United States Patent

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[33] **Japan**
[31] **42/1877**

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[54] **PROCESS FOR GIVING SHAPE-FITTING PROPERTY ON A GARMENT KNITTED WITH FILAMENT YARNS**
10 Claims, No Drawings

[52] **U.S. Cl.** ..... **117/139.4,** 117/139.5 A, 117/161 ZA
[51] **Int. Cl.** **D06m15/66,** D06m 15/72
[50] **Field of Search** ..... 117/139.4, 139.5 A, 161 ZA, 76 T, 121, 126 GS, 138.8 N; 252/8.6; 260/825

[56] **References Cited**
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ABSTRACT: A method and composition for imparting wash durable, shape-fitting properties to a filament yarn knitted garment, whereby a primer comprising a monomer or a prepolymer having the general formula R—Si—X_3, wherein R is a radical having a double bond and X is a silicon atom-bonding organic radical, and a polyorganosiloxane is applied to said garment.

PROCESS FOR GIVING SHAPE-FITTING PROPERTY ON A GARMENT KNITTED WITH FILAMENT YARNS

BACKGROUND OF THE INVENTION

1. Field of Invention

This invention relates to a process for imparting shape-fitting properties to a filament yarn knitted garment, such as hosiery, body stockings, tights, panties, gloves, or brassieres.

2. Description of Prior Art

Garments prepared from knitted filament yarns, such as hosiery, body stockings, tights, panties, gloves or brassieres, will often wrinkle during wear thereby causing the garment to only partially contact the body of the wearer. This places a greater load on the wearer's body at the wrinkling points, which is frequently sufficient to suppress the circulation of the blood and leave unsightly marks when the garment is worn directly on the body without some protective undergarment. To resolve these difficulties, it has been proposed to use high-twisted yarns, or crimp yarns, to impart elasticity to the garment. The fitting properties based on the elasticity of the high-twisted yarns, or crimp yarns, however, is insufficient to prevent the high-contractile forces and partial strains which suppress blood circulation.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a process for rendering shape-fitting properties to a garment knitted with filament yarns which can be worn directly on the wearer's body without a protective undergarment.

It is another object of this invention to provide a process for using specific chemicals to render wash durable shape-fitting properties to a garment knitted with filament yarns.

It is a further object of this invention to provide a process for using specific chemicals to provide wash durable, shape-fitting properties to a garment knitted with twisted filament yarns.

These and other objects have now herein been obtained by treating the knitted garment with a monomer or prepolymer having the general formula $(R—Si—X_3)_q$, wherein R is a radical having a double bond, X is a silicon-atom-bonding organic radical, and q is an integer from 1 to 5, and a polyorganosiloxane.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

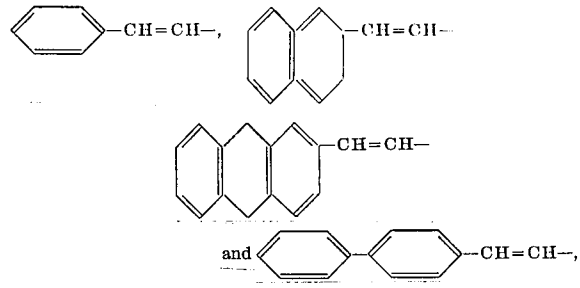
Garments knitted with filament yarns are commonly used in preparing ladies' hosiery. For this purpose, filament yarns of 10 to 30 total deniers, and especially 15 total deniers, e.g., 5 denier × 3 fil., 7.5 denier × 2 fil., or 15 denier × 1 fil. are used. The filament yarns may be twisted, such as in alternate S-twist yarns, and Z-twist yarns, to make the knitted courses. Also, ply yarns having S-twist yarns and Z-twist yarns are frequently used. A crimp yarn which is produced by twisting heat-set detwisting, or by knipping, may be used. A crimping yarn made of conjugate yarn may also be used for knitting the garment to be treated by the process of this invention. Even nontwist yarns may be used to impart a slight stress to the knitted garment. The garment may be knitted with a circular knitting machine, a flat knitting machine, or a warp knitting machine.

The knitted fabric used for this invention is shaped into a garment, such as ladies' seamless hosiery, tights produced with a circular knitting machine, body stockings produced with a circular knitting machine, panties, gloves, etc.

