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2,920,985

COATED POLYMERIC THERMOPLASTIC DIELECTRIC FILM

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No Drawing. Application February 3, 1956
Serial No. 563,192

12 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° C.–175° C.

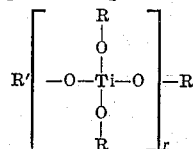
In extending the usefulness of polyethylene terephthalate and like thermoplastic polymeric film dielectric to a wider variety of electrical end uses, it became apparent that the dielectric life of the film required improvement, particularly for use in equipment subjected to high voltage stresses. As 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

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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.

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 low molecular weight polymeric siloxane resin having from 0.05 to 2 silicon-bonded alkoxy radicals per silicon atom, and a titanium organic compound having the formula:



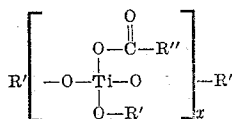
wherein R is a member of the group consisting of alkyl radicals and acyl radicals of the formula $R''C=O$ where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer from 2 to 10, the weight ratio of the siloxane resin to the titanium organic compound ranging from 1/3 to 3/1.

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.

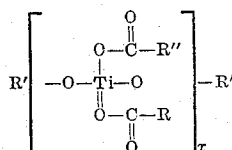
The silicone resins which may be employed in preparing the coating compositions of this invention are those low molecular weight polysiloxanes having 2–50 siloxane Si—O units in the polymer chain. The preparation of these compounds is fully described in U.S.P. 2,584,342 issued to Goodwin and Hunter. These polysiloxanes are prepared by the partial hydrolysis of the silanes of the type R_nSiX_{4-n} where R is a saturated aliphatic radical of less than 7 carbon atoms or a monocyclic aryl radical and X is alkoxy or chlorine and n has a value from 0.9 to 2.1. These partially hydrolyzed polysiloxanes are usually mobile liquids in which the functional groups are alkoxy. These polysiloxanes contain from 0.9 to 2.1 silicon-bonded monovalent hydrocarbon radicals per silicon atom and from 0.05 to 2 silicon-bonded alkoxy radicals per silicon atom, the remaining valences of the silicon being satisfied by oxygen atoms, of an Si—O—Si linkage. A preferred polysiloxane employed in the coating composition of the present invention is dimethyl triphenyl trimethoxy trisiloxane ("Sylkyd" 50—manufactured by the Dow-Corning Corporation). The amount of siloxane resin in the coating may vary from 25% to 75% of the total weight of resin and titanium organic compound, and is preferably within the range of 40–60%.

The titanium organic compounds utilized in the compounding of the coating compositions characteristic of the present invention are preferably either organic esters of orthotitanic acid having a formula $Ti(OR')_4$ where R'

is an alkyl radical containing 1 to 8 carbon atoms, or acyl alkyl polytitanates obtained by the acylation of ortho esters of titanium through the admixtures and reaction of carboxylic acids and water with a titanium ortho ester, as described in U.S.P. 2,621,195 in the name of J. H. Haslam. The alkyl acyl polytitanates have the general formulae:

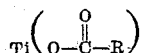


and



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 8. A preferred composition utilized in the process of the present invention is isopropoxy titanium linseed acylate.

The organic esters of orthotitanic acid having the formula $\text{Ti}(\text{OR})_4$ where R is an alkyl radical containing 1 to 8 carbon atoms, may be advantageously plasticized by the addition of organic esters of orthotitanic acid having the formula



wherein an alkyl radical having more than 8 carbon atoms, e.g., tetraoleyl titanate.

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

EXAMPLE 1

Seventy-five parts of dimethyl triphenyl trimethoxy trisiloxane ("Sylkyd" 50)—Dow-Corning, 75 parts of isopropoxy titanium linseed acylate and 2 parts Dow-Corning catalyst XY-24 (a mixture of cobalt and manganese naphthenates and lead octoate) were mixed and coated on polyethylene terephthalate film, air-dried and then heat-set at 150° C. for 30 minutes in an oven. The coated film was tested for corona life at 120° C.

