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COMPOSITION AND METHOD FOR WEATHER-
PROOFING FABRICS

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No Drawing. Filed Sept. 18, 1961, Ser. No. 138,584
4 Claims. (Cl. 260—33.4)

This invention relates to the weatherproofing of fabrics whereby the latter are made resistant to wetting by water. It has particular utility in operations wherein dry-cleaned garments made from a woven fabric are provided with a protective coating which affords a high degree of water-repellency, while at the same time allowing air to pass freely through the fiber interstices.

Basically, the desired results are obtained by treating the fabric with a solution, in an organic solvent, of an alkyl titanate, a critical amount of a glycol, and a vinyl ether polymer.

It is well known in the trade that water repellent garments which have been drycleaned one or more times will have lost substantially all of their original water-repellency. While many compositions are available for restoring this quality, it is necessary to thoroughly remove or otherwise neutralize the residual detergent remaining in the drycleaned garment before such water repellent compositions can be effectively applied. These detergent-removal, pretreating steps are tedious and expensive from a time consumption standpoint. In addition, unless this removal or neutralization step is performed with great care, poor water-repellency is still obtained.

A further disadvantage of many water-repellent compositions now on the market lies in their poor solubility in common drycleaning solvents. This necessitates that the treating bath be used at elevated temperatures to maintain the product in solution, thus introducing both a fume as well as a fire hazard.

In recent years, water repellents have been introduced which are less sensitive to the effect of the residual drycleaning detergents. Many of these are based on combinations of aluminum or titanium esters and various hydrocarbon waxes, as exemplified, for instance in U.S. Pats. Nos. 2,628,170 and 2,628,171. However, considerable detergent sensitivity still remains, so that it is necessary to rinse the drycleaned garments in uncontaminated drycleaning solvent as a special pretreatment prior to application of even these improved water repellents. In addition, they tend to produce a stiff, unwieldy fabric. Moreover, in order to develop their maximum effectiveness, these compositions require that the treated garment be pressed at relatively high temperatures, for example, on a commercial "hot head" press. This results in a still stiffer hand and, in some cases, in actual damage to the garments.

It is, therefore, an object of this invention to provide a novel water-repellent composition adapted to be applied to textiles from organic solvent solution. A more particular object is to provide a composition of this character which can be applied to the textile fabric with good results in either the presence or absence of residual amounts of drycleaning detergent in the fabric material undergoing treatment, the resulting treated product being soft and having excellent water-repellent qualities.

A further object is to provide a water-repellent composition which dissolves readily at room temperatures to form a clear solution in the commonly employed drycleaning solvents, and which retains its life indefinitely except for liquid carry-out, as previously drycleaned

garments containing residual detergent are treated in the solution.

Another object is to provide a composition of the aforesaid character which develops its maximum effectiveness as the treated garments are pressed on a steam press, and which does not require exceptionally high heating during the pressing operation.

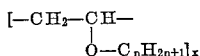
The nature of still other objects of the invention will be apparent from a consideration of the descriptive portion to follow.

We have discovered that the foregoing objects can be achieved by the use of a novel water-repellent composition comprising a long chain, vinyl ether polymer, a tetra-(lower) alkyl titanate and a critical amount, based on the titanate content, of a C_6 - C_9 glycol of the type having at least one secondary hydroxyl group. The water-repellent composition is prepared by dissolving the above components, optionally along with other materials such as hydrocarbon oils and waxes, stearic or other long chain fatty acids, and resins such as polymerized beta-pinene, in an organic solvent or solvent mixture. The conventional practice in carrying out the present invention is to formulate a concentrated solution containing from about 30 to 75% of the solvent, with the latter solution then being diluted with a conventional drycleaning solvent to prepare the final solution with which garments are treated by the drycleaner.

In carrying out the present invention good results have been obtained with compositions containing from about 1 to 4 parts of the titanate ester, from about 2 to 5 parts of the vinyl ether polymer, and from about 0.1 to 0.5 mole of the glycol for each mole of titanate. The lower limit for the glycol varies with the particular titanate ester employed, the purpose of the glycol being to stabilize the ester against hydrolysis. With tetra alkyl titanates wherein the alkyl groups each contain only 3 carbon atoms it may be necessary to use as much as 0.3 mole of the glycol per mole of titanate to effect stabilization, though with esters wherein the alkyl groups contain from 4 to 8 carbon atoms good results are normally obtained with as little as 0.1 mole of the glycol. The factor of stabilization can be readily determined by observing a freshly prepared solution of the composition in an appropriate organic solvent as the solution is allowed to stand for a period of 24 hours at room temperatures. Properly stabilized solutions remain clear for this period, while those containing an insufficient portion of the glycol tend to become cloudy. Simple experimentation thus determines the minimum amount of glycol to be employed, though in no case should the glycol content exceed about 0.5 mole per mole of titanate ester since, as the glycol content exceeds this proportion, the water-repellent qualities of the composition are rapidly lost as garments containing residual detergents are treated therein.

