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[54] **PROCESS FOR IMPARTING HIGH-ELASTIC RECOVERY TO EXTENSIBLE KNITTED OR WOVEN FABRICS AND PRODUCT OBTAINED**

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[30] **Foreign Application Priority Data**

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[51] Int. Cl.D06m 15/66

[58] Field of Search117/161 ZA, 138.8 A, 138.8 E, 117/138.8 F, 138.8 N, 138.8 PV, 139.5 A; 252/8.6; 260/825

[56]

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[57]

ABSTRACT

The present invention relates to a process for imparting high-elastic recovery to extensible knitted or woven fabrics by treating the fabric with an organic solution of low-viscosity containing a hydroxy-terminated dimethylpolysiloxane, a methylhydrogen polysiloxane and an organometallic catalyst.

9 Claims, No Drawings

PROCESS FOR IMPARTING HIGH-ELASTIC RECOVERY TO EXTENSIBLE KNITTED OR WOVEN FABRICS AND PRODUCT OBTAINED

BACKGROUND OF THE INVENTION

Conventional processes are known for producing waterproof fabrics by treating fabrics having relatively low extensibility with organopolysiloxanes. For example, British Pat. No. 1,077,190 describes a process for producing waterproof fabrics by treating a fabric with a highly viscous solution of organopolysiloxanes having a viscosity of from 1,000 to 100,000 c.p.s. In this process, because of the high viscosity of the solution, the interfiber voids on the surface are filled up with the solution, which accordingly can not penetrate sufficiently deeply into the interior of the fabric. In addition, for the purpose of producing waterproof fabrics, the fabric used should have a relatively low extensibility.

SUMMARY OF THE INVENTION

It has now unexpectedly been discovered that the elastic recovery of knitted or woven fabric having a relatively large extensibility can be enhanced without the deminution of extensibility while the elastic recovery of the fabric remains substantially unchanged in both dry and wet states by treating such fabric with a low-viscous solution of organopolysiloxanes such as hydroxy-terminated dimethylpolysiloxane and methylhydrogen polysiloxane dissolved in a suitable organic solvent, said solution uniformly penetrating in an amount of from 1 to 5 percent (as solid) by weight of fabric into the fabric.

An object of the present invention is therefore to provide a process for imparting extensible knitted or woven fabrics with high-elastic recovery in both dry and wet states.

Further object of the present invention is to provide such improved fabrics.

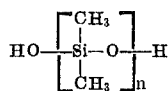
According to the present invention, we provide a process for imparting extensible knitted or woven fabrics with high-elastic recovery, which comprises treating the fabric with an organic solution having a viscosity of less than 400 c.p.s. and containing a hydroxy-terminated dimethylpolysiloxane, methylhydrogen polysiloxane and an organic metal catalyst so that said hydroxy-terminated dimethylpolysiloxane and methylhydrogen polysiloxane can be deposited in an amount of 1 to 5 percent (as solid) by weight of fabric in said fabric, and curing the same at a temperature of from 120° to 200° C.

The knitted or woven fabrics which may be used for the purpose of the present invention have preferably an extensibility of more than 20 percent and include e.g., those composed of textured yarns made of synthetic fibers such as fibers of polyamide, polyester, polyacrylonitrile, polyolefin, polyvinylalcohol etc. Preferred examples of "textured yarns" include crimped yarns such as twist-set-untwist yarns, false twist yarn, stuffer box-treated yarn, edge-crimped yarn, air-jetted yarn and mixtures thereof.

The term "extensibility" used in this specification denotes the percentage of elongation of a sample piece having a width of 5 cm. and a length of 10 cm. when burdened with a load of 1.5 kg. based on the original length of the sample piece.

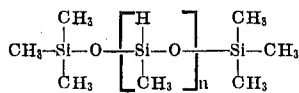
The treating solution used for the process of the present invention may have the following composition:

1. A hydroxy-terminated dimethylpolysiloxane having the following general formula:



in which n is an integer of not less than 500.

