United States Patent Office

3,083,114
Patented Mar. 26, 1963

3,083,114

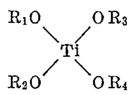
SOLVENT-SOLUBLE WATER-REPELLENCY COMPOSITIONS

Charles Louis Gray, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Dec. 23, 1960, Ser. No. 77,789
6 Claims. (Cl. 106—271)

This invention relates to novel water-repellency agents of the wax and titanate-ester type for textile fiber.

In U.S. Patents Nos. 2,628,170 and 2,628,171 (L. Q. Green) water-repellency agents are described which contain a paraffin wax and a titanium ester, and which are applicable to the fiber from an organic solvent solution (e.g. Stoddard solvent), and are therefore adapted for use in dry-cleaning establishments. The titanate esters suggested for use therein are of the type



wherein the several R's may represent the same or different alkyl radicals, at least some of which may be short-chain radicals, such as isopropyl or butyl, while the remainder may be longer-chain alkyl or aralkyl radicals, such as carnaubyl or benzyl. While paraffin waxes are by themselves usable as water-repellency agents, it has been indicated in said patents that the addition of titanate esters as defined exerts a beneficial influence on the rate of solubility of waxes in organic solvents, while those titanates which bear long-chain alkyl substituents may of themselves contribute to the water-repellency power of the mixture. The use of long-chain esters of titanium would therefore seem to have a special advantege.

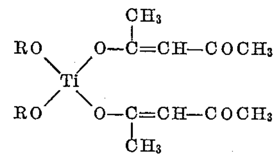
It has been observed, however, that when a fabric has been dry cleaned with anionic or non-ionic detergents (including soap), residual traces of detergent usually remain in the fabric and tend to counteract the subsequent treatment with waxy water-repellency agents, rendering the water-repellency effect weak or unevenly distributed over the fabric.

According to my copending application Serial No. 71,405, filed November 25, 1960, the remedy to the aforegoing problem resides in selecting for the solvent-wax-titanate bath generally defined in said Green patent, U.S.P. 2,628,170, a relatively short-chain alkyl titanate, i.e. one which has no alkyl radicals of more than 8 C-atoms.

More particularly, the titanates most effective for the mentioned purpose are those selected from the group consisting of (*a*) tetraalkyl titanates of 3 to 8 C-atoms in each alkyl radical and (*b*) tetraalkyl titanates as aforementioned in which up to three of said alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula CH_3COCH_2CO—Z, Z being a radical of the group consisting of CH_3, C_2H_5, OCH_3 and OC_2H_5.

The replacement mentioned under (*b*) appears to result from enolization of one of the keto groups of the aceto-acetyl compound, whereupon the enolic compound replaces one, two or three of the OR radicals in the titanate, splitting off the corresponding alcohol ROH, wherein R is an alkyl radical of 3 to 8 C-atoms. For instance, when Z is CH_3, the initial compound is acetyl-

acetone, and the reaction product, if two moles thereof have reacted, will have the formula

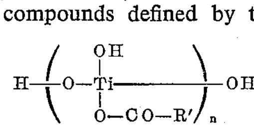


and may be designated dialkyl diacetoacetonyl titanate.

Moreover, the alcohol of formula ROH which splits out in this metathesis, need not be separated from the ester insofar as the objects of this invention are concerned. Accordingly, definition (*b*) above is to be understood as not excluding the presence of such by-product ROH compounds in the mixed titanate esters therein defined.

The above remedy, however, to the principal problem of treating fabric which has been dry cleaned with detergents introduces a new practical problem. The point is that the lower alkyl titanate esters are to a considerable extent sensitive to atmospheric moisture, and therefore, organic solvent solutions containing such lower titanate esters, with or without wax, form a precipitate in a few hours, due to hydrolysis of said esters by atmospheric moisture. It is accordingly a primary object of my present invention to provide means for stabilizing lower aliphatic esters of titanium of the types defined below against rapid hydrolysis by atmospheric humidity. Other objects and advantages of this invention will become apparent as the description proceeds.

Now I have found that lower alkyl titanates of the group above defined can be stabilized against decomposition by atmospheric humidity by incorporating therewith, in quantity of from 0.1 to 0.5 times their own weight, a poly(hydroxytitanium acylate) having not more than on acyl radical per titanium atom, said acyl radical containing from 12 to 18 C-atoms. More particularly, the polyhydroxytitanium acylates usable in this invention are polymeric compounds defined by the formula:



wherein *n* is a variable small integer, greater than one, but probably not exceeding 10, while the radical

—CO—R′

is the acyl radical of a saturated or unsaturated straight-chain aliphatic acid of 12 to 18 C-atoms which is solid at room temperature. Commonly available illustrations of such acids include lauric, palmitic, myristic, stearic and oleic acids.

