

UNITED STATES PATENT OFFICE

2,588,366

METHOD OF RENDERING FABRICS WATER-REPELLENT AND COMPOSITION THEREFOR

Firth L. Dennett, Midland, Mich., assignor to
Dow Corning Corporation, Midland, Mich., a
corporation of Michigan

No Drawing. Application March 9, 1950,
Serial No. 148,733

9 Claims. (Cl. 117—161)

1

This invention relates to a method of rendering fabrics water-repellent.

Siloxanes for treating fabrics to render them water-repellent have heretofore been known. The hydrolysis product of methylhydrogen-dihalogenosilane in particular has been used in this respect.

It is shown in my copending application, Serial No. 126,690, filed November 10, 1949, that water-repellent fabrics with improved laundering and dry cleaning characteristics and improved crease resistance may be obtained by treating them with certain organosiloxanes. Although the method there described allowed the manufacture of greatly improved water-repellent fabrics, certain improvements are to be desired in the results obtained. For instance, some treated fabrics, particularly the smooth-fibered fabrics, such as acetate rayon and nylon, became too slippery. It was found that in the die cutting of stacks of such fabrics, the slippage of some of the individual pieces resulted in imperfect cuttings, with errors in dimensions and form causing an undesirable number of rejects.

A somewhat related problem was that of slippage of the individual yarns in a fabric. This slippage resulted in the obviously undesirable effect of allowing separation of the yarns from one another when the fabric was under stress. The slick, slippery "hand" of treated smooth-fibered fabrics was also undesirable in many applications.

Known methylhydrogenpolysiloxane compositions, when applied to cotton fabrics, have been notoriously poor in resistance to laundering. Treated cotton fabrics have also been found to have too soft a "hand," and a more crisp effect has been desired.

It is an object of the present invention to provide improved methods of rendering fabrics water-repellent.

In accordance with the present invention, fabrics are rendered water-repellent by wetting the fabrics with a mixture of three organosiloxane polymers. The wetted fabrics are then heated at a temperature ranging from 100° to 475° F. for a period of from 5 seconds to one hour.

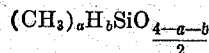
The fabrics which may be treated in accord with the method of this invention include fabrics of natural fibers such as cotton, silk, linen, or wool; and fabrics of synthetic fibers such as nylon, "Orlon," and either viscose or acetate rayon.

The three organosiloxane polymers used in the above stated mixture are as follows:

(I) A methylhydrogenpolysiloxane fluid which contains between 1.0 and 1.5 methyl radicals and between 0.75 and 1.25 hydrogen atoms bonded to silicon per silicon atom, there being a total of 2.0 to 2.25 methyl radicals and such hydrogen atoms

2

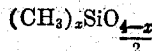
per silicon atom. Fluids of this type may be produced by the hydrolysis and condensation of $\text{CH}_3\text{HSiCl}_2$ alone or by cohydrolyzing and cocondensing it with chlorosilanes such as $(\text{CH}_3)_3\text{SiCl}$; $(\text{CH}_3)_2\text{HSiCl}$; and $(\text{CH}_3)_2\text{SiCl}_2$. These fluids have the general formula



where a has a value of from 1.0 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive.

(II) A methylpolysiloxane fluid which contains between 2 and 2.1 methyl radicals per silicon atom and which has a viscosity of at least 1,000 centistokes and preferably less than 100,000 centistokes. Such fluids have been described in the art and are now commercially available. They have the general formula $(\text{CH}_3)_n\text{SiO}_{4-n}$, where n has a value of from 2.0 to 2.1.

(III) A methylpolysiloxane resin of the general formula



where x has a value of from 1.0 to 1.25. Such resins are well known to the art. They may contain units such as $(\text{CH}_3)_2\text{SiO}$, $(\text{CH}_3)_3\text{SiO}_{.5}$, or unsubstituted silicon in addition to the $\text{CH}_3\text{SiO}_{1.5}$ units which constitute a major portion of the resin. They may be prepared by methods such as those disclosed in U. S. Patent No. 2,486,162 or French Patent No. 927,276. The preferred range of methyl radicals per silicon atom is from 1.05 to 1.15. These resins are normally employed in solution in an appropriate organic solvent, and are added as a solution to (I) and (II) above.

