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2,842,509

**COMPOSITION CONTAINING ORGANOSILOXANE AND POLYIMINE AND METHOD OF TREATING TEXTILES THEREWITH**

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6 Claims. (Cl. 260—29.2)

This invention relates to a substantive method for applying siloxanes to fabrics.

This application is a continuation-in-part of applicant's copending application Serial No. 550,218, filed November 30, 1955, now abandoned.

Prior to this invention siloxanes were generally applied to fabrics by immersing the fabric in an emulsion until it was thoroughly wet and thereafter removing the fabric from the emulsion and drying to cure the siloxane.

In heretofore employed methods this was usually done continuously and the amount of siloxane deposited on the fabric was dependent upon the amount of siloxane in the emulsion which was actually retained by the fabric as it emerged from the bath. That is, the amount of silicone picked up by the fabric was determined solely by the concentration of the siloxane in the treating emulsion. There was little preferential adsorption of the siloxane on the fabric surface. Consequently the fabric was passed through the emulsion until the emulsion was completely removed from the container.

Whereas this method works satisfactorily for continuous operation it does not work satisfactorily for batch operations. This is true because the batch of fabric would be dipped into the emulsion and thereafter removed and dried. Under such conditions only a fraction of the siloxane in the treating bath would be deposited on the fabric. As is well known, siloxane emulsions containing SiH compounds are not stable. These materials are the ones most commonly employed on fabrics. As a result, for batch operations, much of the siloxane would be wasted due to the gelling of the emulsion or for other causes.

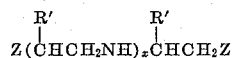
There are many types of fabrics such as knit goods which cannot be continuously passed through an emulsion. Furthermore, it is often desirable to treat finished garments such as sweaters, blankets, or hosiery. These cannot conveniently be treated continuously but must be treated by batch process, that is, a process in which any one batch of emulsion is employed to treat a limited number of pieces of fabric or garments. It would be highly desirable, therefore, to have a system from which all of the siloxane in the emulsion treating bath would be completely adsorbed on the surface of the fabric within a reasonable length of time. In such a system there would be no waste of the siloxane and one could employ much more dilute emulsions than has heretofore been possible in treating fabrics.

It is the object of this invention to provide a novel method for applying siloxanes to fabric in which the siloxane is preferentially adsorbed on the surface of the fabric. Another object is to provide a method for treating fabrics by a batch process. Another object is to provide a method which would be applicable to a wide variety of siloxanes and to all types of fabrics. Other objects and advantages will be apparent from the following description.

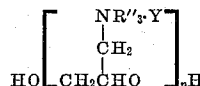
This invention relates to a method of depositing a siloxane on a fabric which comprises immersing the

2

fabric in a siloxane-in-water emulsion containing a non-ionic emulsifying agent and from 2 to 80% by weight based on the weight of the siloxane of a nitrogen compound of the group polyimines of the formula



in which Z is of the group NH<sub>2</sub> or halogen, R' is hydrogen or methyl and x is an integer of at least 4, salts of said polyimines and compounds of the formula



in which R'' is an aliphatic hydrocarbon radical of less than 5 carbon atoms, Y is an acid anion and n has a value of at least 2 and thereafter removing the fabric from the water and drying.

The substantive agents employed in the method of this invention are the polyimines and salts thereof and the defined quaternary ammonium polyglycols. These materials cause a spontaneous deposition of the poly-siloxane in the emulsion on the surface of the fabric. In general, the siloxane is completely adsorbed in less than 60 minutes and generally in less than 15 minutes. The adsorption of the siloxane is indicated by a clearing of the emulsion. This may be measured by light transmission. When the transmission through the treating bath reaches 100%, all of the siloxane has been deposited on the fabric.

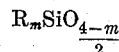
The concentration of the siloxane in the emulsion in the process of this invention is not critical. However, for practical operation, it is preferred that the emulsion be fairly dilute. Ideally the amount of silicone in the emulsion should be that which will give the desired pickup on the fabric. Thus if one desires a 2% weight pickup of siloxane on the fabric the amount of siloxane in the emulsion should be 2% by weight of the weight of the fabric being treated. It should be understood of course that the process of this invention is not limited to those cases in which the siloxane is completely exhausted from the bath in any one operation. This invention also includes the type of operation in which successive batches of fabric are treated from a more concentrated emulsion.

