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POLYTETRAFLUOROETHYLENE COATING COMPOSITIONS, METHOD OF APPLICATION TO SUBSTRATES, COATED SUBSTRATES, AND FILMS

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18 Claims. (Cl. 117—103)

This invention relates to coating compositions, more particularly to liquid modified polytetrafluoroethylene coating compositions which yield relatively thick crack-free films and still more particularly to substrates coated with such compositions.

This application is a continuation-in-part of my earlier application, Serial No. 253,011, filed October 24, 1951, now abandoned.

A customary and convenient form of liquid polytetrafluoroethylene coating composition is a dispersion of colloidal polytetrafluoroethylene in water as disclosed in U. S. Patent 2,478,229 to Berry and U. S. Patent 2,534,058 to Renfrew.

It has long been known that polytetrafluoroethylene films which are deposited on a substrate by a single application of an aqueous suspension of polytetrafluoroethylene tends to develop cracks during the drying and baking steps when the dry film thickness exceeds the order of 1 to 2.5 mils depending upon the particular lot of aqueous polytetrafluoroethylene suspensoid used. Each different lot of suspensoid possesses its own "critical cracking thickness" value which is the dry film thickness above which objectionable cracks develop during drying and/or fusing. The cracks formed during drying of the polytetrafluoroethylene aqueous suspensoid vary in size from unmagnified visual cracks to microscopic cracks. This cracking tends to develop not only in films of uniform thickness greater than about 1 to 2.5 mils but also where such a film thickness occurs accidentally because of poor control in application or because of the shape of the object being coated. Such cracks not only adversely affect the appearance of the article but they lead to premature failure of the coating.

For certain purposes, particularly in the coating of woven glass fabrics and various metals, it is necessary or desirable to have polytetrafluoroethylene films greater than 1.5 mils thick and sometimes even as high as 5 to 10 mils thick. Under very closely controlled conditions, relatively thick crack-free polytetrafluoroethylene films can be built up on a substrate by applying several consecutive thin coats of an aqueous suspension, i. e., of the order of .5 mil or less, each followed by a separate baking or fusing operation after each coat. It is obvious, however, that this method is laborious, cumbersome and costly; and, furthermore, it does not eliminate the need for extreme care in avoiding heavy beads or fatty edges when coating irregularly shaped surfaces.

U. S. Patent 2,539,329 which issued January 23, 1951, to P. F. Sanders discloses a mechanical method of eliminating cracks in polytetrafluoroethylene coatings applied from an aqueous suspension to inorganic fabrics, such as, e. g. woven glass fabrics by calendering, but it is obvious that such a process involves an additional manufacturing operation which increases the cost. Further, the pressure treatment required to close the cracks tends to crush and break at least some of the glass filaments of the woven glass fabric which reduces the tensile strength.

The principal object of this invention is to increase the

"critical cracking thickness" of a film deposiited from a single coat of an aqueous polytetrafluoroethylene coating composition.

Another object of this invention is to provide modified aqueous polytetrafluorcethylene coating compositions which yield in one coat crack-free films substantially thicker than those obtainable with polytetrafluoroethylene alone in one coat.

A further object is to provide liquid modified polytetrafluoroethylene coating compositions which do not crack when applied at dry film thicknesses above the order of 1 to 2.5 mils, this thickness being representative of dry film thickness at which films of polytetrafluoroethylene alone can be expected to crack when applied in a single coat.

A still further object is to provide a liquid modified poyltetrafluoroethylene coating composition which can be applied to a substrate in one coat to yield dry crack free protective coating which is substantially thicker than the thickest dry crack-free film capable of being produced by a particular aqueous polytetrafluoroethylene suspension, the "critical cracking thickness" of which is to be improved.

A still further object is to provide a substrate with thick crack-free modified polytetrafluoroethylene coatings.

A still further object is to provide a relatively thick crack-free unsupported film of modified polytetrafluoroethylene.

A still further object is the provision of a polytetrafluoroethylene coating composition with improved adhesion to metal.

These objects are accomplished by incorporating into an aqueous dispersion of colloidal polytetrafluoroethylene a substantial amount of an aqueous solution of an alkali metal silicate and applying the resulting composition to a substrate.

Any aqueous solution of an alkali metal silicate may be used to blend with the polytetrafluoroethylene aqueous dispersion. The molar ratio of the alkali metal oxide to SiO_2 in the silicate solutions may vary over a wide range, e. g. from 1:1 to 1:4 or higher as long as the silicates are water soluble. Silicate solutions having such widely varying ratios are commercially available.

