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3,065,111

SILANE-SILICONE MIXTURE, METHOD OF PRODUCING THE MIXTURE; TEXTILE TREATED WITH THE MIXTURE; AND METHOD OF IMPREGNATING TEXTILE WITH THE MIXTURE

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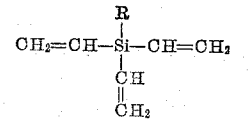
This invention relates to a unique combination of certain silane and silicone polymers and the use of these mixed polymers as a textile finish. More particularly this invention provides mixed polymers of polymerized polyvinylsilanes and polymerized methylsilicones and a process for imparting a durable finish to organic textile fibers.

Organosilicon compounds and polymers have been widely used as textile finishing agents. They have been suggested as water-repellent and stain-resistant finishing agents. They have also been reported to improve abrasion resistance, tear strength and sewability of textiles finished with the organosilicon compounds and polymers. In general, the silicone textile finishes used to impart durable water repellency to fabrics consists of mixtures of two silicones—a monoalkyl silicone and a dialkyl silicone. The dialkyl silicones are relied up to produce the most significant changes in surface characteristics of the textiles, whereas, the monoalkyl silicones having a hydrogen atom attached to the silicon atom produce the durability of the finish that is attainable with such mixtures. A serious weakness of these type finishes is the lack of durability to laundering.

We have found that organosilicon polymers consisting of mixed polymers of a polymerized polyvinylsilane and a polymerized methylsilicone produce outstanding surface finishes on organic textiles and that these new finishes are extremely resistant to removal by laundering and are very resistant to removal by boiling alkaline solutions.

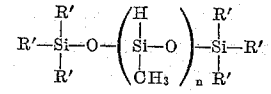
In general, in accordance with this invention, a polyvinylsilane and a methylsilicone are simultaneously polymerized with a peroxide type catalyst in an inert solvent for the monomers and resulting polymers to produce silane-silicone mixed polymers textile finishing agent. The silane-silicone mixed polymers of this invention are applied to textiles by any convenient method such as spraying, immersion, and a conventional textile padding operation. In any case the mixed polymers is fixed on the surface of the textile fibers by heating for a few minutes at an elevated temperature. The silane-silicone mixed polymers finish imparts many desirable new properties to the fibers and textile fabrics made therefrom. Fabrics possess a high degree of water repellency with as little as 0.5% weight add-on of the mixed polymers, and generally possess complete water repellency with 2.0% add-on. Fabrics are given a smooth feel and considerable resistance to abrasion by as little as 0.1% of the mixed polymers. Water-borne stains such as coffee, and ink are repelled by the finish. The tear strength of textiles and especially cellulosic textiles finished with wrinkle resistant and wash-and-wear resins are improved by the silane-silicone finish.

The polyvinylsilanes suitable for use in this invention are compounds with the following structure:



where R is a member of the group of radicals consisting of phenyl, methyl, ethyl, and vinyl.

The methyl silicones suitable for use in this invention have the following structure:



where R′ is a member of the group of radicals consisting of methyl, ethyl, and phenyl, and *n* is an integer ranging from 15 up to about 40. These methyl silicones may be prepared by any suitable method already known to those familiar with silicone synthesis.

The simultaneous polymerization of the polyvinylsilanes and the methyl silicones is carried out by dissolving the organosilicon compounds in a suitable solvent like methyl isobutyl ketone, warming the solution, dissolving a small amount of a peroxy compound, such as benzoylperoxide, and then heating. The polymerization time and temperature are quite variable and range from about 4 minutes at about 116° C. and about 60 to about 120 minutes at 80° C. Intermediate times and temperatures are also suitable, for instance, 30 minutes at 90° C. is good polymerization conditions. The minimum polymerization conditions are about 4 minutes at 80° C. Heating for promotion of polymerization should be terminated as soon as insoluble globules of polymer appear. The polymerized product is ready for application to textiles at this stage. It can be diluted to any desired concentration with more of the inert solvent or it can be emulsified in water with suitable emulsifiers. If the silane-silicone mixed polymers is to be stored for several days before use it should be diluted to about 10% or less concentration or sufficient reducing agent should be added to the solution to destroy the unused peroxide.

Experiments were conducted to determine the necessity of prepolymerizing the polyvinylsilane and methylsilicone. In these experiments it was found that the polyvinylsilane was distilled off if not prepolymerized. Likewise, it was found that it is essential that the methylsilicone be peroxide polymerized, otherwise, the finish was easily removed from the textiles by hot alkaline soap solutions.

