation of orthoesters of titanium through the admixtures and reaction of carboxylic acids and water with a titanium ortho ester, as described in U. S. Patent 2,621,195 in the name of J. H. Haslam. The alkyl alkyl polytitanates have the formulae:



and



where $x=2$ to 10. A preferred composition utilized in the process of the present invention is condensed (partially polymerized) tetrabutyl titanate.

The coating compositions of the present invention may be further modified by the addition of up to 40% by weight of an inorganic filler in the form of fine particles having an average particle size of from 5 millimicrons to 5 microns. The presence of finely divided particles, e. g., finely divided silica particles, helps create an additional barrier against the effects of corona discharge.

The present coating compositions are conveniently applied to thermoplastic polymeric base films from solutions in solvents, said solutions containing, preferably, from 40-60% by weight of 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 a moderately elevated temperature to remove

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solvent. The final step of curing the resin is usually carried out at elevated temperatures, e. g., 100-175° C. for durations from 15-16 minutes, depending upon the nature of the resin employed.

The accompanying drawing is a cross-sectional view illustrative of a typical polymeric thermoplastic-dielectric base film, identified by reference numeral 1 in the drawing, coated on both sides with the coating composition of this invention, indicated in the drawing by the reference numeral 2.

It may be desirable, depending upon the end use for the coated dielectric films of the present invention, to apply subcoatings to the film, e. g., oriented, heat-set polyethylene terephthalate film to improve adhesion between the base film and the resin coating. When applying the subject coating compositions to polyethylene terephthalate film, it is preferred to apply a subcoating which is chemically similar to the base film. Any suitable subcoating may be employed provided that it improves the adhesion between the base film and the present coatings and does not materially adversely affect the original combinations of physical, electrical and chemical properties of the base film. Preferred subcoatings include copolyesters derived by reacting glycol, terephthalic acid or low alkyl ester thereof with a second acid or alkyl ester thereof consisting of sebacic acid, isophthalic acid and hexahydro-terephthalic 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 total weight of acid component. 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 film by lamination over heat and moderate pressure.

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

EXAMPLE 1

Fifty parts of condensed (partially polymerized) tetrabutyl titanate were dissolved in 50 parts of toluene and added to 83.5 parts of a 50% solution of "Glyptal" 2502 (a pentaerythritol phthalate alkyd resin modified with 57% by weight of a soya oil. It has an approximate unreacted hydroxyl content corresponding to 3.7% by weight of pentaerythritol—General Electric Company) in petroleum spirits, and 16 parts of toluene. The mixture was thinned by the addition of 43 parts of toluene. The final mixture had a solids content of 41%. Polyethylene terephthalate film (0.5 mil in thickness) was coated on both sides with this composition and air-dried at room temperature. The coated film was then cured in an oven at 150° C. for 10 minutes.

EXAMPLE 2

Polyethylene film (1.3 mils thick) was coated on both surfaces with a composition identical to that described in Example 1. The coated film was air-dried at room temperature and then cured in an oven at 175° C. for 10 minutes.

EXAMPLE 3

To the coating composition described in Example 1 was added 12.4 parts of estersil (as described in U. S. Patent 2,657,149). The mixture was placed in a ball mill apparatus and was agitated for 20 hours. Polyethylene terephthalate film (0.5 mil thick) was coated on both sides with this composition and air-dried at room temperature. The coated film was then cured in an oven at 150° C. for 10 minutes.

EXAMPLE 4

Eighty-four parts of a 60% solvent (high solvency naphthas) solution of glyceryl phthalate modified with 43% by weight of soya oil and having a content of unreacted hydroxyl corresponding to 5% by weight of

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glycerol; 41 parts of toluene and 100 parts of 50% toluene solution of condensed tetrabutyl titanate were mixed together. The mixture had a solids content of 44.5%. Polyethylene terephthalate film (0.5 mil thick) was coated on both sides with this composition and air-dried at room temperature. The coated film was then cured in an oven at 150° C. for 20 minutes.