For example, an emulsion containing say 10% by weight silicone, based on the weight of the fabric to be treated in any one batch, can be employed to treat five batches of fabric in which a 2% pickup is desired, on all the fabric. The first batch was allowed to remain until 2% pickup was obtained. It can then be removed and a second batch immersed and allowed to remain until 2% pickup is again obtained. This process can be repeated until the bath is entirely exhausted.

The amount of siloxane applied to the fabric is not critical although it has been found in general that the surface becomes saturated at about 3% by weight siloxane based upon the weight of the fabric.

It has been found that the method of this invention can be carried out at any desired pH. Obviously extremely acidic or basic conditions should be avoided so as not to damage the fabric. The preferred pH range is from 2 to 10. This is a decided advantage over most substantive treatments which are quite sensitive to pH.

Siloxanes employed in this invention can be any emulsifiable siloxane of the formula



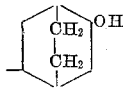
in which R is any monovalent hydrocarbon radical, any hydroxylated monovalent hydrocarbon radical or hydro-

3

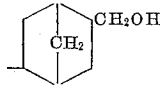
gen and  $m$  has an average value from 1 to 3 inclusive. It is preferred that at least 50% of the R groups in the siloxane be an organic radical.

For the purpose of this invention the siloxane can range from viscous resins to thin fluids. It should be understood that the siloxane can be any homopolymer or copolymer and may contain any combination of siloxane units of the formula  $R_3SiO_{3/2}$ ,  $R_2SiO$  and  $R_3SiO_{1/2}$  together with limited amounts of  $SiO_2$  units.

For the purpose of this invention R can be any monovalent hydrocarbon radical such as alkyl radicals such as methyl, ethyl, butyl and octadecyl; alkenyl radicals such as vinyl, allyl and hexenyl; cycloaliphatic radicals such as cyclohexyl and cyclohexenyl; aryl hydrocarbon radicals such as phenyl, xenyl, tolyl and naphthyl and alkaryl hydrocarbon radicals such as benzyl. R can also be any hydroxylated hydrocarbon radical such as gamma-hydroxypropyl, 5-hydroxybutyl, hydroxycyclopentyl, hydroxycyclohexyl, hydroxyphenyl, 3-hydroxy-methyl-2-methylcyclohexyl

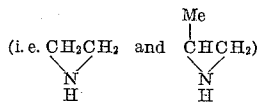


and



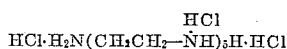
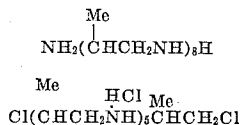
Siloxanes containing the above hydroxylated radicals can be prepared in accordance with the method of the copending application of John L. Speier, Serial No. 463,061, filed October 18, 1954, now abandoned.

The substantive agents employed in the method of this invention can be polyimines derived from ethylenediamine and propylenediamine. These materials can be prepared by the polymerization of ethylene imine or propylene imine



or they may be prepared by the condensation reaction of ethylenediamine or propylenediamine with an ethylenedihalide or a propylenedihalide. In the latter reaction the hydrogen halide evolved reacts with the amino groups to form the imine hydrohalide. Also in this reaction if the dihalide is used in excess some residual halogen atoms will remain on the ends of the molecules. All of these materials are within the scope of this invention provided there is at least 4 alkylene imine units per molecule.

Specific examples of operative imines are those of the formula  $\text{Cl}(\text{CH}_2\text{CH}_2\text{NH})_4\text{CH}_2\text{CH}_2\text{Cl}$ ,



and  $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_{20}\text{H}$ . The sulfates, acetates, nitrates, bromides, formates and any other salts of the imines can also be employed.

The polyglycol quaternary ammonium compounds which are operative as substantive agents in this invention can be prepared by halogenating the methyl group in propylene oxide and thereafter polymerizing this material to a halogenated polypropylene glycol and thereafter reacting the halogenated polyglycol with a tertiary amine of the formula  $\text{R}''_3\text{N}$  in which  $\text{R}''$  is any aliphatic hydrocarbon radical of less than 5 carbon atoms such

4

as methyl, ethyl, vinyl, propyl, allyl, butyl and isopropyl. For the purpose of this invention the Y group in the salt can be any acid anion such as chloride, bromide, iodide, nitrate, sulfate, acetate, formate, propionate and the like.

The salts other than the halides are best prepared by ion exchange with the corresponding halide salts.

