

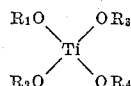
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3,157,661 SOLVENT-SOLUBLE WATER-REPELLENCY COMPOSITIONS CONTAINING WAX, LIQUID TITANIUM ESTER AND STABILIZER

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6 Claims. (Cl. 260-28.5)

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 advantage.

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.

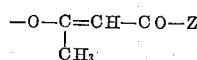
I have now found that when the titanate ester component of the wax and titanate-ester mixture contains only relatively short-chain, aliphatic radicals and is selected from the group defined below, the result is much better, and fabric which has been dry cleaned with detergents may be made water-repellent by such a mixture, to practically the highest initial ratings. Accordingly, the provision of a solvent-soluble water-repellency composition which is capable of being applied with good results to textile material which, as a result of dry cleaning, contains residual detergent deposits in its fiber, may be said to be the primary object of my invention.

On the other hand, it has been known that the lower alkyl titanate esters are to a considerable extent sensitive to atmospheric moisture, and that 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 further object of this 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 the problem defined by said primary object of my invention can be readily solved by

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selecting for the solvent-wax-titanate bath generally defined in said Green patent, U.S. Patent 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 purposes of this invention 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 the O-alkyl radicals have been replaced by the enolic radical

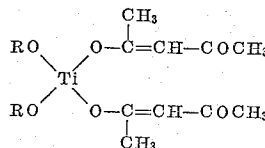


of an aceto-acetyl compound of the formula



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.

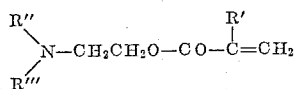
Further details on the metathetical reaction aforementioned may be found in British Patent No. 734,113 or German Patent No. 847,596. The tetraalkyl titanates themselves are well known compounds, and may be exemplified by tetraisopropyl titanate, tetra-n-butyl titanate, tetra-(2-ethylpentyl) titanate and tetra-(2-ethylhexyl) titanate. Any of these may be prepared by reacting the corresponding alcohol of formula ROH with titanium tetrachloride in the presence of ammonia (U.S. Patent 2,187,821).

With the choice of titanium ester as above indicated, I found my invention 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 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.

As for the moisture-sensitivity of the lower titanate alkyl esters, I have found that the titanates hereinabove defined, become considerably stabilized against hydrolysis by atmospheric humidity if a basic acrylate copolymer is added thereto. By this term I mean a copolymer of an alkylaminoethyl acrylate or methacrylate with a neutral acrylic component, and, optionally, a

third olefinic compound, in which the quantity of alkyl-aminoethyl acrylate (or methacrylate) is not less than 10 and not greater than 90% by weight.

The said alkylaminoethyl acrylate may be defined by the formula



wherein R' designates H or CH₃, R'' designates an alkyl radical of 1 to 4 C-atoms, while R''' designates hydrogen or an alkyl radical of 1 to 4 C-atoms. The neutral acrylic component may be an alkyl acrylate or methacrylate in which the alkyl radical may have from 4 to 18 C-atoms, and the optional third olefinic component may be styrene (U.S. Patent 2,737,452, Table VI).

The preparation of such basic acrylic copolymers is described in detail in U.S. Patent 2,737,452 (Catlin and Robbins), and the products prepared there in Examples I, VI, VII and VIII and in Table I may be taken as specific illustrations of the stabilizers particularly suitable for this invention.

The basic copolymers above indicated are soluble in the liquid titanate esters hereinabove defined, especially when some Stoddard solvent or other non-polar solvent is also present. 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 while avoiding contact with the atmosphere, is sufficient.

The quantity of basic acrylic copolymer to be added to the titanate 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 having 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 basic acrylic copolymer 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 and tetrabutyl titanates and the replacement esters of these containing only one enolized radical of an acetoacetyl compound per molecule, the degree of stabilization achieved by the acrylate polymer alone does not rate satisfactory (according to the above definition). Consequently, 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) is positively 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, trichlorethylene, tetrachlorethylene, 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 non-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 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 limits 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 STABILIZED ESTER

Example 1

50 parts of a copolymer prepared from 90 parts of diethylaminoethyl methacrylate and 10 parts of octadecyl methacrylate are entered with stirring, under exclusion of the atmosphere, into an air tight vessel containing 100 parts of tetrabutyl titanate. 10 parts of anhydrous 2-ethyl-1,3-hexanediol are then added with stirring. 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.

Example 2

200 parts of acetylacetone (2 moles) are added slowly with stirring under anhydrous conditions to 284 parts (1 mole) of tetraisopropyl titanate. A small amount of heat develops during the addition. The product is an orange-yellow liquid. Similar results are obtained if the quantity of acetylacetone used in this example is increased up to 300 parts (3 moles), without changing the quantity of the initial titanate. Likewise, replacement of acetylacetone in this example by an equivalent quantity (2 to 3 moles) of propionylacetone, ethyl acetoacetate or methyl acetoacetate gives similar results.

