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TREATMENT OF TEXTILES WITH ALKYL-AMIDOALKENE ORTHOSILICATES

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This invention relates to a novel process for treating textile materials, including in this term fabrics and threads of natural material, as cotton, jute, linen, hemp, wool, and artificial material, as viscose, acetate, etc.

More particularly, this invention relates to the process of waterproofing such materials.

It is an object of this invention to make the materials treated not only water repellent, but also to produce a water repellent effect fast to commercial cleaning methods, particularly the usual dry cleaning.

Other objects will appear hereinafter.

These objects are accomplished according to our invention by treating the textile materials with an organic silicon compound containing at least one long chain fatty radical.

Such compounds may be esters of silicic acid formed with alcohols containing a long chain fatty radical. In this case the bond of the long chain fatty radical with the Si-atom is performed by oxygen, as for instance in tetrahexadecylsilicate $(C_{16}H_{33}O)_4Si$.

Some representatives of this type of compounds are already described in the literature, and known methods can be used to prepare other products of the same type.

Silicic acid esters, for instance, which can be used according to our invention, are easily produced in very good yields by reacting $SiCl_4$ with alcohols containing a long chain fatty radical, generally in the presence of an indifferent solvent. We have found that the radical must contain a chain of at least 12 carbon atoms in order to effect the desired water repellency.

Alcohols suitable for our purposes are, for instance, lauryl alcohol and its higher homologues like myristyl alcohol, cetyl alcohol, stearyl alcohol, or montanyl alcohol. Secondary alcohols of sufficient chain length as mentioned above are also suitable, as for instance, tetradecanol or heptadecanol. Hydroxylated aromatic compounds like ortho-octadecyloxyphenol



are also suitable. Long chain fatty acid amides, in which the amide group is linked with a hydroxylated group like ethanolstearamide



or oxymethylstearamide



are also suitable for our purposes.

The above mentioned hydroxylated compounds

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may first be converted into the corresponding halogenides, submitted to reaction with Mg and finally, after formation of the Grignard compound, reacted with $SiCl_4$.

5 Textiles are treated with the above mentioned compounds by padding them in a solution of these compounds in suitable organic solvents like benzene, kerosene, Stoddard solvent, etc., in a comparatively low concentration of about 0.5-5%, squeezing out the excess of solution and drying at elevated temperatures of 70-160° for a period of several minutes to some hours.

10 Instead of using solutions of the compounds mentioned before in organic solvents, they may also be emulsified and aqueous emulsions applied to textiles in a similar way as described above.

We discovered that it is essential to perform the drying at elevated temperatures. If higher temperatures are used, the time of drying may be considerably shortened. Time and temperature vary individually according to the various silicon compounds.

15 It is amazing that a compound applied to a cloth in a Stoddard solution should not be removed by subsequent dry cleaning by the same solvent, i. e., Stoddard solution. It is our belief that the original monomer silicon compound polymerizes on the cloth during the heating period.

20 Another possible explanation, that some reaction occurs between fabric and silicon compound at higher temperature, seems to us to be less likely. Our opinion appears to be confirmed by the fact that our silicon compounds produce the same water repellent effect on acetate as, for instance, on cotton. In the case of the usual so-called permanent water repellents, mostly quaternary ammonium compounds, it is observed that the effect on acetate is far inferior to that on non-esterified cellulose. This is explained by the fact that a reaction occurs with the cellulose, very probably an etherification of the free hydroxyl groups, which cannot be effected at all, or only to a much smaller extent, on acetate, where at least a part of the hydroxyl groups is already substituted.

25 In order to promote the polymerization of our silicon compounds, a very small amount of HCl may be added to the padding solution, and the same allowed to stand for a prolonged period. In using this procedure we noticed a substantial improvement in some cases where the original spray rating and fastness to dry cleaning were not quite satisfactory.

30 The following examples are given to illustrate

more in detail the preparation of our material and its application to textiles; without, however, limiting our invention to a particular procedure.