The emulsifying agents employed in the process of this invention must be of the non-ionic type. Any non-ionic emulsifying agent may be employed such as, for example, alkyl ethers of polyalkylene glycols such as polypropylene glycol monobutyl ether, polyethylene glycol 2-ethylhexyl ether and polyethylene glycol monobutyl ether and esters of polyhydric alcohols such as glycerol monostearate, polyoxyethylenedistearate and propylene glycol monolaurate. The amount of emulsifying agent is not critical but it is usually employed in amount less than 50% based on the weight of the siloxane.

Preferably the emulsion should contain a catalyst for setting the siloxane. For this reason one may employ water soluble titanates such as triethanolamine titanate, diethanolamine titanate, triethanolamine zirconate and salts such as sodium acetate, zinc acetate and the like.

It has been found that in the treatment of wool fabrics the alkanol amine titanates are of particular utility as catalysts. This is particularly true when the siloxane has hydrogen bonded to at least some of the silicon atoms. The use of the combination of the substantive agents and the alkanol amines gives better deposition of the siloxane on the wool fabric, faster curing and more dependable spray ratings on all types of wool fabric. The concentration of the alkanol amine titanate catalyst relative to the siloxane and the substantive agent is not critical. Excellent results are obtained, for example, when one employs 2% by weight of the substantive agent based on the weight of the siloxane and an amount of the alkanol amine titanate to give 2% by weight titanium metal based on the weight of the siloxane.

If desired, other resinous materials such as aminoplast resins such as melamine aldehyde resins, urea aldehyde resins or combinations thereof may be employed in conjunction with the siloxane.

The treatment of this invention is operative on any type of fabric such as inorganic fabrics such as glass or asbestos and organic fabrics such as paper, cotton, wool, rayon, nylon, Orlon, Dacron, polyacrylonitrilevinylchloride copolymers, linen, silk, cellulose triacetate and leather. The fabrics designated by the terms rayon, nylon, Orlon and Dacron are well known in the textile art. Dacron is a synthetic fiber made by the condensation of dimethyl terephthalate and ethylene glycol. Nylon is any of a series of polyamide resins made by the polymerization of a hexamethylene-diamine salt of adipic acid. Orlon is a synthetic fiber made principally from polyacrylonitrile. Rayon is a manufactured textile fiber or yarn produced from cellulose or with a cellulose base.

In carrying out the process of this invention any type of container may be employed although it is found preferable to use stainless steel since there is practically no deposition of the siloxane on the surface of the vessel. Glass or organic plastic vessels can be employed if desired.

The following examples are illustrative only and should not be construed as limiting the invention which is properly set forth in the appended claims. Organic radicals in the formulas in this specification are often abbreviated by employing the first two letters in the name (i. e. Me for methyl, St for stearyl and Ac for acetic, etc.).

#### Example I

An emulsion was prepared which had the composition 600 ml. of water, .6 g. of siloxane resin having the composition 63 mol percent monomethylsiloxane, 28 mol percent monophenylsiloxane and 9 mol percent diphenyl-

5

siloxane, .06 g. of an alkyl ether of polyethylene glycol as an emulsifying agent and .012 g. of



30 g. of cotton fabric was immersed in the emulsion and agitated. The resinous siloxane had completely deposited on the cotton in 60 minutes.

#### Example 2

Equimolar amounts of ethylenedichloride and diethylenetriamine were condensed by heating the mixture at reflux. The resulting product was a mixture of hydrochlorides of ethylene polyimine having about 8 ethylene units per molecule.

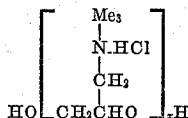
.012 g. of this material was substituted in the emulsion of Example 1 and 30 g. of cotton fabric was immersed therein. The fabric was agitated and complete deposition of the siloxane resin on the cotton took place in 15 minutes.

#### Example 3

An emulsion was prepared employing .45 g. of the siloxane of Example 1, .045 g. of an alkyl ether of polyethylene glycol, .009 g. of the imine hydrochloride of Example 2 and 600 ml. of water. Several nylon hose weighing a total of 30 g. were immersed in this emulsion and the siloxane was completely exhausted on the hose in 15 minutes. The hose were removed from the bath and heated 2 minutes at 220° F. The resulting hose were snag resistant.

#### Example 4

An emulsion was prepared employing .6 g. of the siloxane resin of Example 1, .06 g. of an alkyl ether of polyethylene glycol, .06 g. of the compound



having a molecular weight of 736 and 600 ml. of water. A 30 g. piece of cotton fabric was immersed in the emulsion and the siloxane was completely deposited thereon in 15 minutes. The fabric was then removed from the bath and dried and was water repellent.