Although it has been proposed to provide water repellency to the fibers by treating them with emulsions of silicon resins, such as methyl hydrogen polysiloxane dispersed in water, or by dipping the yarns into solutions of emulsions of methyl-polysiloxane and methyl-hydrogen polysiloxane mixtures and then heat-drying, these processes do not impart wash durable fitting properties to the knitted filament yarns.

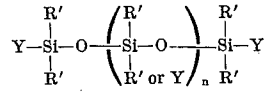
In accordance with the present invention, wash durable fitting properties are imparted to the garment by using a primer comprising:

A. A monomer or prepolymer having no more than five units, having the general formula $R—Si—X_3$, wherein R is selected from the group of $CH_2=CH—$, $CH_3—CH=CH—$,



X is selected from a silicon-atom-bonding organic radical such as $O—CH_3$, OC_2H_5, OC_3H_7, OC_4H_9, OC_5H_{11}, OC_6H_{13}, OC_7H_{15}, OC_8H_{17}, 2-aminoethyl, 3-aminopropyl, 4-aminobutyl and 5-aminophenyl, and

B. a polyorganosiloxane having the general formula



wherein Y is OH or Cl, and more than two Y's are in the formula but the ratio of Y/R' is less than 0.1;

n is an integer of more than 5, preferably from 100 to 3000;

R' is an alkyl group (methyl, ethyl, tertiary-butyl, etc.), an alkenyl group (vinyl, allyl, hexenyl, etc.), a cycloaliphatic hydrocarbon group (cyclohexyl, cyclopentyl, etc.), an alkylaryl group (benzyl, phenylethyl, etc.) or an aryl group (phenyl, toluyl, xylyl, naphthyl, etc.).

The primer (A) and polyorganosiloxane (B) may be applied to the garment knitted with filament yarns in a one-step process by using the mixture of primer (A) and polyorganosiloxane (B) or by sequentially passing the garment through each of (A) and (B). In a two-step process, the garment is dipped into the primer (A) and dried and then dipped into a solution of the polyorganosiloxane (B).

The polyorganosiloxane solution may also contain a modifier such as a monomer or a prepolymer having no more than five units, of the following general formula:

When Y in the polyorganosiloxane is OH, the formulated modifier is:

$$R''—Si—Z_3$$

wherein R'' is selected from the group consisting of an alkyl group (methyl, ethyl, butyl, tertiary-butyl, etc.), an alkenyl group (vinyl, alkyl, hexenyl, etc.), cycloaliphatic hydrocarbon groups (cyclohexyl, cyclopentyl, etc.), an alkyl-aryl group (benzyl, phenylethyl, etc.), and an aryl group (phenyl, toluyl, xylyl, naphthyl, etc.

Z is selected from the group consisting of methoxy, ethoxy, propoxy, iso-propoxy, butoxy, 1-butoxy, and acetyl.

When Y in the polyorganosiloxane used is Cl, the general formula is:

$$R''—C=NOH$$

wherein R'' is the same as defined above.

When a two-step process is used, the solution of the polyorganosiloxane may contain an accelerant together with the modifier.

When Z of the modifier is an acetyl group, the accelerant is selected from the group of dibutyl-tin-diacetate, dibutyl-zinc-diacetate, dibutyl-lead diacetate.

When any of the other modifiers are used, the accelerant may be a salt of an organic carboxylic acid such as lead, tin, antimony, iron, or a barium salt of linoleic acid, stearic acid, acetic acid, or butylic acid.

When the modifier is R''—C=NOH, the accelerant may be an organic amine such as di-n-hexamine.

A nonaqueous solvent such as benzene, toluene, xylene, petroleum ether, perchloroethylene, or chlorobenzene may be used for mixing the polyorganosiloxane, the modifier, and the accelerant.

The quantity of the polyorganosiloxane in the mixture is 70 to 90 weight percent, and the quantity of the modifier is 20 to 1 weight percent. When more than 20 weight percent of the modifier is used, the reaction is not uniform, and when less than 1 percent of the modifier is used, the desired effect is reduced. The quantity of the accelerant is 5 to 0.1 weight percent. When more than 5 weight percent is used, the reaction is too fast and when less than 0.1 weight percent is used, the desired effect is reduced.

The solution, diluted with the nonaqueous solvent, is applied to the garment by dipping or spraying. It is preferably to treat the garment so that each crossing part of knitted warp of filament yarns is immersed. The concentration of the polyorganosiloxane solution is preferably between about 0.1 to 3 weight percent. In amounts of less than 0.1 weight percent, the desired effect is reduced. When more than 3 weight percent of polyorganosiloxane is used, the softness of the garment may be lost.