Example I

104 g. stearyl alcohol were dissolved in 300 ml. dry benzene. The solution was slowly added to 17 g. silicon tetrachloride with stirring. Hydrochloric acid gas was evolved. When the reaction slowed down, the temperature was gradually raised and the mixture refluxed on the boiling water bath for 2.5 hours. At the end of the heating period dry nitrogen was passed through the reaction product to drive out the remaining hydrochloric acid. After elimination of the benzene by distillation a white waxy mass was obtained.

The reaction product corresponds in all probability to the formula $(C_{17}H_{35}O)_4Si$. (Si calculated 2.54%, found 2.40%.)

A piece of gabardine was dipped in a 2.5% solution of the above product in Stoddard solvent, the excess of solution squeezed out by a roller and the fabric then kept for 30 minutes at 120° C. The repellency was tested following the procedure of the 1944 Year Book of the American Association of Textile Chemists and Colorists (pp. 200-211). The initial spray rating was 100 and went down to about 80 after three successive dry cleanings.

Example II

To a mixture of 355 g. commercial stearamide, 40 g. paraformaldehyde and 1000 ml. dry benzene, 15 g. silicon tetrachloride were added. The mixture was heated up to 50° C. with vigorous stirring and after a few minutes the mass thickened, indicating the formation of oxymethylstearamide. The mixture was allowed to cool down to 30° C. To the resulting viscous mass 50 g. silicon-tetrachloride diluted with a substantially equal volume of dry benzene were added, and the temperature gradually raised to 70° C. This temperature was sustained for three hours under continuous stirring. Hydrochloric acid gas was evolved in considerable quantity. At the end of the heating period, dry nitrogen was blown through the reaction mass and eventually the solvent distilled off under reduced pressure. The residue of the distillation was a brown, brittle mass which did not dissolve completely in Stoddard solvent. After elimination of the little insoluble part by filtration, the filtrate was brought to a concentration of 3% and used for padding.

The assumed formula of the product is



(Si found 2.43%, calculated 2.2%.)

Plain weave gray cotton cloth was treated as described in Example I, with the only difference that the padded fabric was heated for three minutes only, to 150° C. Initial spray rating 100; after three consecutive dry cleanings 90.

Similar results as to water repellency were obtained on gabardine and on a fabric consisting of 50% acetate and 50% viscose.

Example III

3.2 g. magnesium turnings were reacted with a solution of 41.5 g. octadecylbromide in 120 ml. dry ether, to which a crystal of iodine had been added. When said turnings were mostly dissolved,

the Grignard solution was added to 11.5 g. silicon tetrachloride dissolved in 50 ml. dry ether under vigorous stirring. After this addition the reaction mass was refluxed on the water bath for 70 minutes. Then the reaction product was decomposed with a few pieces of ice. Decomposition had to be done very cautiously and with as little ice as possible, to avoid formation of emulsions and consequently loss of material. The ethereal layer was washed with water to neutrality, dried with anhydrous sodium sulphate, and the ether distilled off. The residue was a yellowish waxy mass. Yield about 20 g.

Loose wool was padded with a 2.5% Stoddard solution of this material, excess of solvent squeezed out and the wool then heated for 5 minutes to 140° C. Original spray rating 90; after three dry cleanings, 70.

In another padding a few bubbles of dry hydrochloric acid were introduced in the 2.5% Stoddard solution of the material. The hydrochloric acid content determined by titration was 0.2 mg. per 1 ml. solution. This solution was allowed to stand over night and loose wool was padded in it the following day and further treated as described above.

Initial spray rating, 100; hardly affected by three successive dry cleanings.

The above description and examples do not limit the scope of this invention in any way, since numerous modifications may be made without material departure from the salient features of the invention as expressed in the appended claims.

What we claim is:

1. The process of improving textile materials whereby to impart thereto water repellent properties fast to commercial cleaning methods, which comprises treating the raw materials with a solution of an alkylamido-alkene orthosilicate, in which the alkyl group contains at least 12 and not more than 30 carbon atoms, and thereafter heating said treated material at a temperature within the range of approximately 70-160° C.

2. The process of improving textile material which comprises the steps of treating said textile material with a composition including stearamidomethylene orthosilicate, and thereafter heating said treated material at a temperature within the range of approximately 70-160° C., whereby said improved textile material exhibits water repellent properties fast to commercial cleaning methods.

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