The polymeric titanate acylates of the above formula are conveniently prepared by first reacting an alkyl titanate such as tetraisopropyl titanate with one mole of the desired aliphatic acid under anhydrous conditions, and then with a controlled amount of water (usually between 2.5 and three moles) to form the product. The displaced alcohol and any excess water are removed by distillation under vacuum. The resulting polyhydroxytitanium acylates are generally stable to water but not soluble in it. They are soluble, however, in most organic solvents including the non-polar types used in dry-cleaning (e.g. hydrocarbons and chlorinated hydrocarbons).

They are also soluble in the lower alkyl titanates of the group above defined. Therefore the mode of incorporation of the one into the other requires no special technique, except to exclude moisture. Stirring of the polymer into the liquid at room temperature or with moderate warming while avoiding contact with the atmosphere, is sufficient.

The quantity of poly(hydroxytitanium acylate) added to the titanate ester may vary from 10 to 50 parts of the former to 100 parts of the latter. In the case of the higher tetraalkyl esters, for instance those which have 5 to 8 C-atoms in each alkyl radical, and with the mixed titanium esters defined in (*b*) under the definition hereinabove, such quantities of the poly(hydroxytitanium acylate) will achieve satisfactory stabilization. By this I mean that a solution of the titanate ester in Stoddard solvent exposed to the atmosphere in an open container will, if unagitated, remain free of precipitate for at least 48 hours.

If desired, further stabilization may be achieved by adding a small quantity (not over 10 parts by weight per 100 parts of titanate) of a 2-lower alkyl-1,3-hexanediol. Such addition, however, may affect the quality of the water-repellency effect produced eventually by the solvent-titanate-wax composition, and should therefore be avoided, if possible. In the case, however, of tetraisopropyl titanate and the replacement ester of this titanate containing only one enolized radical of an aceto-acetyl compound per molecule, the degree of stabilization achieved by the poly(hydroxytitanium acylate) alone does not rate satisfactory (according to the above definition). Consequently, use of quantities of the poly(hydroxytitanium acylate) approaching the maximum and addition of a small quantity of 2-methyl or 2-ethyl-1,3-hexanediol (4 to 5 parts, and in any event not more than 10 parts per 100 parts of titanate) are recommended in these cases.

For ultimate use, the stabilized titanate compositions above defined may be incorporated into a non-polar organic solvent, for instance Stoddard solvent or other liquid aliphatic hydrocarbon, trichloroethylene, tetrachloroethylene, carbon tetrachloride and mixtures of these, following which, the selected waxy compound may be added and the mixture may be warmed to a moderate temperature (75° to 80° C.) to effect dissolution of the wax. The wax may also be added to the solvent first, if desired.

Also, if desired, the titanate and stabilizer need not be compounded separately, but may be individually added to the polar solvent which contains or will ultimately contain the wax.

As waxy substance in this invention may be used any convenient, commercially available wax which melts in the range of 33° to 90° C. and dissolves in the selected non-polar solvent, for instance paraffin wax, beeswax, or a low-molecular hydrocarbon polymer.

A resin hardener, for instance pentaerythritol abietate, may be added if desired, but is without benefit, and in some cases somewhat detrimental to the water-repellency rating obtained.

The treatment bath applied to the fiber in this invention may comprise from 0.18 to 3.0 parts of the stabilized titanium composition, from 0.5 to 6.0 parts of wax, an optional 0.5 part of wax hardener, and sufficient solvent to make up a total of 100 parts by weight. But for best results, a ratio of stabilized titanium ester to wax within the limits of 0.12:1 to 0.7:1 is recommended.

To facilitate use by the ultimate consumer, a concentrated marketable composition may be prepared which contains the titanate, stabilizer, wax and optional additives, if any, in the mutual proportions above indicated but with a diminished quantity of the solvent, to reduce transportation costs. Such a composition may contain for instance from 0.18 to 3.0 parts of the stabilized titanium composition, from 0.5 to 6.0 parts of wax, from 0 to 0.5 part of a wax hardener and from 9 to 45 parts of a non-polar solvent, the ratio of titanium ester to wax being within the range of 0.12:1 to 0.7:1 by weight.

Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

I. PREPARATION OF THE STABILIZER

Example 1

70 parts of tetraisopropyl titanate are dissolved in 78 parts of a hydrocarbon solvent such as cyclohexane, heptane or the like. Then 70 parts of powdered stearic acid are added with stirring and the mixture is heated until the acid dissolves. After cooling, about 100 parts of water are added and the mixture is stirred slowly. The water is drawn off and another 100 parts of water is added and stirred slowly. This is repeated a total of five times. The reaction mixture is then heated under vacuum until the mass reaches 125° C. The resulting product is poly(hydroxytitanium stearate), as a white solid.

Substitution of equivalent molar amounts of lauric, palmitic, myristic or oleic acid for stearic acid in the above procedure, gives the corresponding poly(hydroxytitanium) laurate, palmitate, myristate or oleate, which are also white solids.

II. PREPARATION OF THE STABILIZED ESTER

Example 2

33.3 parts of poly(hydroxytitanium stearate) are entered with stirring, under exclusion of the atmosphere, into an air tight vessel containing 100 parts of tetrabutyl titanate. The resulting solution is stable to hydrolysis by atmospheric moisture for considerable periods but not indefinitely so. It should therefore be transported and stored in sealed containers.

Tetraamyl titanate, tetraoctyl titanate and the like may be substituted for tetrabutyl titanate with equivalent results.

Example 3

200 parts (2 molar equivalents) of acetylacetone are added slowly with stirring under anhydrous conditions to 284 parts of tetraisopropyl titanate. A small amount of heat develops during the addition. The product is an orange-yellow liquid. Propionylacetone, methyl acetoacetate and ethyl acetoacetate give equivalent results.

To 100 parts of the above solution, 33 parts of poly(hydroxytitanium stearate) are added with stirring, under anhydrous conditions. The resulting orange-yellow solution is stable to hydrolysis for extended periods but not indefinitely so. It should best be transported and stored in sealed containers.

III. PREPARATION OF THE SOLVENT BATH AND TREATMENT OF FIBER

Example 4

A solution of 4 parts of paraffin wax (M.P. 62.8° C.) in 80 parts of Stoddard solvent is prepared by adding the wax to the solvent in small pieces with stirring, and warming if desired. Two parts of the titanium composition prepared in Example 2 are then added. If the use of a wax hardener is desired, 0.5 part of pentaerythritol abietate is dissolved in the solution. Then 14 parts of trichlorethylene are added with stirring.

The resulting solution is now ready for application to cotton fabrics to impart water repellency thereto. The solution is stable to hydrolysis by atmospheric moisture for at least 64 hours under normal conditions of use.

Example 5

A solution of 4 parts of paraffin wax (M.P. 62.8° C.) in 80 parts of Stoddard solvent is prepared by adding the wax to the solvent in small pieces as in Example 4. 1.5

parts of the titanium ester reaction mass obtained in the first paragraph of Example 3 are then added, under anhydrous conditions, with stirring. This is followed by 0.5 part of poly(hydroxytitanium stearate). Then 14 parts of trichloroethylene are added with stirring.

The resulting solution is now ready for application to cotton fabrics to impart water repellency thereto. The solution is stable to hydrolysis by atmospheric moisture for at least 64 hours under normal conditions of use.

Example 6

The solvent solutions prepared in Examples 4 and 5 may be applied to fabric according to the following procedure.

The fabric (cloth or garment) is padded in the solvent solution at room temperature and then centrifuged to give a 40% pickup, on the weight of the fabric. The latter is then air dried for 15 minutes, tumble dried for 20 minutes at 60°–180° F., and pressed for 5 seconds in a flat bed press iron heated with 55 lb. steam.

In the tests made in the development of this invention, the fabric samples were cotton poplin, and before being subjected to the aforegoing treatment they were given a dry cleaning with Stoddard solvent containing a commercial, solvent-soluble, nonionic detergent of the alkanolamide type (i.e. a condensation product of a fatty acid with mono- or diethanolamine). The fabrics were rinsed after the dry cleaning under controlled conditions, whereby to leave calculated deposits (up to 1.5% by weight) of the detergent in the fabric. The fabric samples were then air dried, tumble dried at about 160° F., and allowed to stand in the atmosphere for at least one hour.