#### Example 5

This example shows the operability of the process of this invention over a wide pH range. A series of emulsions were prepared each of which had the composition .45 g. of the siloxane of Example 1, .045 g. of an alkyl ether of polyethylene glycol, .009 g. of a polyethylene imine having more than 4 ethylene units per molecule and 600 ml. of water. The pH of a series of emulsions of this composition was varied by adding ammonia or acidic acid in amounts to give pH's of 2, 4, 6, 7, 8 and 10. 30 g. of cotton fabric was immersed in each of these emulsions. In the one having a pH of 2, the silicone was substantially

6

deposited on the cotton in 30 minutes. In all of the remaining emulsions the silicone was completely deposited on the cotton in 15 minutes.

#### Example 6

An emulsion was prepared having the composition .6 g. of a copolymer of 28 mol percent gamma-hydroxypropylmethylsiloxane, 14.3 mol percent phenylmethylsiloxane and 57.1 mol percent dimethylsiloxane, .012 g. of the polyimine of Example 5, .12 g. of an alkyl ether of polyethylene glycol and 600 ml. of water. 30 g. of cotton fabric was immersed in this emulsion and the siloxane was completely deposited thereon in 60 minutes.

#### Example 7

The base siloxane emulsion employed in this example was prepared by mixing 100 parts by weight of a 30% emulsion of a siloxane mixture having the composition 60% by weight of a 100 cs. copolymer of trimethylsiloxane and methylhydrogensiloxane and 40% by weight of a 10,000 cs. dimethylpolysiloxane fluid, 3.3 parts by weight of a 15% aqueous solution of the polyimine of Example 5 and 10.7 parts by weight of a 20% aqueous solution of sodium acetate. 5.5 g. samples of this base emulsion were then each diluted with 100 ml. water to give the series of emulsions employed below. These emulsions were each placed in a glass jar of about 200 ml. capacity and 5 g. of the various fabrics shown below were then immersed in the emulsion. The jar was then rotated at 40 R. P. M. for 30 minutes. The fabric was then removed from the emulsion and the light transmission of the bath was determined by measuring the transmission of light at 700 m $\mu$ . Each sample of fabric was then removed from the bath, heated 10 minutes at 150° C. and the spray rating was determined. The results are shown in the table below.

Fabric	Spray Rating	Percent Light Transmission	
		Initial	After 30 Minutes
Cotton	100	6	100
Wool	100	3	100
Viscose rayon	100	4	99
Nylon	100	8	86
Orlon	90-100	5	65
Cellulose triacetate	100	4	93
A mixture of Dynel <sup>1</sup> and rayon	100	4	94
Upholstery fabric	100	2	100
Black wool	90	8	100

NOTE.—The upholstery and black wool employed gave very low spray ratings when the siloxane was applied by the conventional modes of application.

<sup>1</sup> Dynel is a copolymer of acrylonitrile and vinylchloride.

#### Example 8

Equivalent results are obtained when the following siloxanes are employed in the process of Example 7 in conjunction with the following substantive agents.

Siloxane <sup>1</sup> In Mol Percent	Substantive Agent
1. .... 10% ViMeSiO, 10% HSiO <sub>2</sub> /2, 20% MeStSiO and 60% Me <sub>2</sub> SiO.	$\begin{array}{c} \text{Me} \\   \\ \text{H}_2\text{N}(\text{CHCH}_2\text{NH})_{10}\text{H} \end{array}$
2. .... 40% Et <sub>2</sub> SiO and 60% MeHSiO	$\text{HNO}_3$ $\text{HNO}_3\text{-H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_{10}\text{CH}_2\text{CH}_2\text{Cl}$
3. .... 10% tolylmethylsiloxane, 89% Me <sub>2</sub> SiO and 1% Me <sub>2</sub> HSiO.	$\left[ \begin{array}{c} \text{R}''_3 \\   \\ \text{N.HAc} \\   \\ \text{CH}_2 \\   \\ \text{HO-CH}_2\text{CHO} \end{array} \right]_n\text{H}$
4. .... 100% EtMeSiO	$\begin{array}{c} \text{Me} \\   \\ \text{SO}_3\text{H}_2\text{-H}_2\text{N}(\text{CHCH}_2\text{NH})_6\text{H-H}_2\text{SO}_4 \end{array}$

<sup>1</sup> Siloxanes 1 to 3 are copolymers.