EXAMPLE 2

In a similar manner to that described in Example 1, 75 parts of "Sylkyd" 50, 75 parts of isopropoxy titanium linseed acylate, and 2 parts Dow-Corning catalyst XY-24, were mixed together and coated on polyethylene terephthalate film, air-dried and then heat-set at 150° C. for 30 minutes in an oven. The coated film was tested for corona life at 23° C.

EXAMPLE 3

Seventy-five parts of "Sylkyd" 50, and 75 parts of tetrabutyl titanate were mixed and applied to polyethylene terephthalate film. The film coating was air-dried and then heat-set at 150° C. for 20 minutes. The coated film was tested for corona life at 23° C.

EXAMPLE 4

Sixty parts of "Sylkyd" 50, 60 parts of tetrabutyl titanate and 44 parts of a 50/50 naphtha solution of tetraoleyl titanate were mixed and coated on polyethylene terephthalate film as in the previous examples. The tetraoleyl titanate was included as a plasticizer for the siloxane-titanate copolymer. The film was heat-set at 150° C. for 25 minutes in an oven. The coated film was tested for corona life at 23° C.

EXAMPLE 5

Seventy-five parts of "Sylkyd" 50, 75 parts of isopropoxy titanium linseed acylate, and 2 parts of Dow-

Corning catalyst XY-24 were mixed together and coated on high-density polyethylene film (density 0.960), air-dried, and then heat-set in an oven for 30 minutes at 125° C. The coated film was tested for corona life at 120° C.

EXAMPLE 6

Seventy-five parts of "Sylkyd" 50, 75 parts of isopropoxy titanium linseed acylate, and 2 parts of Dow-Corning catalyst XY-24 were mixed together and coated on high-density polyethylene film (density 0.960), air-dried, and then heat-set in an oven for 30 minutes at 125° C. The coated film was tested for corona life at 23° C.

EXAMPLE 7

Control sample consisting of uncoated oriented, heat-set, polyethylene terephthalate film.

Table I, below, records the corona life of the inorganic coatings described in Examples 1 to 6. The fifth failure in ten samples was taken as representative of possible corona life. Also listed are the overall thickness (gauge) of the coating, and the temperature at which the corona life of the film was tested. All of the films listed under Examples 1 to 6 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 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 material tested.

TABLE I

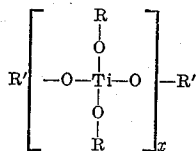
Example	Coating on Polyethylene Terephthalate Film	Overall Thickness (Gauge) of Coating on 0.5 mil Polyethylene Terephthalate Film	Temperature, ° C.	Corona Life at 1,000 volts/mil, 5th failure in 10 samples
1-----	50/50 "Sylkyd" 50/TRLNA.	0.61	120	116
2-----	50/50 "Sylkyd" 50/TRLNA.	0.86	23	165
3-----	50/50 "Sylkyd" 50/TBT.	0.53	23	31
4-----	60/60/12 "Sylkyd" 50/TBT/Tolt.	0.54	23	29
5 ¹ -----	50/50 "Sylkyd" 50/TRLNA.	0.59	120	105
6 ¹ -----	50/50 "Sylkyd" 50/TRLNA.	0.62	23	190
7-----	Polyethylene Terephthalate Film-Control (No Coating) 0.5 mil gauge.	0.00	23	10

"Sylkyd" 50—dimethyl triphenyl trimethoxy siloxane—Dow-Corning.
TRLNA—isopropoxy titanium linseed acylate.
Tolt—tetra oleyl titanate.
TBT—tetra butyl titanate.
¹ Coating on 1 mil high-density polyethylene film.

As can be seen from the table listed above, the use of coatings composed of organic titanium esters or alkyl acyl polytitanates and low molecular weight polysiloxane resins containing at least .05 to 2.1 bonded silicon alkoxy radicals per silicon atom, having substantially increased the corona life at 1,000 volts per mil at both 23° C. and 120° C. These coatings have a main polymer chain which is completely inorganic substituents Si and Ti to prevent too much cross-linking which would cause excessive brittleness. Many of these inorganic compounds have the added advantage of being liquids, and consequently can be mixed and applied as a coating, so that no solvents or fillers are necessary. These coatings extend the usefulness of polyethylene terephthalate, high-density polyethylene, and like thermoplastic film dielectric to a variety of end uses, particularly for use in equipment subjected to high voltage stresses. As employed herein "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.