When the two-step procedure is used, the garment is first pretreated with a primer (A). For this purpose, a solution of 1–20 weight percent of the primer is prepared with an organic solvent such as methanol, perchloroethylene, or petroleum ether. If the concentration of the primer is higher than 20 percent, the garment tends to lose its softness. A polymerization catalyst such as triethoxy-titane, may be used when the solution is intended to be dipped or sprayed onto the garment.

The treated garment is dried at a relatively low temperature, such as between room temperature and 50° Centigrade. During the treatment, the primer is polymerized and is adhered to the filament yarns of the garment. In selecting the particular primer, therefore, it is necessary to consider the affinity of the particular primer for the particular filament yarn.

After the pretreatment, the garment is treated with a nonaqueous solution of a polyorganosiloxane containing the modifier and the accelerant. The polyorganosiloxane and the modifier is reacted on the filament to form a slippery covering over the polymerized primer covered filament yarn.

When a one-step procedure is used, the garment is treated with the nonaqueous solution of the primer and the organosiloxane diluted with the nonaqueous solvent containing, if necessary, the modifier or the accelerant by dipping or spraying the garment with the solution so as to immerse each of the crossover parts of the filament yarn.

The garment treated with the solution is dried at a relatively low temperature such as between about room temperature and 50° Centigrade. In the one-step process, the primer is partially polymerized and adhered to the filament yarn, and the polyorganosiloxane is reacted so as to adhere to the product so as to make the filament yarn slippery. This slipperiness is wash durable.

The shape-fitting properties of the garment treated by the process of the present invention is imparted by the slippery movement of the filament yarns which reduces the tensile strength built up by partial contacts with the body. This shape-fitting characteristic can be demonstrated by the following test procedure.

A hosiery knitted with a circular knitting machine using twisted nylon filament of 5 d. × 3 fil. (knitted by alternate S-twist and Z-twist yarns) are treated as follows:

The shape-fitting properties of the hosiery treated by both the one-step and two-step processes were measured by observing the degree of wrinkles appearing at the ankles and knees of the garments when worn by 10 different ladies. The degree of wrinkles are classified in the following 10 types.

Shape-Fitting Property	Degree Of Wrinkling Produced Upon Bending The Leg
10	No wrinkling is found for any person.
9	No wrinkling is found for 9 of the 10 persons.
8	Wrinkling is found for 2 to 4 persons but the wrinkles readily disappear.
7	Wrinkling is found for 2 to 4 persons but the wrinkles disappear slowly.
6	Wrinkling remains for 2 to 4 persons.
5	Degree of wrinkling is too high.
4	Wrinkling remains for 5 to 7 persons.
3	Degree of wrinkling is too high.
2	Slack and wrinkle remain for all 10 persons.
1	Degree of slack and wrinkle is too high.

EXAMPLE

Hosiery knitted with a circular knitted machine by using each twisted nylon filament yarn of 5d. × 3 fil. was treated by the two-step process or the one-step process using the following solutions, and dried at 40° Centigrade. The shape-fitting properties of each hosiery treated by said process is shown in the table.