The mixture is made up of from 15 to 45 per cent by weight of the methylhydrogenpolysiloxane fluid (I), 10 to 30 per cent of the methylpolysiloxane fluid (II), and 20 to 65 per cent of the methylpolysiloxane resin (III). As was stated above, the methylsiloxane resin (III) is preferably added as a solution. Both the amount and type of solvent for this solution are immaterial, and the actual weight of solvent present is not included in the 35 to 65 per cent (III) called for. The composition of the mixture may be varied within the prescribed limits above in accordance with the fabric to be treated and the desired "hand" to be obtained.

Catalysts may be added to the organosiloxane mixture above, and the mixture then used to wet the fabric. Alternatively, the fabric may be wetted with the organosiloxane mixture and the fabric dipped in a solution of the catalyst. Such catalysts include metallic salts such as sodium bicarbonate and sodium aluminate, and the metallic salts of carboxy acids such as the acetates, hexoates, octoates and naphthenates of lead, iron, zinc, manganese, and cobalt. These cata-

3

lysts are not necessary to the practice of the invention; however, since they merely speed-up the curing rate.

The organosiloxane mixture may be applied directly to the fabric. However, it is preferred to extend the organosiloxane mixture by diluting with a liquid hydrocarbon, chlorohydrocarbon, ether, or alcohol, such as benzene, dioxane, ethanol, methylene dichloride or the like in order to minimize the amount of siloxane employed.

The organosiloxane mixture may likewise be extended by the preparation of an aqueous emulsion, which emulsion preferably contains an emulsifying agent decomposable by heating. The quaternary ammonium halides are examples of such emulsifying agents. They are decomposed on heating for a brief period. Examples of such halides are the alkylarylammonium chlorides, such as trimethylbenzylammonium chloride and hexadecyldimethylbenzylammonium chloride. Non-cationic emulsifying agents, such as the amide condensation products of fatty acids with organic amines, are preferred in the treatment of cotton, wool, and rayon. An example of such a non-cationic emulsifying agent is the product known as "Pluramine S-100," marketed by the Kearny Manufacturing Company, Inc., Kearny, New Jersey. If desired, the siloxane mixture may be thinned with any of the above indicated solvents in order to facilitate emulsification. After emulsification, the solvent may be removed under vacuum, if desired.

Emulsions of methylhydrogenpolysiloxanes frequently liberate hydrogen upon standing. In order to avoid this effect, it is desirable to add an organic acid such as acetic acid to the emulsion in order to inhibit the evolution of hydrogen. The quaternary ammonium salts function well as emulsifying agents in such acid systems.

The siloxane mixture either straight or as a solution or emulsion may be applied to the fabric in any appropriate manner. Thus, the mixture may be applied to the fabric by the use of conventional equipment such as a padder or quetch. The fabric may then be dried to remove water or solvent.

The material should be applied to the fabric in such an amount that there is a pick-up of between one and five per cent of the organosiloxane mixture (not including solvent or water) based upon the weight of the fabric.

The fabric is then heated to between 100° and 475° F. for from five seconds to one hour. This heating effects liberation of a major portion of the hydrogen which is bonded to the silicon in the methylhydrogenpolysiloxane. The siloxane present is polymerized by this heating to an insoluble polymer in the fabric, whereby the fabric is rendered permanently hydrophobic. When a heat decomposable emulsifying agent is employed, it is also decomposed during this heating.

The present invention is of particular importance in the hydrophobing of nylon, acetate rayon, and cotton. It has been found that by the use of the mixture of organosiloxanes disclosed herein, as compared to prior organosiloxane treatments, nylon and rayon fabrics may be effectively hydrophobed without being excessively slippery to the touch or in contact with one another. When used on cotton fabrics, the products of this invention develop a water-repellency which is much more resistant to laundering than was heretofore possible with organosiloxane treatments, and furthermore produce a treated fabric which has a more crisp "hand."

4

The following organosiloxanes were prepared for use in the examples below. Parts given are by weight.

A mixture of 1,000 parts of $\text{CH}_3\text{HSiCl}_2$ and 51.5 parts of $(\text{CH}_3)_3\text{SiCl}$ was added to 750 parts of benzene. This mixture was then cooled to 20° C. To this mixture 675 parts of isopropyl alcohol were added over a period of 10 minutes and then 783 parts of water were added over a period of one hour, whereby to effect hydrolysis. An additional 750 parts of benzene were then added to the reaction mixture. The product was washed six times with water and strip distilled at 3 mm. pressure to 115° C. to remove the benzene and the lower boiling products. There were obtained 475 parts of a trimethylsiloxy end-blocked methylhydrogenpolysiloxane, which is referred to as product (I) in the examples.