I claim:

1. A polymeric thermoplastic dielectric substantially non-porous base film having a continuous adherent coating consisting essentially of a mixture of a low molecular weight polymeric siloxane resin having from 0.05 to 2 silicon-bonded alkoxy radicals per silicon atom, and a titanium organic compound having the formula:

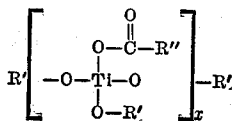


wherein R is a member of the group consisting of alkyl radicals and acyl radicals of the formula $R''C=O$ where R'' is alkyl, R' is an alkyl radical containing from 1 to 8 carbon atoms, and x is an integer of from 2 to 10, the weight ratio of siloxane resin to titanium organic compound ranging from 1/3 to 3/1.

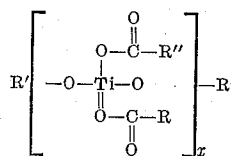
2. The product of claim 1 wherein the base film is polyethylene terephthalate film.

3. The product of claim 1 wherein the base film is heat-set, polyethylene terephthalate film oriented substantially the same degree in both directions.

4. A polymeric thermoplastic dielectric substantially non-porous base film having a continuous adherent coating consisting essentially of a mixture of a low molecular weight polymeric siloxane resin having from 0.05 to 2 silicon-bonded alkoxy radicals per silicon atom, and a titanium organic compound selected from the group consisting of esters of orthotitanic acid having the formula $Ti(OR)_4$ wherein R is an alkyl radical containing 1 to 8 carbon atoms, and acyl alkyl polytitanates of the formulae:



and



wherein R' is an alkyl radical containing from 1 to 8 carbon atoms, R'' is alkyl, and x is an integer from 2 to 8, the weight ratio of siloxane resin to titanium organic compound ranging from 1/3 to 3/1.

5. The product of claim 4 wherein the base film is polyethylene terephthalate film.

6. The product of claim 4 wherein the base film is heat-set polyethylene terephthalate film oriented substantially the same degree in both directions.

7. Substantially non-porous polyethylene terephthalate film having a continuous adherent coating consisting essentially of a mixture of dimethyl triphenyl trimethoxy trisiloxane and tetrabutyl titanate, the weight ratio of trisiloxane to titanate ranging from 1/3 to 3/1.

8. The product of claim 7 wherein the tetrabutyl titanate is plasticized with tetraoleyl titanate.

9. Heat-set polyethylene terephthalate film oriented substantially the same degree in both directions having a continuous adherent coating consisting essentially of a mixture of dimethyl triphenyl trimethoxy trisiloxane and tetrabutyl titanate, the weight ratio of trisiloxane to titanate ranging from 1/3 to 3/1.

10. The product of claim 9 wherein the tetrabutyl titanate is plasticized with tetra oleyl titanate.

11. Polyethylene terephthalate film having a continuous adherent coating consisting essentially of a mixture of dimethyl triphenyl trimethoxytrisiloxane and isopropoxy titanium linseed acylate, the weight ratio of trisiloxane to linseed acylate ranging from 1/3 to 3/1.

12. Heat-set polyethylene terephthalate film oriented substantially the same degree in both directions having a continuous adherent coating consisting essentially of a mixture of dimethyl triphenyl trimethoxy trisiloxane and isopropoxy titanium linseed acylate, the weight ratio of trisiloxane to linseed acylate ranging from 1/3 to 3/1.

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UNITED STATES PATENT OFFICE
Certificate of Correction

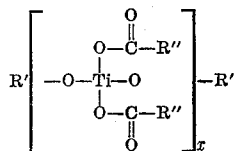
Patent No. 2,920,985

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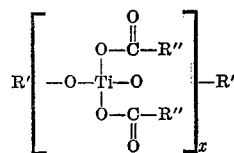
Richard Thomas McBride

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 14 to 19, the formula should appear as shown below instead of as in the patent:



line 33, after "wherein" insert —R is—; column 6, lines 2 to 7, claim 4, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 26th day of July 1960.

[SEAL]

Attest:

KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.