As indicated above, the compositions hereof are formulated using about 1 to 4 parts of the tetra-(lower) alkyl titanate ester, these and other parts expressed herein being on a weight basis. A preferred range is from about 1.5 to 3 parts. The titanate ester is selected from the group consisting of those wherein each alkyl group contains from 3 to 8 carbon atoms, representative compounds being tetraisopropyl titanate, tetra-n-propyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate, diisopropyl-di-n-butyl titanate, tetraamyl titanate, tetra-n-hexyl titanate, tetrakis (2-ethylbutyl) titanate and tetrakis (2 ethylhexyl) titanate. Of these compounds, it is preferred to use tetraisopropyl titanate, a compound which normally requires from about 0.25 to 0.3 mole of glycol per mole of titanate for effective stabilization as the latter is dissolved in an organic solvent.

The composition contains from about 2 to 5 parts, and preferably 2.5 to 4 parts, of a vinyl ether polymer. A preferred polymer is polymerized vinyl octadecyl ether, though good results can be obtained with any polymer having the general formula,



wherein n has a value of from about 12 to 22 and x has a value of at least 5, the upper limit on the value of x being that imposed as a solvent-insoluble product is obtained. In the case of the vinyl octadecyl ether polymer noted above, n has a value of 18 and x has an average value of about 9.

The glycol employed in the composition is one containing from 6 to 9 carbon atoms, and wherein, of the two hydroxyl groups, at least one is secondary in nature. Good results can be obtained, for example, with 2-methyl-2,4-pentanediol, 2,2-dimethyl-1,3-pentanediol and 2-ethyl-1,3-hexanediol. The preferred compound for use in the present invention is 2-methyl-2,4-pentanediol, otherwise known commercially as hexylene glycol.

To the titanate, glycol and ether polymer components of the composition may also be added various of the materials which are presently employed in water-repellent compositions. Thus, the mixture may include a hydrocarbon wax (paraffin or scale) in amounts up to about 50% of the weight of ether polymer employed. Mineral oil, which acts as an extender and plasticizer can be used in amounts up to those substantially equaling the content of ether polymer, and the preferred compositions of this invention contain from 50 to 100% of mineral oil, based on polymer weight. Similarly, the preferred compositions also include from about 10 to 25%, in terms of the weight of ether polymer, of a polymerized bicyclic monoterpene hydrocarbon such as polymerized beta-pinene. It is also possible to add a long chain fatty acid such as stearic acid in amounts up to about 50%, based on the weight of ether polymer. Still other conventional ingredients can also be employed in the composition, if desired.

The composition is normally prepared by dissolving the various components mentioned above in a suitable organic solvent such as carbon tetrachloride, perchlorethylene, trichlorethylene, Stoddard solvent and other petroleum hydrocarbon solvents commonly used in drycleaning. A clear solution can be prepared in most instances using as little as 30% of solvent, though somewhat larger amounts (i.e., 50%) are used in most instances. Solutions of this character hold up well during storage, and while they tend to become turbid during cold weather, they readily become clear on being warmed to room or slightly higher temperatures. The use of the polymerized beta-pinene component in the composition has been found to facilitate clarification of such solutions at temperatures of about 75° F., the pinene also acting to maintain the solution in a clear condition at somewhat lower temperatures than would otherwise be the case.

In using the water-repellent solution in the treatment of either new or drycleaned garments, the fabric is either dipped in or otherwise impregnated with a relatively dilute solution of the product. The extent of dilution will depend somewhat on liquid takeout, or amount of solution retained in the fabric after it has been allowed to hang or has been subjected to a centrifuging step preparatory to being heated at conventional drying temperatures (usually about 140° F.) to remove contained solvent. In general, good results are obtained with solutions containing a total of from about 5 to 20% by weight of the various non-solvent components. We find that from about 1.5 to 10 pounds of solid constituent in the solution will effectively treat 100 pounds of garments, though it is preferred to use from about 2.5 to 5 pounds of solids per 100 pounds of garments.

The examples given below illustrate the practice of the invention in various of its embodiments. The Spray Rat-

ings referred to therein were obtained using Standard Test Method No. 22-1952 of the American Association of Textile Chemists and Colorists (AATCC), the cotton poplin swatches or other fabric garments employed in the tests having been first cleaned in a solvent containing from about 0.5 to 1% of an active detergent. At the end of the cleaning cycle the excess detergent solution was removed by centrifuge extraction and the fabric dried without rinsing or other treatment, the dried fabric so obtained being found to contain from about 0.1 to 0.25% by weight of the active detergent.