A mixture of 9.3 parts by weight of decamethyltetrasiloxane and 735 parts of octamethylcyclotetrasiloxane was prepared. To this mixture there was added .56 part of KOH. This mixture was then heated at 160° C. for 8 hours. The mixture was then cooled to about 100° C. and CO_2 in the form of Dry Ice was added over a period of 30 minutes. This mixture was then filtered and flash distilled to 250° C. at 1 mm. pressure. There were obtained 625 parts of a trimethylsiloxy end-blocked dimethylpolysiloxane fluid having a viscosity of 1,000 centistokes, which is referred to as product (IIA) in the examples.

A mixture was prepared of 1.5 parts by weight of decamethyltetrasiloxane and 735 parts of octamethylcyclotetrasiloxane. To this mixture there were then added .56 part of KOH. This mixture was then agitated and heated at 160° C. for 8 hours. The mixture was then cooled to about 100° C. and CO_2 in the form of Dry Ice added over a period of 30 minutes. The mixture was then filtered and flash distilled to 250° C. at 1 mm. pressure. There were obtained 630 parts of a trimethylsiloxy end-blocked dimethylpolysiloxane fluid having a viscosity of 12,500 centistokes, which is referred to as product (IIB) in the examples.

A mixture was prepared of 1.2 parts by weight of decamethyltetrasiloxane and 735 parts of octamethylcyclotetrasiloxane. To this mixture there were then added .56 part of KOH. The mixture was then agitated and heated at 160° C. for 8 hours. The mixture was then cooled to 100° C. and CO_2 in the form of Dry Ice added over a period of 30 minutes. The mixture was then filtered and flash distilled to 250° C. at 1 mm. pressure. There were thereby obtained 620 parts of a trimethylsiloxy end-blocked dimethylpolysiloxane having a viscosity of 30,000 centistokes, which is referred to as product (IIC) in the examples.

A mixture of 1345 g. of CH_3SiCl_3 and 128 g. of $(\text{CH}_3)_2\text{SiCl}_2$ was diluted with 500 g. of toluene and added slowly to a mixture of 6,000 g. of water, 500 g. of toluene, and 1,500 g. of n-butanol. The temperature of the reaction mixture was held at less than 25° C. throughout the addition. When the reaction was complete, the organic layer was washed free of HCl, dried over sodium sulfate, and filtered. The filtered resin solution was adjusted to 33 per cent resin solids by the addition of a small amount of toluene. This resin solution is referred to as product (IIIA) in the examples.

A mixture of 1317 g. of CH_3SiCl_3 and 130 g. of $(\text{CH}_3)_2\text{SiCl}_2$ was diluted with 500 g. of toluene and hydrolyzed by the procedure of (IIIA) above.

5

After washing, drying, and filtering, the resin solution was adjusted to 33 per cent by weight of resin solids. This solution is referred to in the examples as product (IIIB).

Example 1

A mixture was made of 30 parts of the methylhydrogenpolysiloxane fluid (I), 20 parts of 30,000 centistokes methylpolysiloxane fluid (IIC), and 150 parts of the 33 per cent methylpolysiloxane resin solution (IIIA). To this mixture was added 3133 parts of toluene, giving a 3 per cent solution based on the organosilicon content. When samples of nylon and acetate rayon are treated with this solution, and then heated at a temperature of 150° C. for 10 minutes, a spray rating (AATCC standard test method 22-41) of 90-100 is obtained. The fabrics have a soft, full "hand," and show no slippage effect when in contact with one another.

Example 2

The following mixtures were made:

- A. 20 parts (I), 20 parts 12,500 centistokes methylpolysiloxane fluid (IIB), 180 parts 33 per cent (IIIA).
- B. 45 parts (I), 30 parts 12,500 centistokes methylpolysiloxane fluid (IIB), 75 parts 33 per cent (IIIA).
- C. 35 parts (I), 10 parts 12,500 centistokes methylpolysiloxane fluid (IIB), 165 parts 33 per cent (IIIA).
- D. 30 parts (I), 20 parts 1,000 centistokes methylpolysiloxane fluid (IIA), 150 parts 33 per cent (IIIA).
- E. 30 parts (I), 20 parts 12,500 centistokes methylpolysiloxane fluid (IIB), 150 parts 33 per cent (IIIB).