Following the aforegoing details, the several titanate compositions set forth in the examples below were tested, with the results there indicated. In all tests, the treatment bath consisted of titanium ester and polymeric stabilizer in the quantities indicated, 4 parts of paraffin wax, M.P. 145° F., pentaerythritol abietate or ethyl-hexanediol where indicated, 80 parts of Stoddard solvent, and sufficient trichlorethylene to make a total of 100 parts of solution. The ratings stated in the table, are standard A.A.T.C.C. spray ratings, having the following meanings: 100—excellent (no wetting or sticking to fabric); 90—very good; 80—good; 70—fair; 50—poor; 0—completely wetted.

Stability to atmospheric humidity was measured in each case by placing a sample of the water-repellent solution, contained in a beaker, in a desiccator jar containing warm water. The jar was covered and the air within the jar was allowed to reach 100% relative humidity at a temperature of about 72° F. (i.e. room temperature). The bath life was determined by periodic observations for the first appearance of cloudiness and precipitation. A bath was considered unusable when there was sufficient precipitate developed to cause spotting of the fabric.

Example 7

Ester: Tetrabutyl titanate, 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.5 part
Resin hardener: Pentaerythritol abietate, 0.5 part
Results:
  Initial spray rating: 100
  Bath life: Over 64 hours

Example 8

Ester: Tetrakis(2-ethylhexyl)titanate, 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.5 part
Resin hardener: Pentaerythritol abietate, 0.5 part
Results:
  Initial spray rating: 90
  Bath life: Over 64 hours

Example 9

Ester: Replacement product of 1 mole of tetraisopropyl titanate and 2 moles of acetylacetone, including the isopropyl alcohol which splits off in the reaction, 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.5 part 2-ethyl-1,3-hexanediol, 0.1 part
Resin hardener: Pentaerythritol abietate, 0.5 part
Results:
  Initial spray rating: 100
  Bath life: Over 64 hours

Essentially the same results are obtained if the ester in this example is replaced by one derived from 1 mole of tetraisopropyl titanate and 2.5 or 3 moles of acetylacetone, or from 1 mole of the mentioned titanate and from 2 to 3 moles of propionylacetone.

Example 10

Ester: (Same as in Example 9), 1.125 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.375 part
Resin hardener: (As in Example 9), 0.5 part
Results:
  Initial spray rating: 80
  Bath life: Over 64 hours

Example 11

Ester: (Same as in Example 9), 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.5 part
Results:
  Initial spray rating: 100
  Bath life: Over 64 hours

Example 12

Ester: Replacement product of 1 mole of tetraisopropyl titanate and 2 moles of ethyl acetoacetate, including the isopropyl alcohol which splits off in the reaction, 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.5 part
Resin hardener: Pentaerythritol abietate, 0.5 part
Results:
  Initial spray rating: 100
  Bath life: Over 64 hours

Essentially the same results are obtained if the ester in this example is replaced by the corresponding ester derived from methyl acetoacetate or by using an ester derived from a larger quantity, up to three moles, of either acetoacetate.

Example 13

Ester: Tetraisopropyl titanate, 1.5 parts
Stabilizer: Poly(hydroxytitanium stearate), 0.75 part 2-ethyl-1,3-hexanediol, 0.15 part
Resin hardener: Pentaerythritol abietate, 0.5 part
Results:
  Initial spray rating: 100
  Bath life: Over 69 hours

Similar results are obtained in any of the above examples if the poly(hydroxytitanium stearate) there mentioned is replaced by another long-chain poly(hydroxytitanium acylate), as for instance the oleate, palmitate, margarate or laurate.

It will be understood that the details of the above examples may be varied widely within the skill of those engaged in this art.

In lieu of paraffin wax, indicated generally for use in Examples 4, 5 and 6, may be employed beeswax, petrolatum wax, low molecular-weight polyethylenes, or in general any hydrophobic wax-like material melting within range of 33° to 90° C. From the view point of efficiency and solubility, waxes melting at about 60°–70° C. are preferred.

In lieu of pentaerythritol abietate, any other wax hardener may be employed, for instnace: limed rosin, polymerized terpene resin or polymerized petroleum resin.

Although cotton poplin has been specifically named in the above examples and tests, the novel compositions of this invention are applicable to all sorts of textile materials which have been dry cleaned with detergents, including garments and fabrics made of cotton, viscose rayon, nylon, wool, polyethylene terephthalate and polyacrylonitrile fiber. The detergents that have been used on said textile material may be anionic or non-ionic detergents (such as soap, condensation products of long-chain fatty acids with mono- or diethanolamine, etc.) and the quantity thereof left on the fiber may be as high as 1.5% by weight.