In carrying out the operations of the examples, the dry-cleaned fabrics were dipped in a water-repellent solution prepared by first incorporating about 50 parts by weight of the indicated nonsolvent components in 50 parts by weight of solvent (usually 35 parts carbon tetrachloride and 15 parts Stoddard solvent) and then diluting this 50-50 solution with 5 times its volume of solvent. The fabrics dipped in this solution, after being centrifuged or otherwise freed of excess liquid, had a 35% retention of the treating liquid. The resulting fabrics after being dried a few minutes at room temperatures and then for about 30 minutes at 140° F., we found to contain about 3.5% by weight of the various non-volatile components of the particular treating solution employed. In cases where raincoats or other garments were dipped in the treating bath, each was accompanied by a swatch of cotton poplin, and the swatch was thereafter employed in making the Spray Rating determination.

Briefly, the Spray Rating of the treated fabrics was measured by pouring a measured amount of water through a spray head and onto a stretched piece of fabric held at a 45° angle, at a set distance from the spray head. The amount of wetting is compared with a standard chart and rated from 0 for complete wetting of the fabric to 100 for no wetting.

Example 1

In this operation, the fabric was treated with a water-repellent solution prepared as described above, using:

	Parts
Tetraisopropyl titanate	1
Hexylene glycol (0.474 mole/mole of titanate)	0.2
Polymerized octadecyl vinyl ether	2

The treated fabric had a Spray Rating of 100.

Example 2

A mixture was prepared containing 24 lbs. of a polymerized octadecyl vinyl ether, 12 lbs. of white mineral oil, 12 lbs. of tetraisopropyl titanate, 1.8 lbs. hexylene glycol (0.355 mole/mole of titanate), 30.1 lbs. Stoddard solvent and 20.1 lbs. carbon tetrachloride. 1 gallon of this was diluted with 5 gallons of Stoddard solvent. 5 garments and 5 cotton swatches, all of which had been cleaned with a commercial drycleaning detergent and dried, were immersed in the solution. The garments and swatches were then centrifuged to remove excess solution and the excess solution combined with the original solution. The garments and swatches were dried at 140° F. and pressed on a commercial steam press. Both the garments and swatches had Spray Ratings of 100. Seven more sets of garments and swatches were treated in turn in the same manner. All garments and swatches had Spray Ratings of 100 and all had a soft, pleasant hand.

The foregoing operation was repeated, except that here one side of each garment was pressed on a commercial "hot head" press while the other was not pressed. Both sides had a Spray Rating of 100.

Example 3

Two solutions were prepared. One contained 24 lbs. of a polymerized octadecyl vinyl ether, 12 lbs. of white mineral oil, 1.8 lbs. of hexylene glycol (0.355 mole/mole of titanate), 12 lbs. of tetraisopropyl titanate, 35.5 lbs.

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carbon tetrachloride and 14.7 lbs. of Stoddard solvent. The second solution contained 18 lbs. of a polymerized octadecyl vinyl ether, 3 lbs. of a solution containing 65% polymerized B-pinene in Stoddard solvent, 15 lbs. of white mineral oil, 2.2 lbs. hexylene glycol (0.434 mole/mole of titanate), 12 lbs. tetraisopropyl titanate, 35.7 lbs. carbon tetrachloride and 14.1 lbs. Stoddard solvent.

On being cooled, the first solution became turbid at 16.5° C., while the second did not become turbid until 14.5° C. On rewarming, the second solution became clear at room temperature (75° F.), while the first solution did not become clear until 95° F.

One gallon of each solution was diluted with 5 gallons of Stoddard solvent. Garments and swatches, which had been drycleaned, were immersed in these solutions, centrifuged and dried at 140° F. All the garments had a Spray Rating of 100. The swatches were tested for stiffness on a Drape-Flex Stiffness Tester. The swatches treated with the second solution were less stiff than those treated with the first solution (12.8 in. vs. 13.9 in. bending length).

The foregoing data show the improved results which are obtained by incorporating the polymerized beta-pinene in the composition.

Example 4

In this operation, water-repellent solutions were prepared having the same general composition as that (incorporating the polymerized beta-pinene) described above in Example 3, except that here the tetraisopropyl titanate content was held at 6% in one series, at 9% in another, and at 12% in still a third. In each series the content of glycol was varied, as indicated in Table I below. Those compositions marked with an asterisk (*) were unstable due to the use of insufficient glycol. It will be seen that approximately 0.3 mole of glycol per mole of titanate is required to stabilize the latter. Also, poorer Spray Ratings are obtained as the content of glycol approaches or exceeds 0.5 mole per mole of titanate.