To 100 parts of the above solution, 33 parts of a copolymer prepared from 35 parts of diethylaminoethyl methacrylate and 65 parts of octadecyl methacrylate are added with stirring, under anhydrous conditions. The resulting orange-yellow solution is stable to hydrolysis by atmospheric moisture for extended periods but not indefinitely so. It should best be transported and stored in sealed containers.

II. PREPARATION OF THE SOLVENT BATH AND TREATMENT OF FIBER

Example 3

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 75 hours under normal conditions of use.

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 as in Example 3. 1.5 parts of the titanium ester reaction mass obtained in the first paragraph of Example 2 are then added, under anhydrous conditions, with stirring. This is followed by 0.5 part of a copolymer prepared from 35 parts of diethylaminoethyl methacrylate and 65 parts of octadecyl methacrylate. 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 75 hours under normal conditions of use.

Example 5

The solvent solutions prepared in Examples 3 and 4 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 160°-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 that were to be subjected to the foregoing treatment were cotton poplin, and were first given a dry cleaning with Stoddard solvent containing a commercial, solvent-soluble, nonionic detergent of the alkylamide 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.

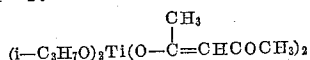
Following the foregoing details, the several titanate compositions set forth in the examples below were tested, with the results there indicated. In all tests, the treatment bath consisted of 1.5 parts of the titanium ester, 0.5 part of polymeric stabilizer, 4 parts of paraffin wax, M.P. 145° F., pentaerythritol 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 6

(a)
Ester: Diisopropyl-diacetoacetonyl-titanate—



Stabilizer: Copolymer of diethylaminoethyl methacrylate (35 parts) and octadecyl methacrylate (65 parts).

Results:

Initial spray rating—100.

Bath life—Over 75 hours.

(b) The same results were obtained when the stabilizer

used was a copolymer of the same two monomers but in the ratio of 90 parts of the amine to 10 parts of the neutral acrylate.

(c) In a similar example, except using a copolymer containing only 20% of the basic acrylate (with the same other component), the results were as follows:

Initial repellency rating—100.

Bath life—75 hours.

(d) In the three instances above, addition of pentaerythritol abietate to the treatment bath (0.5 part per 100 parts total) resulted in an inferior initial rating of the water-repellency. (Dropped to 80 or 90.)

Example 7

15 Ester: Diisopropyl-diacetoacetonyl-titanate.

Stabilizer: Copolymer of tert-butylaminoethyl methacrylate (30 parts) and octadecyl methacrylate (70 parts).

Results:

Initial spray rating—100.

20 Bath life—Over 75 hours.

Addition of pentaerythritol abietate in this case did not affect the initial spray rating.

Example 8

25 Ester: Diisopropyl-diacetoacetonyl-titanate.

Stabilizer: Copolymer of diethylaminoethyl acrylate (31 parts) and octadecyl methacrylate (69 parts).

Results:

Initial spray rating—100.

30 Bath life—Over 75 hours.

Addition of pentaerythritol abietate in this case did not affect the initial spray rating.

Example 9

35 Ester: Tetra-n-butyl titanate.

Stabilizer: Copolymer of diethylaminoethyl methacrylate (90 parts) and octadecyl methacrylate (10 parts).

40 In this case, the treatment bath contained also 0.75 part of 2-ethyl-1,3-hexanediol (0.75 part per 100 parts total).

Results:

Initial spray rating—100.

45 Bath life—Over 75 hours.

Example 10

45 Ester: Tetrakis(2-ethylhexyl) titanate.

Stabilizer: Terpolymer of diethylaminoethyl methacrylate (10 parts), oleyl methacrylate (50 parts) and styrene (40 parts).

50 Results:

Initial spray rating—100.

Bath life—Over 75 hours.

Example 11

55 To 150 parts of the orange-yellow, liquid reaction mass of acetylacetone and tetraisopropyl titanate obtained in the first paragraph of Example 2, are added with stirring, under anhydrous conditions, 50 parts of a 50% kerosene solution of a terpolymer as defined in Example 10.

60 Two parts of the resulting orange-yellow solution and 4 parts of paraffin wax are added with moderate warming to 94 parts of a mixed solvent made up of equal parts of Stoddard solvent and trichlorethylene. The resulting solution has a bath life of over 48 hours. When applied to cotton poplin by padding, centrifuging, drying and pressing as indicated under Example 5, an initial water-repellency rating of 100 is imparted to the fabric.