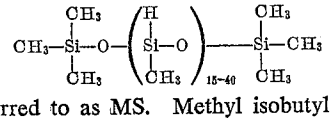
The silane-silicone mixed polymers can conveniently be applied to textiles by conventional textile finishing equipment—the fabric is wet-out on a padder and then heated at an elevated temperature using an oven or heated cans. The heating or curing temperature is important. To insure a finish that is durable to laundering and alkaline solutions it must be cured at about 150° C. or higher temperature for at least five minutes.

The silane-silicone mixed polymers is applicable to both hydrophilic and hydrophobic organic textile fibers. Suitable fibers include cotton, chemically modified cottons, resin finished cottons, rayon, nylon, Dacron, Orlon, wool, and blends of these fibers, and leather. Textiles containing these fibers and treated with the silane-silicone mixed polymers are made highly water repellent with about 1% add-on. Smaller amounts improve tear strength, resistance to abrasion, sewability, and resistance to water-borne stains. Other goods such as paper and glass fabric can be given a water repellent finish with the silane-silicone mixed polymers of this invention.

Catalysts suitable for use in this invention are per-

oxides which readily form free radicals when heated or exposed to light. Thus the catalyst may be any of the peroxides commonly used to promote free radical reactions that are soluble in the solvent used to dissolve the silane and silicone of this invention. Appropriate catalysts include benzoyl peroxide, tert-butyl hydroperoxide, tert-butyl peroxide, and benzoyl butyl peroxide.

The following examples illustrate this invention. The water repellency test used in evaluating the fabrics in this invention is the American Standards for Testing Materials (ASTM) method D583–54. The test for permanency of the silane-silicone mixed polymers finish was that of boiling for one hour in an aqueous solution containing 0.5% laundry soap and 0.2% sodium carbonate. In the examples, the term "part" refers to parts by weight. For convenience tetravinylsilane will be referred to as TVS; phenyl trivinylsilane will be referred to as PTVS; and methylsilicones, having structures of:



will be referred to as MS. Methyl isobutyl ketone will be refered to as MIBK.

EXAMPLE 1

A. *Polymerization of One Part TVS Per One Part MS*

Thirty-six parts of TVS, and 36 parts of MS were dissolved in 48 parts of MIBK. This solution was divided into twelve equal portions of about 10 ml. each and treated as shown in Table I below. The solutions were heated to the indicated reaction temperature and then about 0.7 part (about 1.0% of the weight of the silicon compounds) of benzoyl peroxide was added and the temperature was held constant for the times specified in Table I, then cooled to 27° C.

TABLE I

Solution No.	Reaction temp., ° C.	Reaction time, min.	Appearance of hot polymer solution at end of reaction time	Viscosity of polymer solutions at 27° C. in centipoises
1	27	60	Clear	2.333
2	70	30	do	2.601
3	80	30	do	2.601
4	90	30	White, colloidal	3.707
5	100	30	do	8.856
6	80	60	Slightly turbid, colloidal	2.641
7	80	90	White, colloidal	3.655
8	80	120	do	8.698
9	80	150	White, colloidal with insoluble globules.	8.660
10	80	180	do	8.681
11	80	210	do	8.712
12	80	240	do	8.724

B. *Application of 1:1 Ratio of TVS:MS to Textiles*

Most of the twelve solutions described in Table I were diluted with MIBK and applied to a cotton print cloth so as to be able to determine the durability of the silane-silicone mixed polymers finish to boiling soap and soda solutions. Three percent solutions and 1% solutions were made. The print cloth was padded through the solutions so as to obtain about 80 to 100% wet pickup. The wet fabrics were then placed in a forced draft oven at 165° C. for 10 minutes. The cured fabrics were then rinsed in hot water for 10 minutes and air dried and air equilibrated for about 24 hours. Spray ratings were obtained on the fabrics. The same fabrics were then boiled for one hour in a solution containing 0.5% soap and 0.2% sodium carbonate. After rinsing 10 minutes in hot water and again air drying and equilibrating for 24 hours, the spray rating of each fabric was again obtained. The spray ratings before and after the soap boil are shown in Table II. Analysis of Tables I and II shows that it is necessary to polymerize the silane-silicone mixture by application of heat before it is applied to fabric to get water repellency. The analysis also shows that all the polymer solutions that contained insoluble globules of polymer produced a finish that did not withstand the soap and soda boil; polymer solutions which did not contain insoluble visible globules produced a finish that was very resistant to water rinsing and soap and soda boil.