Each mixture was diluted to 3 per cent organosilicon content with toluene. Samples of acetate rayon gabardine, plain-weave nylon, rayon and nylon taffetas, muslin, and cotton twill were dipped in each solution and then cured at 150° C. for 10 minutes. Spray ratings on the treated fabrics ran from 70 to 100, and the following general trends were noted: As the percentage of methylhydrogenpolysiloxane (I) is decreased below about 30 (based on the total organosiloxane components), the spray rating gradually decreases. As the percentage of methylpolysiloxane fluid (IIA, B, C) is decreased, the fabrics become less slippery but begin to show a stiffer "hand" and have less resistance to "mark-off" or creasing. Increasing this component causes a drop in water-repellency and results in a more slippery fabric, but improves the resistance to "mark-off." As the percentage of methylpolysiloxane resin (IIIA) is decreased, the slippage of the fabric increases; raising this percentage produces a stiffer fabric with less water-repellency and a somewhat brash "hand." The monomethyl-trimethyl polysiloxane resin (IIIB) compares favorably with the monomethyl-dimethyl polysiloxane resin (IIIA), with the exception that on cotton it imparts somewhat less resistance to laundering. It was indicated that the composition of Example 1 is preferable for maximum water-repellency, wash resistance and resistance to "mark-off"; and for minimum slippage of smooth-fibered fabrics.

Example 3

A mixture of 60 g. of the 33 per cent methylpolysiloxane resin (IIIA), 32 g. of 12,500 centistokes methylpolysiloxane fluid (IIB), 48 g. of

6

methylhydrogenpolysiloxane fluid (I) and 43 g. of methylene dichloride was made. This was added slowly, with extremely rapid agitation, to a solution of 2 g. of cetyldimethylbenzylammonium chloride in 30 g. of water. The resulting emulsion was diluted to a 4 per cent concentration of organosiloxane components by the addition of water. Samples of plain-weave nylon were dipped in the 4 per cent emulsion and cured for 5 minutes at 150° C. The cured samples were found to have a spray rating of 100. A sample was washed for 45 minutes at 130° F. in a 0.5 per cent soap solution. After rinsing and drying, the spray rating remained unchanged at 100. The treated samples had no undesirable slippage properties.

Example 4

When samples of nylon fabric are treated with the 3 per cent solution of Example 1, and cured for 1 minute at a temperature of 450° F., results are obtained comparable to the results of the treatment in Example 3.

Example 5

In order to illustrate the effect of the presence of the methylpolysiloxane resins, two emulsions were prepared as follows:

A. A mixture of 48 g. of methylhydrogenpolysiloxane fluid (I), 32 g. of 12,500 centistokes methylpolysiloxane fluid (IIB), and 40 g. of methylene dichloride was slowly added to a rapidly agitated solution of 3 g. of "Pluramine S-100" in 75 g. of water. The resulting emulsion was diluted by the addition of water to a 3 per cent concentration of the organosiloxane components.

B. A mixture of 48 g. of methylhydrogenpolysiloxane fluid (I), 32 g. of 12,500 centistokes methylpolysiloxane fluid (IIB), 40 g. of methylene dichloride, and 120 g. of the 33 per cent solution of methylpolysiloxane resin (IIIA) was slowly added to a rapidly agitated solution of 4 g. of "Pluramine S-100" in 100 g. of water. The resulting emulsion was diluted with water to a 3 per cent concentration of organosiloxanes.

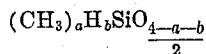
Samples of tan poplin, grey poplin, cotton gabardine, and mixed acetate-viscose rayon fabrics were dipped in these emulsions and cured for 10 minutes at 150° C. Spray ratings were taken on all samples, then the samples were washed for 45 minutes at 130° F. in a water solution containing 0.5 per cent soap and 0.2 per cent sodium carbonate. After rinsing and drying, the spray ratings were again determined, and the cycle repeated through a total of three washes. The initial spray rating and the rating after each wash are tabulated below for both the "A" and "B" treatments.

Fabric	Spray Rating							
	Initial		1st Wash		2nd Wash		3rd Wash	
	A	B	A	B	A	B	A	B
Tan poplin....	100	100	80	100	70	80	70	80
Grey poplin....	100	100	70	90	70	80	70	80
Cot. gabardine.....	100	90	70	90	70	80	70	80
Ac. and Vis. rayon.....	100	90	70	70	70	70	70	70

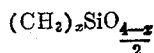
The rayon which had been treated with the "B" emulsion, containing methylpolysiloxane resin, showed much less slip than that treated with the "A" emulsion.