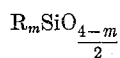
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## Example 9

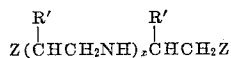
Wool flannel fabric was treated with the siloxane composition of Example 7. The siloxane emulsion was employed in amount to give 2% by weight siloxane based on the weight of the wool fabric. The emulsion was added to a tank of water along with 2% by weight of the polyimine of Example 5 based on the weight of the siloxane and 2% by weight titanium based on the weight of the siloxane, said titanium being added in the form of triethanolamine titanate. The wool fabric was immersed in the treating emulsion and the siloxane was exhausted on the fabric in 12 minutes. The fabric was then removed from the treating bath and cured 9 minutes at 200° F. The spray rating was 100.

That which is claimed is:

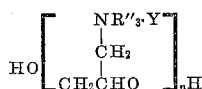
1. A method of depositing a siloxane on a fabric which comprises immersing the fabric in a siloxane-in-water emulsion containing (1) a organo siloxane of the unit formula



in which R is selected from the group consisting of monovalent hydrocarbon radicals, hydroxylated monovalent hydrocarbon radicals and hydrogen atoms and  $m$  has an average value from 1 to 3 inclusive, (2) a non-ionic emulsifying agent and (3) from .2-80% by weight based on the weight of the siloxane of a nitrogen compound selected from the group consisting of polyimines of the formula



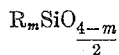
in which Z is of the group consisting of  $NH_2$  groups and chlorine atoms, R' is of the group consisting of hydrogen and methyl radicals and  $x$  has a value of from 4 to 20 inclusive, salts of said polyimines and compounds of the formula



in which R'' is an aliphatic hydrocarbon radical of less than 5 carbon atoms, Y is an acid anion and  $n$  has a value of from 2 to 6 inclusive and thereafter removing the fabric from the water and drying it.

2. A method in accordance with claim 1 wherein the organosiloxane is a methylhydrogensiloxane.

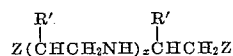
3. A composition of matter consisting essentially of a siloxane-in-water emulsion containing (1) a organosiloxane of the unit formula



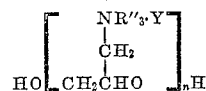
in which R is selected from the group consisting of monovalent hydrocarbon radicals, hydroxylated monovalent hydrocarbon radicals and hydrogen atoms and  $m$  has an average value from 1 to 3 inclusive, (2) a non-ionic

8

emulsifying agent and (3) from .2-80% by weight based on the weight of the siloxane of a nitrogen compound selected from the group consisting of polyimines of the formula



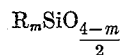
in which Z is of the group consisting of  $NH_2$  groups and chlorine atoms, R' is of the group consisting of hydrogen and methyl radicals and  $x$  has a value of from 4 to 20 inclusive, salts of said polyimines and compounds of the formula



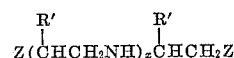
in which R'' is an aliphatic hydrocarbon radical of less than 5 carbon atoms, Y is an acid anion and  $n$  has a value of from 2 to 6 inclusive.

4. A composition in accordance with claim 3 wherein the organosiloxane is a methylhydrogensiloxane.

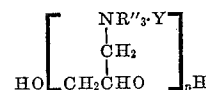
5. A method of depositing a siloxane on a fabric which comprises immersing the fabric in a siloxane-in-water emulsion containing (1) an organosiloxane of the unit formula



in which R is of the group consisting of monovalent hydrocarbon radicals, hydroxylated monovalent hydrocarbon radicals and hydrogen atoms, at least some of the silicon atoms in said siloxane having hydrogen bonded thereto and  $m$  has an average value from 1 to 3 inclusive, (2) a non-ionic emulsifying agent, (3) from .2-80% by weight based on the weight of the siloxane of a nitrogen compound selected from the group consisting of polyimines of the formula



in which Z is of the group consisting of  $NH_2$  groups and chlorine atoms, R' is of the group consisting of hydrogen and methyl radicals and  $x$  has a value of from 4 to 20 inclusive, salts of said polyimines and compounds of the formula



in which R'' is an aliphatic hydrocarbon radical of less than 5 carbon atoms, Y is an acid anion and  $n$  has a value of from 2 to 6 inclusive and (4) an alkanol amine titanate catalyst.

6. A method in accordance with claim 5 in which the organosiloxane is a methylhydrogensiloxane and the alkanol amine titanate is triethanolamine titanate.

No references cited.