TABLE II.—DURABILITY OF FINISH ON PRINT CLOTH

Solution used (from Table I)	Concentration of solution used on the fabric, percent	Spray rating	
		After water rinse	After the soap and soda boil
1	3	0	0
3	3	80	70
3	1	50	0
6	3	80	70
6	1	50	50
7	3	80	70
7	1	60	50
8	3	80	70
8	1	70	60
9	3	70	0
9	1	50	0
10	3	70	0
10	1	50	0
11	3	50	0
11	1	50	0
12	3	70	0
12	1	0	0

EXAMPLE 2

Use of One and One-Half Part of TVS Per Four Parts of MS

Seven and one-half parts of TVS and 20 parts of MS were dissolved in 17.3 parts of MIBK to form a clear solution. The solution was heated to 116° C. then 0.3 part of benzoyl peroxide was added. After 4 min. the solution was cooled rapidly to about 27° C. The clear solution was diluted with MIBK to a total weight of 2,750 grams to form a 1% silane-silicone solution. The 1% solution was used to pad six pieces of cotton print cloth. The wet pickup of solution was about 90% in each case. The fabrics were cured at the temperatures and times shown in Table III. The spray ratings and breaking strengths reported in the table were obtained after the fabrics had been boiled one hour in soap and soda solution.

TABLE III.—SOME PROPERTIES OF PRINT CLOTH TREATED WITH A 1% SOLUTION OF SILANE-SILICONE MIXED POLYMERS

Cure time, min.	Cure temp., ° C.	Test results obtained after fabric had been boiled 1 hour in a soap and sodium carbonate solution		
		Spray rating	Breaking strength (lbs.)	Flex abrasion (cycles)
Untreated control fabric		0	45.6	1,230
240	30	50	45.1	1,718
3	90	50	44.1	1,440
4	150	60	40.8	1,516
10	150	70	41.8	1,523
5	160	70	43.0	1,423
10	165	80	43.2	1,513

EXAMPLE 3

Solutions were made of the reagents shown in Table IV. Methyl isobutyl ketone was the solvent in each case. Solutions 2 through 7 contained TVS and MS. Solution 1 contained only TVS while 8 and 9 contained only MS. The purpose of solutions 1, 8, and 9 was to demonstrate the need for both of the silicon compounds in the system. Solution polymerization was carried out at the temperature and time shown in Table IV. After polymerization, the solutions were cooled to about 27° C. and diluted with more MIBK so as to produce a 3% solution with respect to the total silicon containing materials present. Cotton cloth was padded in the solu-

tions and then cured 10 minutes at the indicated temperature. Spray ratings were determined after the cure and again after the fabrics had been boiled for one hour in soap and soda solution.

When TVS was polymerized and used alone the original spray rating was only 50 and it fell to 0 when the fabric was boiled. With MS alone, the original spray rating was 90 and it fell to 0 after the boil. Polymerization of MS improved the durability of this finish, but it still fell to 50 after the boil. Table IV shows that good durability was obtained with the mixed polymers finish when the ratio of the two silicon compounds was varied considerably.

TABLE IV.—DURABLE WATER REPELLENCY OBTAINED WITH SILANE-SILICONE MIXED POLYMERS

Solution No.	Concentration of reagents				Polymerization conditions		Conc. of silicon compound in solution used to treat fabric	Type of cotton fabric treated	Cure conditions		Spray rating	
	TVS, gms.	MS, gms.	MIBK gms.	Benzoyl peroxide gms.	Temp., °C	Time, min.			Time, min.	Temp., °C	After cure, no wash	After 1 hr. soap and soda boil
1	20	0.0	40	0.6	80	90	3	Broadcloth	10	160	50	0
2	50	10	40	0.6	80	90	3	do	10	160	100	70
3	30	30	40	0.6	80	120	3	do	10	160	100	70
4	10	50	40	0.6	80	90	3	do	10	160	100	90
5	5.3	53.3	40	0.6	80	90	3	do	10	160	100	70
6	30	30	40	0.6	80	90	3	Print cloth	10	165	80	70
7	30	30	40	0.6	80	120	3	do	10	165	80	70
8	0.0	30	40	0	27	90	3	Broadcloth	10	165	90	0
9	0.0	60	40	0.6	80	90	3	do	10	160	90	50

EXAMPLE 4

Two parts of phenyltrivinylsilane, four parts of MS and 0.004 part of benzoyl peroxide (0.1% catalyst based upon the total weight of silicon compounds) were dissolved in 3 parts of methyl isoamyl ketone. The solution was heated rapidly until it began to boil (time required about 3 minutes) then it was cooled to about 27° C within five minutes after it had started to boil. The solution remained clear. The solution was then diluted with an additional 193 parts of methyl isoamyl ketone. The silane-silicone solution was used to pad cotton print cloth. The wet fabric was then cured (heated in a forced-air oven to fix the finish) for 10 minutes at 160° C. The print cloth was water repellent, smooth, with good hand and repelled drops of ink.