2. A methylhydrogen polysiloxane having the following general formula:



in which n is an integer from 15 to 50.

3. An organometallic catalyst, for example, zinc caprylate, tin caprylate, zirconium caprylate, dibutyl tin dilaurate, dibutyl tin dicaprylate, dibutyl tin diacetate, dibutyl tin oxide, alkyl titanate, zinc naphthenate, tin naphthenate, zirconium naphthenate, ferric naphthenate, cobalt naphthenate, zinc formate, zirconium formate, zinc acetate, zirconium acetate etc.

The foregoing components are dissolved in an organic solvent in which the organopolysiloxanes are soluble and which does not deteriorate the texture of the fabric and is inactive to said substances. Preferred examples of organic solvents which may be used for the purpose of the present invention include hydrocarbons having carbon atoms of not more than 10 such as petroleum benzene, gasoline, benzene, toluene, xylene, trichloroethylene, perchloroethylene and ethylacetate.

Further, better results may be obtained by adding suitable additives such as e.g., sodium alcoholate, ester silane, polyalkyl silicate etc. These additives serve to improve the elastic recovery and washability of the final products because they are capable of cross-linking with aforesaid polysiloxanes so as to increase the degree of the polymerization.

Sodium alcoholates are represented by the general formula: RONa , in which R is an alkyl group having less than five carbon atoms. Polyalkyl silicate is a polymer obtained by partially hydrolyzing organosilicates represented by the general formula: $(\text{RO})_n\text{Si}$, in which R is an alkyl group having less than five carbon atoms. Ester silanes are represented by the general formula:

$\text{R}_n\text{Si}(\text{OR}')_{4-n}$, in which R is an alkyl group having less than five carbon atoms and R' is an alkyl group having less than five carbon atoms, and n is an integer of from 1 to 3.

The treating solution of the present invention must be applied to the fibers uniformly, and for this purpose, the dimethylpolysiloxane of the present invention should be dissolved in the organic solvent so as to give a low viscosity. It is essential that the viscosity of the treating solution at 20° C. used in the present invention is less than 400 c.p.s. (as measured by using a conventional rotary viscometer [type BL available from Tokyo Keiki Seizo-sho. K.K., Japan]). If the viscosity is higher than that level, the liquid is liable to remain only the surface of the fabric, thus covering the interfiber voids so that it hardly is possible to obtain the desired elastic recovery. The preferred blending proportions of the components are for example as follows:

Five to 30 (preferably 10 to 25) weight parts of methylhydrogen polysiloxane and 0.1 to 5 weight parts of organometal catalyst per 100 weight parts of dimethyl polysiloxane. The organic solvent should be used in sufficient amounts so that the liquid viscosity will stay below 400 c.p.s.

There are various methods for applying the treating solution to the fabric, but it is advantageously effected e.g., either by immersing the fabric in the treating solution and then squeezing it, or by coating or spraying the solution to the fabric. The amount of deposition of the organopolysiloxanes should be 1.0 to 5.0 percent by weight of the fabric. If such amount is less than 1.0 percent, unsatisfactory elastic recovery may be obtained, while if it is more than 5.0 percent, the feel of and extensibility of the fabric may be deteriorated.

After treating the fabric, it is dried e.g., at 50° to 120° C. under lowest possible tension to remove the organic solvent. The fabric is then cured e.g., at 120° to 200° C. under lowest possible tension thereby effecting the cross-linkage of the organopolysiloxanes with the fibers and the reaction between each of the organopolysiloxanes. It is desirable to treat the fabric under minimum tension. Such low-tension treatment will permit the extensibility prior to the treatment to be carried over to the resultant article.

The article thus obtained has a high-elastic recovery never seen in conventional bulky articles and its elasticity can be equal to that of elastomer fibers. It is thus possible to obtain articles having high-elastic recovery being equal to that of the elastomer fibers by subjecting extensible fabric to the treatment according to the present invention. Articles thus obtained are free from deterioration of color fastness and washability, and can minimize production costs.

The following nonlimitative examples illustrate the invention.