The term "critical cracking thickness" as used throughout the specification and claims means the dry film thickness above which cracks develop in a film deposited from one coat of an aqueous dispersion of polytetrafluoroethylene. Throughout the specification and claims the terms "dispersion," "suspensoid" and "suspension" are used synonymously to denote a composition which contains discrete particles distributed uniformly throughout a liquid medium. The term "crack" means a linear rupture or fissure which extends from the outer surface of a film partially or completely through the film to the substrate beneath, such fissure being at least large enough to be visible to the naked eye or when magnified one hundred times under good illumination. The terms "crack-free" and "free of cracks" mean that the film in question contains an average of not more than one of the above defined cracks for each 100 sq. centimeters of film surface area.

A method of determining the critical cracking thickness of a polytetrafluoroethylene suspensoid consists of (1) pouring an aqueous suspensoid of polytetrafluoroethylene in a container having a slightly tilted bottom in an amount that when the water is evaporated the thickness of the dry film at one end of the pan will be about .1 mil thick and about 10 mils thick at the opposite end, (2) drying the film at about 100° C. until substantially all of the water has evaporated, (3) baking or fusing at the required temperature and (4) examining the coating by the naked eye, or under magnification if necessary, to determine the greatest thickness at which no cracks are present.

In a copending application, Serial No. 241,170, filed August 9, 1951, now U. S. Patent 2,681,324, there is disclosed a method of improving the critical cracking thickness of aqueous polytetrafluoroethylene compositions by incorporating organic polymeric materials which are film forming and produce crack-free films thicker than the thickest film capable of being produced from an aqueous suspensoid of the polytetrafluoroethylene. The invention described in this application differs from the earlier one mentioned above in that the modifying material for the polytetrafluoroethylene is an aqueous solution of an alkali metal silicate.

The following detailed description is given by way of illustration and not limitation. The parts and percentages are on a weight basis.

EXAMPLE I

	Per cent by wt.	
Aqueous polytetrafluoroethylene suspensoid:		
Polytetrafluoroethylene	46.0	
Octyl phenyl polyglycol ether	2.8	91.0
Water	51.2	
37.6% aqueous solution of sodium silicate		9.0
		100.0

The 37.6% sodium silicate solution contained 10.6% Na_2O and 27.0% SiO_2, which is equivalent to a molar ratio (Na_2O to SiO_2) of 1 to 2.5.

The above composition was prepared by adding the sodium silicate solution to the polytetrafluoroethylene suspensoid with moderate stirring. The above composition was cast into a film on a chromium plate at room temperature, dried at 230° F. and fused by heating above the fusion temperature of polytetrafluoroethylene which corresponds to 621° F. A crack-free film was formed which was approximately 2.5 mils thick. The film was cold drawn to a thickness of 1 mil. The tensile strength of a sample 1"x.001"x¼" registered 2.5 lbs. on a Scott tester which is equivalent to 10,000 lbs. per sq. inch of cross-sectional area. The dielectric strength of the drawn film corresponded to 2500 volts per mil.

EXAMPLE II

A crack-free film was prepared from a composition similar to that described in Example I by casting a film on a polished chromium plate followed by drying at about 230° F. and then heating above 621° F. to fuse the polytetrafluoroethylene. A second coat was cast on the fused film attached to the chromium plate, followed by drying and fusing under the same conditions. The fused film was stripped from the chromium plate. It had a milky appearance, was free of cracks and had an average thickness of 6.2 mils.

The dielectric strength of the fused film as stripped from the chromium plate was 500 volts per mil of thickness. After cold drawing the film to three times its original length to a thickness of approximately 2 mils the average dielectric strength was increased to 1120 volts per mil.

EXAMPLE III

The unstretched fused film of Example II as stripped from the chromium plate was subjected to hot working or rolling by passing between heated (270° F.) even speed calender rolls, twice in one direction and then twice in the opposite direction.

The calendering or rolling operation reduced the average thickness of the film from 6.2 mils to 3.1 mils and the average dielectric strength was increased from 500 volts per mil to 1190 volts per mil.