EXAMPLE 5

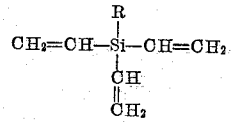
A silane-silicone solution was prepared exactly as described for solution No. 4 in Table IV of Example 3. The solution containing 3% of silicon containing compounds was used to finish a number of fabrics. The fabrics finished were as follows:

(*a*) Acetate rayon
(*b*) Nylon sateen cloth
(*c*) Flame-retardant treated cotton poplin. This fabric had been treated with about 12% THPC-APO flame retardant [Textile Research J. 27, 260–266 (1957)] to make it highly flame resistant.
(*d*) Acrilan cloth
(*e*) Cotton-nylon (50% cotton and 50% nylon)
(*f*) Aminized cotton sheeting (cloth containing 0.5% nitrogen in the form of aminoethyl groups)

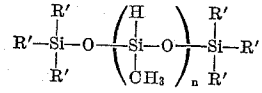
Each fabric was wet out in the MIBK solution, then the excess solution was removed mechanically by passing the wet fabric through two squeeze rolls, and finally the fabrics were heated for 10 minutes at 150° to 160° C. All of the fabrics had a spray rating of 100. After a one hour soap and soda boil, the flame-retardant treated cotton fabrics still had a spray rating of 80.

We claim:

1. A textile finishing agent comprising a liquid mixture of homopolymers of about 5.3 to 50 parts by weight of a polyvinyl silane having the structure:

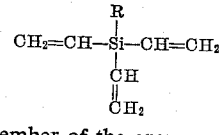


wherein R is a member of the group consisting of phenyl, methyl, ethyl, and vinyl and about from 50 to 10 parts by weight of a methyl silicone having the structure:

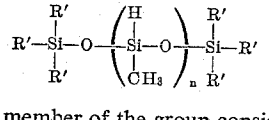


wherein R′ is a member of the group consisting of methyl, ethyl, and phenyl and *n* is an integer of from 15 to 40, said mixture of homopolymers being insufficiently polymerized to exhibit visible insoluble globules of polymer in the liquid.

2. The method of producing a textile finishing agent which comprises simultaneously heating a solution, in an inert solvent and in the presence of a peroxide catalyst, of a mixture comprising about from 5.3 to 50 parts by weight of a polyvinylsilane having the structure:



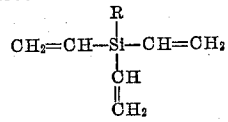
wherein R is a member of the group consisting of phenyl, methyl, ethyl, and vinyl and about from 50 to 10 parts by weight of a methyl silicone having the structure:



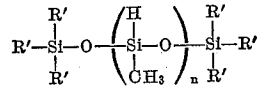
wherein R′ is a member of the group consisting of methyl, ethyl, and phenyl and *n* is an integer of from 15 to 40, said heating being carried out for a period of about from 4 to 120 minutes at a temperature of about from 116° C. to 80° C., and terminating the reaction while the reaction mixture is still liquid and before visible, insoluble globules of polymer have formed, to obtain a liquid mixture of homopolymers of said polyvinyl silane and methyl silicone.

3. A water-repellent, abrasion-resistant, stain-resistant organic textile comprising an organic textile impregnated with a heat-insolubilized mixture of homopolymers of

about from 5.3 to 50 parts by weight of a polyvinyl silane having the structure:



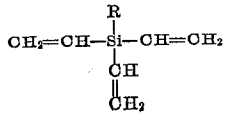
wherein R is a member of the group consisting of phenyl, methyl, ethyl, and vinyl and about from 50 to 10 parts by weight of a methyl silicone having the structure:



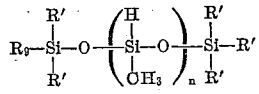
wherein R′ is a member of the group consisting of methyl, ethyl, and phenyl and *n* is an integer of from 15 to 40, said mixture of homopolymers before application to the textile and before insolubilization having been a liquid mixture insufficiently polymerized to exhibit visible, insoluble globules of polymer in the liquid.

4. The textile product of claim 3 wherein the insolubilized mixture of homopolymers is present in about from 0.5 to 2.0% by weight of the fabric.

5. The method of producing a water-repellent, abrasion-resistant, stain-resistant organic textile which comprises impregnating an organic textile with a solution in an inert solvent of a liquid, incompletely polymerized mixture of homopolymers of about from 5.3 to 50 parts by weight of a polyvinyl silane having the structure:



wherein R is a member of the group consisting of phenyl, methyl, ethyl, and vinyl and about from 50 to 10 parts by weight of a methyl silicone having the structure:



wherein R′ is a member of the group consisting of methyl, ethyl, and phenyl and *n* is an integer of from 15 to 40, said mixture of homopolymers being incompletely polymerized to be still free from visible, insoluble globules of polymer, and curing the impregnated fabric at an elevated temperature to dry the fabric and to insolubilize the mixture of homopolymers.

6. The method of claim 5 wherein the textile is impregnated with an amount of solution to provide about from 0.5 to 2.0 by weight of mixed homopolymers in the dried product.

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