I claim as my invention:

1. A process of imparting water-repellency to textile material whose fibers are contaminated with residual quantities of an organic detergent material from a prior dry cleaning, which comprises treating said material with an organic solvent bath containing a wax, a liquid titanium ester and a stabilizer against atmospheric humidity for the latter, said titanium ester being a liquid composition selected from the group consisting of (*a*) tetraalkyl titanates of 3 to 8 C-atoms in each alkyl radical and (*b*) tetraalkyl titanates as aforementioned in which up to three of said alkyl radicals have been replaced by the enolic radical of an aceto-ethyl compound of the formula

$$CH_3COCH_2CO—Z$$

Z being a radical of the group consisting of CH_3, C_2H_5, OCH_3 and OC_2H_5, and said stabilizer being a solvent-soluble, poly(hydroxytitanium acylate) having one acyl radical per titanium atom said acyl radical being a straight-chain, aliphatic acyl radical of 12 to 18 C-atoms which is solid at room temperature, said titanate ester being present in quantity bearing a ratio of from 0.12:1 to 0.7:1 to the weight of the wax in said solvent bath.

2. A composition of matter comprising as active ingredients essentially 100 parts by weight of a liquid titanium ester and from 10 to 50 parts by weight of a stabilizer for the same against atmospheric humidity, said titanium ester being a liquid composition selected from the group consisting of (*a*) tetraalkyl titanates of 3 to 8 C-atoms in each alkyl radical and (*b*) tetraalkyl titanates as aforementioned in which up to three of said alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula $CH_3COCH_2CO—Z$, Z being a radical of the group consisting of CH_3, C_2H_5, OCH_3 and OC_2H_5, and said stabilizer being a solvent-soluble, poly(hydroxytitanium acylate) having one acyl radical per titanium atom, said acyl radical being a straight-chain aliphatic acyl radical of 12 to 18 C-atoms which is solid at room temperature.

3. A composition of matter as in claim 2, said stabilizer being poly(hydroxytitanium stearate).

4. A marketable concentrate for use in making textile fabric water repellent, consisting essentially of 0.18 to 3.0 parts of a stabilized titanate as defined in claim 2, 0.5 to 6.0 parts of wax, 0 to 0.5 part of a wax hardener, and 9 to 45 parts of a non-polar organic solvent selected from the group consisting of liquid aliphatic hydrocarbons, trichlorethylene, tetrachloroethylene, carbon tetrachloride and mixtures thereof, the ratio of titanate ester to wax being within the range of 0.12:1 to 0.7:1 by weight.

5. A process of imparting water-repellency to textile material whose fibers are contaminated with residual quantities of an organic detergent material from a prior dry cleaning, which comprises treating said textile material with an organic solvent bath containing a wax, a liquid titanium ester selected from the group consisting of (*a*) tetraalkyl titanates of 3 to 8 C-atoms in each alkyl radical and (*b*) tetraalkyl titanates as aforementioned in which up to three of said alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula $CH_3COCH_2CO—Z$, Z being a radical of the group consisting of CH_3, C_2H_5, OCH_3 and OC_2H_5, and a solvent-soluble, poly(hydroxytitanium acylate) having one acyl radical per titanium atom said acyl radical being a straight-chain, aliphatic acyl radical of 12 to 18 C-atoms which is solid at room temperature, said titanate ester being present in quantity bearing a ratio of from 0.12:1 to 0.7:1 to the weight of the wax in said solvent bath, and said poly(hydroxytitanium acylate) being present in quantity corresponding by weight to from 10 to 50 percent by the weight of said titanate ester.

6. A composition of matter adapted for use as an adjuvant to wax-type water-repellency compositions and consisting essentially of a liquid titanium ester and a solvent-soluble poly(hydroxytitanium monoacylate), said titanium ester being a liquid composition selected from the group consisting of (*a*) tetraalkyl titanates of 3 to 8 C-atoms in each alkyl radical and (*b*) tetraalkyl titanates as aforementioned in which up to three of said alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula $CH_3COCH_2CO—Z$, Z being a radical of the group consisting of CH_3, C_2H_5, OCH_3 and OC_2H_5, and the acyl radical of said poly(hydroxytitanium monoacylate) being a straight-chain aliphatic acyl radical of 12 to 18 C-atoms which is solid at room temperature, said poly(hydroxytitanium monoacylate) being present in quantity corresponding by weight to from 10 to 50 percent of the weight of said titanate ester.

References Cited in the file of this patent

UNITED STATES PATENTS

2,628,170 Green ---------------- Feb. 10, 1953