65 In the same example if the terpolymer is omitted, the bath develops a precipitate within 15 hours.

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

Thus, in lieu of octadecyl methacrylate named as component of the copolymer in Examples 6 to 9, one may

use other neutral acrylates such as butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, dodecyl methacrylate, octadecyl acrylate or oleyl methacrylate.

In lieu of the terpolymer named in Example 10, other terpolymers may be used, for instance the one made up of

Diethylaminoethyl methacrylate (20 parts),
Lauryl methacrylate (50 parts) and
Styrene (30 parts).

(See Table VI in U.S. Patent 2,737,452.)

In lieu of the ester designated in Examples 6, 7 and 8 any other of the replacement products indicated in the first paragraph of Example 2 (including the isopropyl alcohol liberated in the reaction) may be used.

In lieu of paraffin wax, indicated generally for use in Examples 2, 3 and 11, 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 viewpoint 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 instance: limed rosin, polymerized terpene resin or polymerized petroleum resin.

This application is a continuation-in-part of my application Serial No. 69,565, filed November 16, 1960, now abandoned.

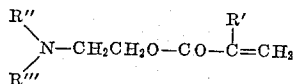
I claim as my invention:

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 a bath consisting essentially of a non-polar organic solvent, a wax, a liquid titanium ester and a stabilizer, said wax being one which melts within the range of 33° to 90° C. and is soluble in non-polar organic solvents, said titanium ester being a compound 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 the O-alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula



Z being a radical of the group consisting of CH_3 , C_2H_5 , OCH_3 and OC_2H_5 , said titanate 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 stabilizer being a basic acrylate copolymer containing neutral acrylic components and basic components selected from the group consisting of alkylaminoethyl acrylates and alkylaminoethyl methacrylates, said stabilizer being present in quantity bearing a ratio of from 0.1:1 to 0.5:1 to the weight of said titanate in the solvent bath.

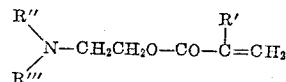
2. A process as in claim 1, said basic acrylate copolymer being a polymer formed from 10 to 90 parts of an alkylaminoethyl acrylate of the formula



wherein R' designates H or CH_3 , R'' designates an alkyl radical of 1 to 4 C-atoms, while R''' is selected from the

group consisting of hydrogen and an alkyl radical of 1 to 4 C-atoms; and from neutral olefinic compounds selected from the group consisting of, neutral alkyl esters of acrylic acid and neutral alkyl esters of methacrylic acid said neutral alkyl ester being present in an amount of from 90 to 10 parts by weight, respectively, of said alkylaminoethyl acrylate.

3. A composition of matter consisting essentially of as active ingredients essentially 100 parts by weight of a liquid titanium ester, and from 5 to 50 parts by weight of a basic acrylate copolymer, 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 the O-alkyl radicals have been replaced by the enolic radical of an aceto-acetyl compound of the formula $\text{CH}_3\text{COCH}_2\text{CO}-\text{Z}$, Z being a radical of the group consisting of CH_3 , C_2H_5 , OCH_3 and OC_2H_5 , and said basic acrylate copolymer being a polymer formed from 10 to 90 parts of an alkylaminoethyl acrylate of the formula



wherein R' designates H or CH_3 , R'' designates an alkyl radical of 1 to 4 C-atoms, while R''' is selected from the group consisting of hydrogen and an alkyl radical of 1 to 4 C-atoms; and neutral olefinic compounds selected from the group consisting of, neutral alkyl esters of acrylic acid and neutral alkyl esters of methacrylic acid said neutral alkyl ester being present in an amount of from 90 to 10 parts by weight, respectively, of said alkylaminoethyl acrylate, said composition of matter being liquid at room temperature, and being readily miscible with non-polar organic solvents containing paraffin wax to produce a water-repellency agent for textile fiber.

4. A marketable concentrate for use in making textile fabric water repellent, consisting essentially of from 0.18 to 3.0 parts of a stabilized titanate as defined in claim 3, from 0.5 to 6.0 parts of wax which melts within the range of 33° to 90° C. and is soluble in non-polar organic solvents, from 0 to 0.5 part of a wax hardener, and from 9 to 45 parts of a non-polar organic solvent selected from the group consisting of liquid aliphatic hydrocarbons, trichlorethylene, tetrachlorethylene, 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 according to claim 2 in which process styrene is utilized in an amount of from 30 to 40 parts by weight of said alkylaminoethyl acrylate.

6. A composition of matter according to claim 3, said composition containing styrene in an amount of from 30 to 40 parts by weight of said alkylaminoethyl acrylate.

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