EXAMPLES

In the examples, the samples were cured by means of a conventional short-loop baking machine (available from Hirano Kinzoku Kogyo K.K., Japan). The extensibility and elastic recovery were determined in the following manner:

1. Extensibility:

The extensibility was determined by using a tensile tester, Autograph P-100 (available from Shimadzu Seisakusho, K.K., Japan) under the following conditions:

Weight of Load	1,500 g.
Length of sample	10 cm.
Width of sample	5 cm.
Tensile speed	10 cm./min.
Chart speed	20 cm./min.

2. Elastic recovery:

A similar tester and samples to those described above were used for determining the elastic recovery. The sample was loaded with a suitable load so as to stretch the sample to a length of 80 percent of the elongation, which was obtained when loaded with a load of 1,500 grams. The sample was left for 1 minute. The sample was relaxed and left for 3 minutes in relaxed state, (without tension). The elastic recovery rate is the percentage of the recovery of the elongation during the relaxed state and can be defined as follows:

Elastic recovery rate = $(c/b) \times 100$ in which b is the length by which the sample was stretched and c is the length by which the sample was recovered (and $a+b-c$ is the length of the sample after being stretched and then retained in relaxed state for 3 minutes without tension, where a is the length of the prestretched sample).

3. The extensibility and elastic recovery in wet state were determined in a similar manner to that described above after the removal of the water content of the sample, which has been immersed in water for 10 minutes by using a filter paper.

EXAMPLE 1

Two-stage interlock fabric (jersey) and twill-knitted fabric knitted by using nylon bulky yarn (70 deniers/2 filaments) were respectively immersed in a solution having the following composition (viscosity: 40 c.p.s.) and were squeezed to give polysiloxanes (as solid) amounting to 0.5%, 1.0%, 3.0%, 5.0%, and 7.0% by weight of the fabric respectively:

Composition of the solution: part by weight

Dimethyl polysiloxane	2.7
Methylhydrogen polysiloxane	0.3
Phenyltriethoxysilane	0.03
Dibutyl tin dilaurate	0.03
Trichloroethylene	96.94

The trichloroethylene was removed off by heating at 80° C. The fabric was then cured by using a short-loop baking machine at 155° C. for 3 min. under lowest possible tension.

The jersey and twill thus obtained had the extensibility and elastic recovery values shown in tables 1 and 2, respectively.

Key to Tables

- A. Amount of polysiloxane deposited as solid (percent by weight of the fabric)
- B. Extensibility
- C. Elastic recovery (in dry state)
- D. Elastic recovery (in wet state)
- E. Antipilling property (determined as class)

TABLE 1 (2-stage interlock jersey)

A	0	0.5	1.0	3.0	5.0	7.0
B	61.1	242.0	227.1	209.0	184.1	81.9
C	78.0	93.5	93.8	94.0	94.0	94.0
D	74.1	75.2	91.2	92.7	94.0	94.0
E	1	1	4	5	5	5

TABLE 2 (Twill knitted fabric)

A	0	0.5	1.0	3.0	5.0	7.0
B	52.3	177.0	147.6	117.7	106.8	70.3
C	76.1	93.5	93.7	93.9	94.0	94.0
D	73.2	80.1	92.8	93.0	93.4	93.7
E	1	1	3	4	4	5

It is apparent from the tables that when the deposited amount of polysiloxanes is less than 5 percent (by weight of the fabric) substantial increase of extensibility can be obtained. Amounts greater than 5 percent will decrease the extensibility sharply and the feeling of the treated fabrics will also largely deteriorate. The elastic recovery in dried state is likely to be almost independent on the changes of the deposited amounts of the polysiloxanes, while the elastic recovery in wet state significantly decreases when the deposited amount of polysiloxanes is less than 1 percent by weight of the fabric. The antipilling property shown in tables 1 and 2 was determined by means of the method according to Japanese Industrial Standard (JIS) L-1076-1967, which is similar to the so-called ICI method. The antipilling property will be advantageous when the deposited amount of the polysiloxanes is more than 1 percent by weight of the fabric.