Treatment	Shape-fitting property: No washing	Shape-fitting property: After washing with 5% of soap solution for 5 minutes
(1)—— No treatment. (Control.)	2	1
(2)—— 0.1% perchloroethylene solution of: (B) polydimethylsilanol (85%). (C) methyltriacetoxysilane (10%). (D) dibutyltindiacetate (5%). (Control.)	8	3
TWO-STEP PROCESS		
(3)—— 1. 1% perchloroethylene solution of: (A) triethoxyvinylsilane. 2. Treating with (2).	10	10
(4)—— 1. Treating with (3)-1. 2. 0.1% perchloroethylene solution of: (B) polydimethylsilanol (85%). (C) triethoxymethylsilane (15%).	9	9
(5)—— 1. Treating with (3)-1. 2. 0.1% perchloroethylene solution of: (B) polydimethyloxanechloride (85%). (C) acetoxim (10%). (D) di-n-hexylamine (5%).	9	9
(6)—— 1. 1% petroleum benzene solution of: (A) triisopropyloxyvinylsilane. 2. 0.1% petroleum benzene solution of: (B) polyphenylmethylsilane (85%). (C) methyltriacetoxysilane (15%).	8	8
(7)—— 1. 1% petroleum benzene solution of: (A) triisopropyloxyvinylsilane. 2. 0.1% petroleum benzene solution of: (B) polyphenylmethylsilanol (85%). (C) triisopropyloxyethylsilane (12%). (D) barium butylate (3%).	8	8
(8)—— 1. A% petroleum benzene solution of: (A) triisopropyloxyvinylsilane. 2. 0.1% petroleum benzene solution of: (B) polyphenylmethylsiloxanechloride (85%). (C) diethylketoxime (15%).	8	8
(9)—— 1. 1% petroleum ether solution of: (A) tri-t-butyloxyallylsilane. 2. 0,1% petroleum ether solution of: (B) polydiphenylsilanol (85%). (C) triacetoxyphenylsilane (15%).	8	8
(10)—— 1. 1% petroleum ether solution of: (A) tri-t-butyloxyallylsilane. 2. 0.1% petroleum ether solution of: (B) polydiphenylsiloxanechloride (85%). (C) diphenylketoxime (12%). (D) dibutyl-tin-diacetate (3%).	7	7
(11)—— 1. 1% xylene solution of: (A) tri-amino-propylvinylsilane. 2. 0.1% xylene solution of: (B) polyvinylmethylsilanol (85%). (C) triacetoxyvinylsilane (15%),	10	10
(12)—— 1. 1% xylene solution of: (A) tri-amino-propylvinylsilane. 2. 0.1% xylene solution of: (B) polyvinylmethylsilanol (85%). (C) tripropyloxyoinylsilane (15%).	9	9
(13)—— 1. 1% xylene solution of: (A) tri-amino-propylvinylsilane. 2. 0.1% xylene solution of: (B) polydiethyl-silanol (85%). (C) triacetoxyethylsilane (12%). (D) dibutyl-zinc-diacetate (3%).	10	10

Treatment		Shape-fitting property: No washing	Shape-fitting property: After washing with 5% of soap solution for 5 minutes
(14)	1. 1% xylene solution of: (A) tri-amino-propylvinylsilane. 2. 0.1% xylene solution of: (B) polydiethylsilanol (85%). (C) triethoxyallylsilane (15%).	9	9
(15)	1. 1% toluene solution of: (A) triethoxy-styrylsilane. 2. 0.1% toluene solution of: (B) polycyclohexylsilanol (85%). (C) triacetoxybutylsilane (15%).	8	8
	ONE-STEP PROCESS		
(16)	0.1% petroleum benzene solution of: (A) triethoxyvinylsilane (10%). (B) polydimethylsilanol (85%). (C) triethoxymethylsilane (5%).	9	9
(17)	0.1% petroleum benzene solution of: (A) triisopropyloxyvinylsilane (15%). (B) polyphenylmethylsilanol (85%).	9	9
(18)	0.1% petroleum benzene solution of: (A) triethoxyallylsilane (15%). (B) polydimethylsilanol (85%).	9	9
(19)	0.1% petroleum benzene solution of: (A) triisopropyloxyallylsilane (10%). (B) polyphenylmethylsilanol (75%). (C) triisopropyloxyethylsilane (5%).	8	8
(20)	0.1% perchloroethylene solution of: (A) triethoxystyrylsilane (15%). (B) polydimethylsilanol (85%).	9	8
(21)	0.1% xylene solution of: (A) tri-aminopropylvinylsilane (15%). (B) polydimethylsilanol (85%).	9	9
(22)	0.1% xylene solution of: (A) tri-aminopropylallylsilane (15%). (B) polyphenylmethylsilanol (85%).	8	8
(23)	0.1% xylene solution of: (A) tri-4-aminobutylstyrylsilane (15%). (B) polydiphenylsilanol (85%).	8	8

Stress-strain Diagram

In order to demonstrate the changes of physical properties of the hosiery, stress-strain diagrams were measured by the tension tester for the samples of (1), (2) control (3), (5), (6) and (10) as listed above.

Conditions:	
stretch rate	10 cm./min.
recording rate	20 cm./min.
test sample of hosiery	20 cm. × 10 cm.
gripping width	5 cm.
elongation ratio	max. 50%
repeating turns	2 turns
full scale	2 kg.