EXAMPLE IV

A standard square-weave glass fabric, identified as

Owens-Corning Fiberglas Corporation's ECC–112 and having the following specification:

Mil thickness	3.0
Yarn size	450½
Thread count	40 x 39
Ounces per sq. yd	2.09

was given three dip coats of the following dispersion:

	Per cent by wt.
Polytetrafluoroethylene	46.0
Octylphenyl polyglycol ether	2.8
Water	51.2
	100.0

The coated fabric was dried by passing through a heated tower in which the air temperature was about 250–300° F. The thickness of the dry coated glass fabric at this stage was approximately 4.7 mils and there were microscopic cracks in the coating. The cracked coating was calendered to close the cracks and then subjected to an air temperature of 700–800° F. to sinter the coating. The coated fabric was further coated by dipping in the sodium silicate-polytetrafluoroethylene composition of Example I and then dried and fused by subjecting to an air temperature of 700–800° F. There were no cracks in the dried sodium silicate-polytetrafluoroethylene coating. The dry thickness after the second composition was applied corresponded to 6.7 mils.

In this example it is preferred to coat the glass fabric with unmodified polytetrafluoroethylene before coating with the aqueous sodium silicate containing composition, since the latter has a solvent action on the glass filaments.

The dry film pick-up of the second composition amounted to 2 mils thickness, i. e., approximately 1 mil on each side. In another experiment in which the second composition was the same as the first, i. e., an unmodified aqueous suspensoid of polytetrafluoroethylene, the pick-up of the dry film was only .2 mil or .1 mil on each side and after drying there were cracks in the surface of the coating.

The polytetrafluoroethylene-sodium silicate coated glass fabric sample of this example was divided into four portions designated A, B, C and D. The A sample was not processed further and served as the control. The B sample was given a heat and pressure treatment by passing it four times between heated (270° F.) smooth, even speed, calender rolls under pressure. Sample C was calendered between unheated uneven speed steel rolls operating under pressure, such as used for milling rubber. Sample D was cold worked on both sides by scraping each side with a knife blade while the sample was supported on a hard smooth surface. After the mechanical surface treatment of samples B, C and D they were rendered more transparent. Each sample was then tested for dielectric strength with the following results:

Table I

Sample	Mils Thickness	Dielectric Strength—Volts/Mil		
		Average	Maximum	Minimum
A	7.3	517	702	432
B	6.5	597	771	483
C	6.5	1,103	1,292	953
D	6.7	950	1,088	811

The above data indicate that hot or cold working of the coating increases the dielectric strength.

The coated glass fabric sample of this example showed no loss in weight after soaking three weeks in water. The coating was not affected in any manner as a result of the three week water soak. This was surprising since the sodium silicate introduced into the coating composition is water sensitive.

EXAMPLE V

A crack-free unsupported film 4.0 mils thick was prepared from the following composition in a single coat:

	Per cent by wt.	
Aqueous polytetrafluoroethylene suspensoid:		
Polytetrafluoroethylene	46.0	
Octyl phenyl polyglycol ether	2.8	65.0
Water	51.2	
37.6% aqueous solution of sodium silicate		35.0
		100.0

The above composition was thoroughly mixed and cast on a chromium plate. The film was dried at 230° F. and then further heated to at least 621° F. to sinter or fuse the film. The dry film was stripped from the chromium plate. It was milky-white and was rendered more transparent when the surface was cold worked by scraping with a knife blade when supported by a hard surface.

EXAMPLE VI

A crack-free unsupported film 3.0 mils thick was prepared from the following composition in a single coat:

	Per cent by wt.	
Aqueous polytetrafluoroethylene suspensoid:		
Polytetrafluoroethylene	46.5	
Octyl phenyl polyglycol ether	2.8	90
Water	50.7	
29.1% aqueous solution of potassium silicate		10
		100

The 29.1% potassium silicate solution contained 20.8% SiO_2 and 8.3% K_2O. The above composition was thoroughly mixed and cast on a chromium plate. The film was dried at about 200° F. and then further heated to at least 621° F. to sinter or fuse the film. The dry milky-white film was stripped from the chromium plate. It was crack-free, 3.0 mils thick and the dielectric strength was 300 volts per mil thickness. By drawing the film down to 1.5 mils thickness the dielectric strength was increased to 1000 volts per mil thickness. The transparency of the milky-white film was increased by cold rolling.

EXAMPLE VII

Steel and copper panels (4" x 12") were prepared for coating by sanding with #240 sandpaper. Each primer composition illustrated in Table 2 below was sprayed on one-half of the prepared surface of a copper and steel panel and cured for 3 minutes at 750° F.