From the observation described above, it appears that the deposition of the polysiloxanes in an amount of from 1 to 5 percent by weight of the fabric is most favorable.

EXAMPLE 2

A similar process to that described in example 1 was performed with the exception of using the polysiloxanes in such amount that they would be deposited in the fabric in an amount of 2 percent by weight of the fabric (calculated as solid).

The amount of trichloroethylene was changed stepwise so as to give the viscosities of the solution of 10, 40, 120, 250, 400, 500 and 1,000 c.p.s., respectively. The obtained results are shown in tables 3 and 4. The results obtained are likely to be substantially independent on the treating time.

Key to Tables

- A. Viscosity of the solution (c.p.s.)
- B. Extensibility (percent)
- C. Elastic recovery percent (in a dry state)
- D. Elastic recovery percent (in wet state)

TABLE 3 (2-stage interlock jersey)

A	0	10	40	120	250	400	500	1,000
B	61.0	242.5	214.0	167.8	125.6	100.8	90.3	89.9
C	78.0	94.2	93.3	90.4	90.4	87.7	82.7	80.2
D	74.1	93.5	93.0	91.2	91.4	90.0	76.3	75.5

TABLE 4 (Twill knitted fabric)

A	0	10	40	120	250	400	500	1,000
B	52.3	150.2	130.0	115.7	107.9	89.9	85.4	80.2
C	76.1	93.0	93.5	94.2	92.4	90.1	85.3	80.7
D	73.2	92.3	91.5	90.4	90.7	89.4	74.3	72.4

From the tables, it is apparent that when the viscosity of the polysiloxanes-containing solution is not more than 400 c.p.s. good extensibility and elastic recovery rates both in dry and wet states can be obtained; while these values are lowered by using the polysiloxanes solution having a viscosity of more than 400 c.p.s.

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EXAMPLE 3

A three-stage interlock fabric of nylon bulky yarn (70 deniers/2 filaments; jersey) was immersed in a treating solution having the following composition, and was then dried at 80° C. to remove off the trichloroethylene.

Composition of the Solution (part by weight)

Dimethylpolysiloxane	2.8
Methylhydrogen polysiloxane	0.7
Dibutyl tin diacetate	0.02
Trichloroethylene	96.48
Viscosity of the solution	40 cps.

The fabric was cured at 160° C. for 3 minutes under a lowest possible tension by using the conventional short-loop baking machine to yield a fabric having an improved extensibility, and elastic recovery as shown in table 5.

TABLE 5

Condition	Sample	Extensibility %	Elastic Recovery %
Dry	Nontreated	48.2	70.2
	Treated	92.6	91.2
Wet	Nontreated	47.1	69.8
	Treated	114.2	90.9

EXAMPLE 4

A similar treatment to that described in example 3 was performed using the nylon jersey with the exception of employing the following treating solutions:

Composition of the solution (part by weight)

Dimethylpolysiloxane	3.0
Methylhydrogen polysiloxane	0.3
Metallic sodium ethylate	0.02
Dibutyl tin diacetate	0.02
Trichloroethylene	96.66
Viscosity of the solution	50 cps.

Organopolysiloxanes (3.5 percent calculated as solid) was thus deposited on the fabric. The fabric was then dried at 80° C. to remove off the solvent, and was cured at 160° to give a fabric having improved extensibility and elastic recovery as shown in table 6. The curing was performed in an analogous manner to that described in example 3.

Key to Table

- A. Extensibility before washing (percent)
 B. Extensibility after washing five times (percent)
 C. Elastic recovery before washing (percent)
 D. Elastic recovery after washing five times (percent)

TABLE 6

Condition	Sample	A	B	C	D
Dry	Nontreated	48.2	50.0	70.2	68.1
	Treated	130.2	128.7	94.3	95.0
Wet	Nontreated	47.1	49.0	69.8	66.6
	Treated	133.1	130.0	94.6	91.5

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The washing test was performed by using a Hitachi SC-AT Model 3 Washing Machine (commercial product available from Hitachi Seisaku-sho K.K., Japan) and washed in a solution of 1 g./l. of Emal (an anionic washing agent available from Kao Sekken K.K., Japan) at 40° C. for 10 minutes. Excellent elastic recovery in wet state, good extensibility and improved elastic recovery after washing for 5 minutes was particularly observed.