TABLE II.—FIRST STRETCHING-SHRINKING S-S DIAGRAM

	Elongation, percent	Treatment stated in Table I, g. (1)	(2)	(3)	(5)	(6)	(10)
Stretching	10	30	20	10	10	10	10
	20	160	100	50	80	90	80
	30	300	220	170	205	210	220
	40	440	380	290	330	320	350
	50	600	530	410	460	440	510
Shrinking	40	185	190	160	190	190	200
	30	55	60	50	70	70	70
	20	10	10	10	10	10	10
	10	0	0	0	0	0	0

TABLE III.—FIRST STRETCHING-SHRINKING S-S DIAGRAM

	Elongation, percent	Treatment stated in Table I, g. (1)	(2)	(3)	(5)	(6)	(10)
Stretching	10	0	0	0	0	5	5
	20	50	40	20	40	40	40
	30	200	180	130	160	160	170
	40	380	320	160	300	280	320
	50	580	530	410	460	430	510
Shrinking	40	170	180	160	180	180	190
	30	50	50	50	60	60	60
	20	10	10	10	10	10	10
	10	0	0	0	0	0	0

TABLE III. FIRST STRETCHING-SHRINKING S-S DIAGRAM

These tests show that the tension strength of these samples (3), (5), (6), (10) treated by this invention under stretching were extremely low in comparison with those of samples (1) or control sample (2). It was also found that the size of the hysteresis loop of the S—S diagram of the samples (3), (5), (6) and (10) treated by this invention, were extremely small in comparison with those of samples (1) and control sample (2).

Moreover, the differences in the hysteresis loop in the First stretching-shrinking and the Second stretching-shrinking were minor.

The results of the stress-strain diagram measurements show that each hosiery treated by (3), (5), (6) and (10) of this invention has good shape characteristics, good softness and elasticity, which latter characteristics determine the shape-fitting properties.

It should be understood that numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

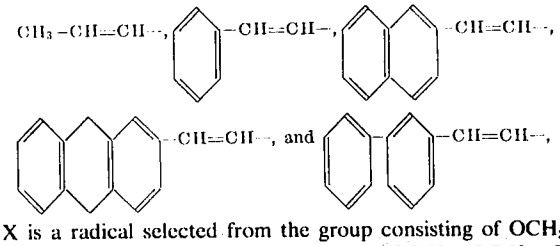
What is claimed and intended to be covered by Letters Patent is:

1. A process for imparting good shape-fitting characteristics to a filament yarn knitted garment, which comprises applying to said garment a combination of:

A. a primer of the general formula:

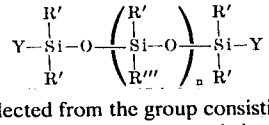
$$(R—Si—X_3)_q$$

wherein R is selected from the group consisting of $CH_2=CH—$,



X is a radical selected from the group consisting of OCH_3, OC_2H_5, OC_3H_7, OC_4O_8, OC_5O_{11}, OC_6H_{13}, OC_7H_{15}, OC_8H_{17}, 2-aminoethyl, 3-aminophenyl, 4-aminobutyl, and 5-aminophenyl, and q is an integer of from 1–5;

B. a polyorganosiloxane having the general formula:



wherein Y is selected from the group consisting of OH and Cl and R''' is selected from the group consisting of R' and Y, and wherein the ratio of Y/R' is less than 0.1;

n is an integer of more than 5;

R' is selected from the group consisting of an alkyl group, an alkenyl group, a cycloaliphatic hydrocarbon group, an alkylaryl group and an aryl group.

2. The process of claim 8, wherein said garment is first immersed in A, dried and immersed in B.

3. The process of claim 1, wherein said garment is immersed into an admixture of A and B.

4. The process of claim 1, wherein n in the formula of B is an integer of from between 100 and 3000.

5. The process of claim 8, wherein said combination contains a modifier such that when Y in the polyorganosiloxane is OH, said modifier is characterized by the formula:

$$(R'—Si—Z_3)_q$$

wherein R'' is selected from the group consisting of an alkyl group, an alkenyl group, a cycloaliphatic hydrocarbon group,

an alkyl-aryl group, an aryl group, Z is selected from the group consisting of methoxy, ethoxy, propoxy, isopropoxy, butoxy, 1-butoxy, and acetyl, and wherein q is an integer of from 1 to 5;

when Y in the polyorganosiloxane is Cl, said modifier is characterized by the formula:

$$R''—C=N—OH$$

wherein R'' is the same as defined above.