Table 2

	Composition of Primer						
Ratio of Polytetrafluoroethylene to Potassium Silicate	91/9	83.3/16.7	76.6/23.4	71.4/28.6	66.7/33.3	62.5/37.5	58.8/41.2
60% Polytetrafluoroethylene Suspensoid* percent	82.0	69.0	59.5	52.8	47.2	42.8	39
27% Potassium Silicate Solution** do	18.0	31.0	40.5	47.2	52.8	57.2	61

*The polytetrafluoroethylene suspensoid consisted of 60% of polytetrafluoroethylene, 3% of the sodium salt of a mixture of long chain alcohols, predominantly laurylalcohol and 37% water.

**The potassium silicate solution was a 27% aqueous solution in which the molar ratio of K_2O to SiO_2 was 1 to 3.91, which corresponds to 7.7% K_2O and 19.3% SiO_2 on a weight basis.

Three coats of the following polytetrafluoroethylene suspensoid coating composition were sprayed over the entire surface of each copper and steel panel, coating both the primed and unprimed surface:

	Per cent by wt.
Polytetrafluoroethylene suspensoid (same as used in primer composition)	78.3
Water	8.5
Sodium salt of a mixture of long chain alcohols, predominantly lauryl alcohol	1.9
Non-ionic dispersing agent *	1.3
Toluene	10.0
	100.0

* Polyethylene glycol ether of an alkylated phenol.

Each successive coat of the above composition was cured by heating for 5 minutes at 750° F. The resistance of the cured films to stripping from the copper and steel panels was measured by a Scott tensile tester. The results are recorded below in Table 3.

Table 3

	Pounds Required to Pull a 1" Strip From Panel							
Ratio of Polytetrafluoroethylene to Potassiun Silicate in Primer	(1)	91/9	83.3/16.7	76.6/23.4	71.4/28.6	66.7/33.3	62.5/37.5	58.8/41.2
Copper	<0.5	<0.5	1.0	3.5	3.8	3.3	2.5	2.6
Steel Panel	<0.5	0.5	1.0	3.3	4.5	4.0	2.7	----------

[1] Control no primer.

The examples illustrate blending the aqueous sodium or potassium silicate solutions with the polytetrafluoroethylene. It is to be understood that it is within the scope of this invention to use a mixture of sodium silicate and potassium silicate solutions for modifying the critical cracking thickness of the polytetrafluoroethylene aqueous dispersions.

Additional tests on the coatings and films derived from the compositions of this invention show that the crack-free coatings also possess the desirable properties of coatings derived from polytetrafluoroethylene alone, namely, good electrical properties, chemical and solvent resistance, corrosion resistance, and resistance to the adhesion or sticking of extrinsic substances applied thereto.

In the preferred examples the coatings are applied by dipping the substrate to be coated in the composition or by casting the composition on the surface by well known techniques. In addition, the coatings may be applied by doctor knife, doctor roller, reverse roll doctor, and other well known techniques in the art of coating surfaces with liquid coating compositions. The coatings may be applied to one or both surfaces of the substrate to be coated.

An important advantage of the products of this invention is an economic one. The alkali metal silicate costs but a small fraction of the cost of polytetrafluoroethylene and provides a blending material which does not detract from many of the desirable properties of polytetrafluoroethylene.

Thus it is seen that the problem of cracking of relatively thick polytetrafluoroethylene coatings deposited from aqueous dispersions which heretofore has restricted or prevented the full utilization of polytetrafluoroethylene finishes, has been solved in an unexpected way by modi-

fying the aqueous dispersion of polytetrafluoroethylene with another chemically dissimilar material.

In the examples the ratio of dry sodium or potassium silicate to dry polytetrafluoroethylene varies between about 6 to 94 and 41 to 59. It is to be emphasized that these ratios illustrate the preferred embodiment. In certain applications where film strength is not important, the ratio of silicate to polytetrafluoroethylene may be as high as 50 to 50, and useful products may be produced with less silicate than the preferred ranges.

The polytetrafluoroethylene dispersion and/or the mixture of the silicate solution and polytetrafluoroethylene dispersion may contain modifying agents, such as pigments, dyes, soluble chemical substances, inhibitors, dispersing agents, and other modifiers well known in the coating composition art, to color, stabilize or otherwise modify the chemical or physical properties of the codispersions or the films derived therefrom, provided any such modifying agent employed is innocuous to the composition and its components.