EXAMPLE 5

Ninety-one parts of a 55% solvent (high solvency naphthas) solution of glyceryl phthalate modified with 60% by weight of soya oil, 34 parts of toluene and 100 parts of a 50% toluene solution of condensed tetrabutyl titanate were mixed together. The mixture had a solids content of 44.5% solids. Polyethylene terephthalate film (0.5 mil thick) was coated on both sides with this composition and air-dried at room temperature. The coated film was then cured in an oven at 150° C. for 15 minutes.

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on the film was due only to the gravitational forces of 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.

Table I, below, records the corona life of the coatings described in Examples 1-7. The fifth failure in 10 samples was taken as a representative of possible corona life. Also listed is the overall thickness (gauge) of the coated film.

TABLE I.—DIELECTRIC LIFE (CORONA RESISTANCE) OF POLYETHYLENE TEREPHTHALATE AND POLYETHYLENE FILM COATED WITH COPOLYMERS OF TITANIUM ORGANICS AND ALKYD AND/OR PHENOLIC RESINS AT 23° C.

Example No.	Film Type	Coating	Overall Gauge (Thickness in Mils)	Dielectric Life at 1,000 volts/mil (Time to 5th failure of 10 samples, Hrs.)
Control	Polyethylene Terephthalate	None	0.5	10.0
1	do	50/50 Cond. TBT/ ¹ "Glyptal" ² 2502. ³	1.01	193.0
Control	Polyethylene	None	1.3	25.0
2	do	50/50 Cond. TBT/ ¹ "Glyptal" ² 2502.	1.86	212.0
3	Polyethylene Terephthalate	50/50/12 Cond. TBT/ ¹ "Glyptal" ² 2502/Estersil. ³	1.06	125.0
4	do	50/50 Cond. TBT/Soya Oil Modified Alkyd Resin.	1.08	114.0
5	do	do	1.06	113.0
6	do	50/50 Cond. TBT/Fatty Ester Modified Phenolic Varnish.	1.13	172.0
7	do	24/76 Isopropoxy Titanium Oleate/ ¹ "Glyptal" ² 2502.	1.60	45.0

¹ Partially polymerized tetrabutyl titanate.

² High hydroxy-containing alkyd resin—Gen. Elec. Co.

³ Described in U. S. P. No. 2,657,149.

EXAMPLE 6

Sixty-seven parts of a 60% solvent solution of phenolic varnish modified with 66% fatty ester, 80 parts of a 50% solution of toluene condensed tetrabutyl titanate, and 15 parts of toluene were mixed together. The mixture had solids content of 48.6%. Polyethylene terephthalate film (0.5 mil thick) was coated on both sides with this composition and air-dried at room temperature. The coated film was cured at 150° C. for 10 minutes.

EXAMPLE 7

Twenty parts of isopropoxy titanium oleate (isopropoxy oleyl titanate), 64 parts of a 50% solution of "Glyptal" 2502 (a pentaerythritol phthalate alkyd resin modified with 57% by weight of a soya oil. It has an approximate unreacted hydroxyl content corresponding to 3.7% by weight of pentaerythritol—General Electric Company) in petroleum spirits, and 116 parts of xylene were mixed together. The final mixture had a solids content of 42%. Polyethylene terephthalate film (0.5 mil in thickness) was coated with this composition and air-dried at room temperature.

The coated films of the foregoing examples were subjected to the dielectric life test as described below.

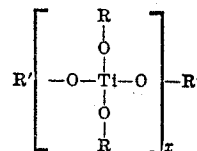
Dielectric life test

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

As can be seen from the table above, the use of coatings composed of organic titanium esters with an alkyd or phenolic resin has substantially increased the corona life of the dielectric base film. These coatings extend the usefulness of polyethylene terephthalate, polyethylene, high-density polyethylene, and like thermoplastic film dielectric to a variety of end uses, particularly for use in equipment subjected to high voltage stresses.