6. The process of claim 5, wherein said garment is first immersed in (A), dried and then immersed in an admixture of (B), said modifier, and an accelerant such that when Z of said modifier is an acetyl group, the accelerant is selected from the group consisting of dibutyl-tin-diacetate, dibutyl-zinc-diacetate, and dibutyl-lead-diacetate,

when Z of said modifier is selected from the group consisting of methoxy, ethoxy, propoxy, isopropoxy, butoxy, and 1-butoxy, the accelerant is selected from the group consisting of an organic carboxylic acid salt of a metal selected from the group consisting of lead, tin, antimony, iron and barium, and when said modifier is R'—C=NOH, said accelerant is an organic amine.

7. The process of claim 6, wherein said metal salt is a metal salt of linoleic acid, stearic acid, acetic acid, or butylic acid.

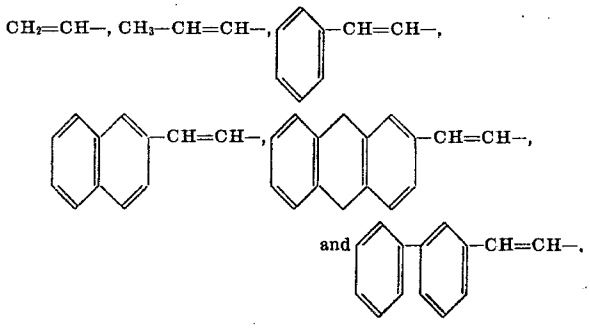
8. The process of claim 1, wherein said primer is in the form of a nonaqueous solution.

9. A process for producing a garment having wash-durable, shape-fitting properties which comprises applying to said garment a combination of:

A. a primer of the general formula:

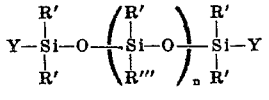
$$(R—Si—X_3)_q$$

wherein R is selected from the group consisting of



X is a radical selected from the group consisting of OCH_3, OC_2H_5, OC_3H_7, OC_4O_8, OC_5O_{11}, OC_6H_{13}, OC_7H_{15}, OC_8H_{17}, 2-aminoethyl, 3-aminophenyl, 4-aminobutyl and 5-aminophenyl, and q is an integer of from 1–5;

B. a polyorganosiloxane having the general formula:



wherein Y is selected from the group consisting of OH, Cl and R''' is selected from the group consisting of R' and Y and wherein the ratio of Y/R' is less than 0.1;

n is an integer of more than 5;

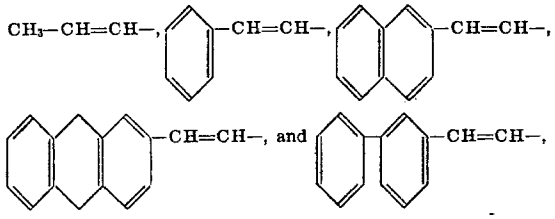
R' is selected from the group consisting of an alkyl group, an alkenyl group, a cycloaliphatic hydrocarbon group, alkylaryl group, and an aryl group.

10. A process for imparting good shape-fitting characteristics to a filament yarn knitted garment, which comprises: applying to said garment a combination of:

A. 20 to 1 weight percent of a primer in a nonaqueous solvent, said primer having the general formula:

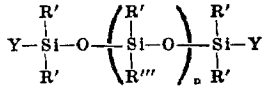
$$(R—Si—X_3)_q$$

wherein R is selected from the group consisting of $CH_2=CH—$,



X is a radical selected from the group consisting of OCH_3, OC_2H_5, OC_3H_7, OC_4O_8, OC_5O_{11}, OC_6H_{13}, OC_7H_{15}, OC_8H_{17}, 2-aminoethyl, 3-aminophenyl, 4-aminobutyl, and 5-aminophenyl, and q is an integer of from 1–5;

B. 70 to 90 weight percent of a polyorganosiloxane in a nonaqueous solution, said polyorganosiloxane having the general formula:



wherein Y is selected from the group consisting of OH or Cl and R''' is selected from the group consisting of R' or Y, and wherein the ratio of Y/R' is less than 0.1;

n is an integer of more than 5;

R' is selected from the group consisting of an alkyl group, an alkenyl group, a cycloaliphatic hydrocarbon group, an alkylaryl group and an aryl group.

* * * * *