The products of this invention are particularly useful in coating heat resistant surfaces, such as, metals, ceramics, glass fabrics, asbestos fabrics, woven wire fabrics and heat treated polyacrylonitrile fabrics. The compositions of this invention adhere to copper better than the aqueous dispersion of polytetrafluoroethylene alone. The coating compositions of this invention are also useful for coating substrates which have a decomposition temperature below the fusion temperature of polytetrafluoroethylene, such as, cotton, nylon, rayon, and various synthetic resins, in which case the baking temperature must be below the fusion temperature of the substrate.

Specific uses for the products of this invention include, in addition to coated glass fabrics and unsupported films described in the specific examples, anti-sticking coatings for muffin tins or cookie sheets, electrically insulated coatings for wire, spark plugs, condensers and corrosion resistant interior coatings for metal tanks containing corrosive chemical materials.

In coating wire and other metal surfaces with the compositions of this invention, where the maximum adhesion of the coating to metal is desired, the metal surface may be primed with the polytetrafluoroethylene-chromic acid compositions disclosed in U. S. Patent 2,562,117 or the polytetrafluoroethylene-chromic acid-phosphoric acid compositions disclosed in U. S. Patent 2,562,118.

It is apparent that many widely different embodiments of this invention can be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as defined in the appended claims.

I claim:

1. A liquid coating composition comprising an aqueous dispersion of polytetrafluoroethylene and an aqueous solution of at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate, said alkali metal silicate being present in an amount of about 6.0% to 50.0% of the combined weight of polytetrafluoroethylene and said alkali metal silicate, the molar ratio of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

2. The product of claim 1 in which the alkali metal silicate is sodium silicate.

3. The product of claim 1 in which the alkali metal silicate is potassium silicate.

4. A substrate having a surface coating comprising polytetrafluoroethylene and at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate, said alkali metal silicate being present in an amount of about 6.0% to 50.0% of the combined weight of polytetrafluoroethylene and said alkali metal silicate, the molar ratio of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

5. The product of claim 4 in which the substrate is glass fabric.

6. The product of claim 4 in which the substrate is metal.

7. The product of claim 4 in which the substrate is copper.

8. The process of preparing crack-free polytetrafluoroethylene films which comprises blending an aqueous solution of at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate with an aqueous dispersion of polytetrafluoroethylene, spreading the resulting blend in the form of a film on a substrate, heating to remove the aqueous medium, further heating above 621° F. to sinter the film, cooling the sintered film and stripping the sintered film from said substrate, said alkali metal silicate being present in an amount of about 6.0% to 50.0% of the combined weight of polytetrafluoroethylene and said alkali metal silicate, the molar ratio of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

9. The process of claim 8 in which the alkali metal silicate is sodium silicate.

10. The process of claim 8 in which the alkali metal silicate is potassium silicate.

11. The process of preparing crack-free polytetrafluoroethylene coatings on a substrate which comprises blending an aqueous dispersion of polytetrafluoroethylene with an aqueous solution of at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate, applying said blend to a substrate, heating to remove the aqueous medium, further heating above 621° F. to sinter the coating, and cooling the sintered coating, said alkali metal silicate being present in an amount of about 6.0% to about 50.0% of the combined weight of polytetrafluoroethylene and said alkali metal silicate, the molar ratio of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

12. The process of claim 11 in which the alkali metal silicate is sodium silicate.

13. The process of claim 11 in which the alkali metal silicate is potassium silicate.

14. The process of claim 11 in which the substrate is glass fabric.

15. The process of claim 11 in which the substrate is metal.

16. The process of claim 11 in which the substrate is copper.

17. A film comprising polytetrafluoroethylene and uniformly distributed throughout at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate, said alkali metal silicate being present in an amount of about 6.0% to 50.0% of the combined weight of polytetrafluoroethylene and alkali metal silicate, the molar ratio of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

18. The process of preparing crack-free shaped articles which comprises blending an aqueous dispersion of polytetrafluoroethylene with an aqueous solution of at least one water-soluble alkali metal silicate from the group consisting of sodium silicate and potassium silicate, shaping the blend, heating to remove the aqueous medium, further heating to at least 621° F. to sinter the composition and cooling the sintered composition, said alkali metal silicate being present in an amount of about 6.0% to 50.0% of the combined weight of polytetrafluoroethylene and alkali metal silicate, the molar ration of alkali metal oxide to silicon dioxide in the alkali metal silicate being at least 1:1.

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