I claim:

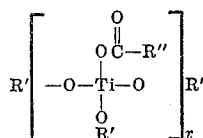
1. A polymeric thermoplastic dielectric base film having an adherent continuous cured coating consisting essentially of (A) a resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, and (2) alkyd resins prepared from the interreaction of a polybasic carboxylic acid and a polyhydric alcohol, and at least 35% by weight, based on the total weight of reactants, of at least one member of the group consisting of fatty acids containing at least 8 carbon atoms and fatty oils, said alkyd resins having an unreacted hydroxyl content corresponding to at least 3% by weight of the polyhydric alcohol, and (B) a titanium organic compound having the formula:



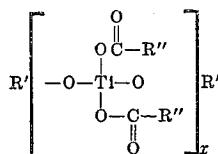
where R is a member of the group consisting of alkyl radicals and acyl radicals of the formula R'C=O, where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10.

2. A product, according to claim 1, wherein the titania

nium organic compound is selected from the group consisting of organic esters of orthotitanic acid having the formula $Ti(OR)_4$, wherein R is an alkyl radical containing from 1 to 8 carbon atoms and alkyl acyl polytitanates of the formulae:

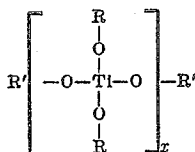


and



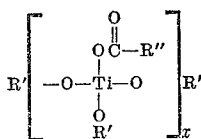
where R' is an alkyl radical containing from 1 to 8 carbon atoms, R'' is an alkyl radical and x is an integer from 2 to 10.

3. Polyethylene terephthalate base film having an adherent continuous cured coating consisting essentially of (A) a resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, and (2) alkyd resins prepared from the interreaction of a polybasic carboxylic acid and a polyhydric alcohol, and at least 35% by weight, based on the total weight of reactants, of at least one member of the group consisting of fatty acids containing at least 8 carbon atoms and fatty oils, said alkyd resins having an unreacted hydroxyl content corresponding to at least 3% by weight of the polyhydric alcohol, and (B) a titanium organic compound having the formulae:

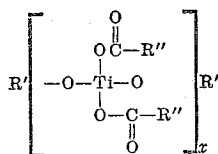


where R is a member of the group consisting of alkyl radicals and acyl radicals of the formula $R''C=O$, where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10.

4. A product, according to claim 3, wherein the titanium organic compound is selected from the group consisting of organic esters of orthotitanic acid having the formula $Ti(OR)_4$, wherein R is an alkyl radical containing from 1 to 8 carbon atoms and alkyl acyl polytitanates of the formulae:



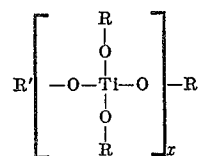
and



where R' is an alkyl radical containing from 1 to 8 carbon atoms, R'' is an alkyl radical and x is an integer from 2 to 10.

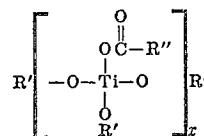
bon atoms, R'' is an alkyl radical and x is an integer from 2 to 10.

5. Balanced, heat-set polyethylene terephthalate base film having an adherent continuous cured coating consisting essentially of (A) a resinous compound selected from the group consisting of (1) phenol-formaldehyde resins, and (2) alkyd resins prepared from the interreaction of a polybasic carboxylic acid and a polyhydric alcohol, and at least 35% by weight, based on the total weight of reactants, of at least one member of the group consisting of fatty acids containing at least 8 carbon atoms and fatty oils, said alkyd resins having an unreacted hydroxyl content corresponding to at least 3% by weight of the polyhydric alcohol, and (B) a titanium organic compound having the formula:

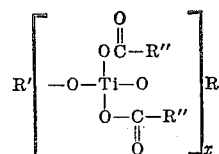


where R is a member of the group consisting of alkyl radicals and acyl radicals of the formula $R''C=O$, where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10.

6. A product, according to claim 5, wherein the titanium organic compound is selected from the group consisting of organic esters of orthotitanic acid having the formula $Ti(OR)_4$, wherein R is an alkyl radical containing from 1 to 8 carbon atoms and alkyl acyl polytitanates of the formulae:



and



where R' is an alkyl radical containing from 1 to 8 carbon atoms, R'' is an alkyl radical and x is an integer from 2 to 10.

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