That which is claimed is:

1. The method of rendering organic fabrics water-repellent, which comprises wetting the fabrics with a mixture of from 15 to 45 per cent by weight of a methylhydrogenpolysiloxane fluid of the general formula

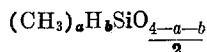


where a has a value of from 1.0 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25; 10 to 30 per cent by weight of a methylpolysiloxane fluid containing between 2.0 and 2.1 methyl radicals per silicon atom and having a viscosity of from 1,000 to 100,000 centistokes; and 20 to 65 per cent by weight of a methylpolysiloxane resin of the general formula

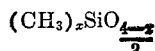


where x has a value of from 1.0 to 1.25; and heating the wetted fabrics at a temperature of 100° F. to 475° F. for a period of from 5 seconds to 1 hour, whereby the fabrics are rendered water-repellent and slip-resistant.

2. The method of rendering organic fabrics water-repellent, which comprises wetting the fabrics with an aqueous emulsion of a mixture of from 15 to 45 per cent by weight of a methylhydrogenpolysiloxane fluid of the general formula



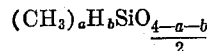
where a has a value of from 1.0 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25; 10 to 30 per cent by weight of a methylpolysiloxane fluid containing between 2.0 and 2.1 methyl radicals per silicon atom and having a viscosity of from 1,000 to 100,000 centistokes; and 20 to 65 per cent by weight of a methylpolysiloxane resin of the general formula



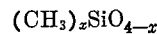
where x has a value of from 1.0 to 1.25; which emulsion contains a heat decomposable emulsifying agent, and heating the wetted fabric at a temperature of from 100° to 475° F. for a period of from 5 seconds to 1 hour, whereby the fabrics are rendered water-repellent and the emulsifying agent is decomposed.

3. An organosiloxane mixture for rendering organic fabrics water-repellent comprising from

15 to 45 per cent by weight of a methylhydrogenpolysiloxane fluid of the general formula



where a has a value of from 1.0 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25; 10 to 30 per cent by weight of a methylpolysiloxane fluid containing between 2.0 and 2.1 methyl radicals per silicon atom and having a viscosity of from 1,000 to 100,000 centistokes; and 20 to 65 per cent by weight of a methylpolysiloxane resin of the general formula



where x has a value of from 1.0 to 1.25.

4. The method of claim 1 in which the methylhydrogenpolysiloxane fluid is a trimethylsiloxy end-blocked methylhydrogenpolysiloxane, the methylpolysiloxane fluid is a trimethylsiloxy end-blocked dimethylpolysiloxane, and in which the methylpolysiloxane resin is a copolymer containing $(\text{CH}_3)_2\text{SiO}_{1.5}$ units and units of the group consisting of $(\text{CH}_3)_2\text{SiO}$ and $(\text{CH}_3)_3\text{SiO}_{0.5}$ units.

5. The method of claim 2 in which the methylhydrogenpolysiloxane fluid is a trimethylsiloxy end-blocked methylhydrogenpolysiloxane, the methylpolysiloxane fluid is a trimethylsiloxy end-blocked dimethylpolysiloxane, and in which the methylpolysiloxane resin is a copolymer containing $(\text{CH}_3)_2\text{SiO}_{1.5}$ units and units of the group consisting of $(\text{CH}_3)_2\text{SiO}$ and $(\text{CH}_3)_3\text{SiO}_{0.5}$ units.

6. The method of claim 5 in which the emulsifying agent is a quaternary ammonium halide.

7. The organosiloxane mixture of claim 3 in which the methylhydrogenpolysiloxane fluid is a trimethylsiloxy end-blocked methylhydrogenpolysiloxane, the methylpolysiloxane fluid is a trimethylsiloxy end-blocked dimethylpolysiloxane, and in which the methylpolysiloxane resin is a copolymer containing $(\text{CH}_3)_2\text{SiO}_{1.5}$ units and units of the group consisting of $(\text{CH}_3)_2\text{SiO}$ and $(\text{CH}_3)_3\text{SiO}_{0.5}$ units.

8. An aqueous emulsion of the organosiloxane mixture of claim 7.

9. The emulsion of claim 8 in which the emulsifying agent is a quaternary ammonium halide.

FIRTH L. DENNETT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,386,259	Norton	Oct. 9, 1945
2,392,805	Biefeld	Jan. 15, 1946