TABLE I

6% Titanate		9% Titanate		12% Titanate	
Mole G/ Mole T ¹	Spray Rating	Mole G/ Mole T	Spray Rating	Mole G/ Mole T	Spray Rating
0.237 *	90	0.158 *	100	0.118 *	100
0.472	90	0.316	90-100	0.236 *	100
0.708	70	0.474	90	0.355	100
				0.474	100
				0.592	90-100

¹ Mole G/Mole T = moles of glycol per mole of titanate.

* Indicate solution clouded on standing for 24 hours.

Example 5

The water-repellent solution of Example 3 (containing polymerized beta-pinene and 0.434 mole glycol per mole of titanate) was used to successively treat 20 garments totaling 40 lbs. in weight. The Spray Rating of each garment was 100. On the other hand, when this operation was repeated using a similar solution, but with 0.474 mole glycol per mole of titanate, the Spray Rating had fallen to 80 by the time the 20th garment had been processed. This indicates the desirability of using the least amount of glycol possible commensurate with obtaining a stable solution.

Example 6

In this operation water-repellent solutions were prepared using the following composition:

	Parts
Polymerized octadecyl vinyl ether	18
Polymerized beta-pinene	3
Mineral oil	15
Tetra-n-butyl titanate	12
Carbon tetrachloride	35
Stoddard solvent	14.1

and 2-ethyl-1,3-hexandiol in varying proportions, as in

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indicated in Table II below. Each formulation was diluted with five times its volume of Stoddard solvent in the usual fashion. With this (C₄) tetraalkyl titanate, a stable solution was reached at approximately the 0.1 mole/mole of titanate level. However, as indicated by the Spray Rating data of Table II, those fabrics treated with solutions of the higher glycol content gave increasingly poorer results, again pointing to the desirability of using amounts of glycol not materially larger than those required for stabilization.

TABLE II

Glycol Content, Parts by Wt.	Moles Glycol per Mole of Titanate	Spray Rating
0.5	0.096	90
1.0	0.192	90+
1.5	0.288	90+
2.0	0.384	80
2.5	0.480	70

It should be observed that a strong synergistic effect is obtained as a glycol-stabilized titanate ester is employed in connection with a vinyl ether polymer. This is evidenced by the following tests:

A solution containing 2.0% tetraisopropyl titanate and 0.3% hexylene glycol in Stoddard solvent was prepared. A swatch of cotton poplin which had been drycleaned using a commercial drycleaning detergent and dried, was immersed in the solution, passed through squeeze rolls and dried for 30 minutes at 15° C. The fabric was then pressed on a commercial steam press. This fabric had a Spray Rating of 0. A second solution was prepared containing 4% of a polymerized octadecyl vinyl ether in Stoddard solvent, and drycleaned cotton fabric treated as before. This fabric had a Spray Rating of 0. A third solution was prepared containing 2% tetraisopropyl titanate, 0.3% hexylene glycol and 4% of the polymerized octadecyl vinyl ether. The drycleaned fabric treated with this solution had a Spray Rating of 100.

We claim as our invention:

1. A composition for rendering fabric water-repellent, said composition comprising a solution in an organic solvent of from 2 to 5 parts of a C₁₂-C₂₂ alkyl vinyl ether polymer, from 1 to 4 parts of a tetraalkyl titanate wherein the alkyl groups each contain from three to eight carbon atoms, and a C₆-C₉ glycol of the type having at least one secondary hydroxyl group, said glycol being present in an amount ranging from 0.1 to 0.5 mole per mole of said titanate, which amount is at least sufficient to stabilize the titanate against hydrolysis.

2. The composition of claim 1 wherein the non-solvent portion of said composition comprises from about 2 to 5 parts of polymerized vinyl octadecyl ether and from about 1 to 4 parts of tetraisopropyl titanate, and wherein the glycol employed is hexylene glycol.

3. A composition for rendering fabric water-repellent, said composition being a solution in an organic solvent wherein the non-solvent components comprise from about 2 to 5 parts of a C₁₂-C₂₂ alkyl vinyl ether polymer; from about 1 to 4 parts of a tetraalkyl titanate wherein the alkyl groups each contain from 3 to 9 carbon atoms; an amount effective to stabilize said titanate against hydrolysis of a C₆-C₉ glycol of the type having at least one secondary hydroxyl group, said amount ranging from about 0.1 to 0.5 mole per mole of titanate; from 50 to 100% of white mineral oil, based on the weight of vinyl ether polymer; and from about 10 to 25%, based on the weight of said vinyl ether polymer, of a polymerized beta-pinene.

4. The composition of claim 3 wherein the vinyl ether polymer is polymerized octadecyl vinyl ether, the titanate is tetraisopropyl titanate, and the glycol is hexylene glycol.

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