EXAMPLE 5

A similar process to that described in example 4 was performed with the exception that an ester silane [$C_6H_5Si(OC_2H_5)_3$] substituted for the metallic sodium ethylate. No washing test was made in this example. The fabric obtained also had improved extensibility and elastic recovery as shown in table 7.

Key to Table

- A. Extensibility (percent)
 B. Elastic recovery (percent)

TABLE 7

Condition	Sample	A	B
Dry	Nontreated	48.2	70.2
	Treated	129.3	92.3
Wet	Nontreated	47.1	69.8
	Treated	130.1	91.7

EXAMPLE 6

A similar treatment to that described in example 4 was carried out with the exception of substituting diethoxy pentasilane for the metallic sodium ethylate. The properties of the fabric thus obtained are shown in table 8. No washing test was made.

Key to Table

- A. Extensibility (percent)
 B. Elastic recovery (percent)

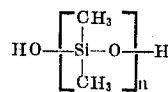
TABLE 8

Condition	Sample	A	B
Dry	Nontreated	48.2	70.2
	Treated	129.3	92.3
Wet	Nontreated	47.1	69.8
	Treated	130.1	91.7

60 What is claimed is:

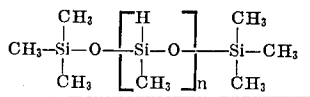
1. A process for imparting high-elastic recovery to extensible bulky knitted or woven fabrics composed of textured yarns made of synthetic fibers having an extensibility of more than 20 percent, which comprises applying to the fabric an organic solution containing

1. a hydroxy-terminated dimethylpolysiloxane having the general formula:



75 in which n is an integer not less than 500;

2. a methylhydrogen polysiloxane having the general formula:



in which *n* is an integer from 15 to 50, the ratio of methylhydrogen polysiloxane to dimethylpolysiloxane is 5 to 30 parts by weight of methylhydrogen polysiloxane based upon 100 parts by weight of dimethylpolysiloxane; and

3. an organic metallic catalyst, dissolved in an organic solvent capable of dissolving said polysiloxanes and utilized in an amount to give a solution having a viscosity of not more than 400 c.p.s. so that 1.0 to 5.0 percent by weight of the fabric, of polysiloxanes are deposited as solid on said fabric, and then curing the polysiloxane treated fabric at an elevated temperature.

2. The process of claim 1 in which said fabric is composed of textured yarn selected from the class consisting of polyamide, polyester, polyacrylonitrile, polyolefin, polyvinylalcohol and mixtures thereof.

3. The process of claim 2 in which said textured yarn is twist-set-untwist yarn, false twist yarn, stuffer box-treated yarn or mixtures thereof.

5 4. The process of claim 1 in which the treating solution further contains at least one member selected from the class consisting of sodium alcoholate, ester silane and polyalkyl silicate.

10 5. The process of claim 1 in which said organometallic catalyst is at least one member selected from the class consisting of zinc caprylate, tin caprylate, zirconium caprylate, dibutyl tin dicaprylate, dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin oxide, alkyl titanate, zinc naphthenate, tin naphthenate, zirconium naphthenate, ferric naphthenate, cobalt naphthenate, zinc formate, zirconium formate, zinc acetate and zirconium acetate.

15 6. The process of claim 1 in which said organic solvent is a hydrocarbon having carbon atoms of from one to 10.

20 7. The process of claim 6 in which said hydrocarbon is one member selected from the class consisting of petroleum benzene, gasoline, benzene, toluene, xylene, trichloroethylene, perchloroethylene and ethyl acetate.

8. The process of claim 1 in which said fabric is cured at a temperature of from 120° to 200° C.

25 9. The product of the process of claim 1.

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