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Tanahashi

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[54] **METHOD OF PRODUCING AN ACRYLIC FIBER HAVING AN IMPROVED TOUCH LIKE ANIMAL HAIR**

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[52] **U.S. Cl.** ..... **117/138.8 UA,** 117/139.5 A, 117/161 UZ, 117/161 UT, 117/161 UN, 117/161 UC, 117/161 ZA

[51] **Int. Cl.** **B44d 1/09,** C10m 3/22

[58] **Field of Search** ..... 117/138.8 UA, 139.5 A, 117/139.5 C, 139.5 Q, 161 UZ, 161 ZA; 8/115.6; 252/8.9; 260/827

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[57] **ABSTRACT**

There is disclosed a process for improving the tactile qualities of acrylic fibers comprising treatment thereof with effective quantities of a mixture of suitable proportions of an acrylonitrile copolymer containing certain amounts of a comonomer containing a long-chain alkyl group and suitable proportions of a silicone polymer. Tactile qualities resemble those of animal hair fibers.

10 Claims, No Drawings

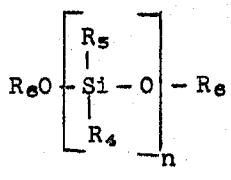
METHOD OF PRODUCING AN ACRYLIC FIBER HAVING AN IMPROVED TOUCH LIKE ANIMAL HAIR

This invention relates to a process for imparting to acrylic fiber improved tactile qualities. More particularly, this invention relates to such a process wherein the acrylic fiber is treated with a sufficient quantity of a mixture of (A) an acrylic copolymer containing a comonomer having a long-chain alkyl group and (B) a silicone resin so as to provide the desired tactile qualities.

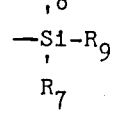
Acrylic fibers have been developed for and used in fiber applications wherein advantage is taken of their resemblance to wool and other animal hair fibers in physical properties. However, contrary to the tactile qualities associated with wool and other animal hair fibers, acrylic fibers have a very harsh touch and a noticeable feeling of frictional resistance. Thus, the acrylic fibers do not possess the tactile qualities associated with fine wool fibers and other animal hair fibers such as cashmere.

Because of the deficiency of acrylic fibers in tactile qualities, softening treatments are generally applied thereto. One previous method of modifying the tactile properties involved treating the fiber with a copolymer containing 4 to 30 mole percent of a monomer having a long-chain alkyl group and 70 to 96 mole percent of acrylonitrile or another unsaturated vinyl monomer. Such method, however, produced a slippery feel which was at the same time sticky and resulted in undesirable agglutinations of individual fibers. Problems resulted in spinning the thus treated fiber because it did not become sufficiently opened during the carding operation and caused excessive nep formation as well as windings around the card. Yarn spun from yarn thus processed was non-uniform and of low commodity value. Although processing can be improved by use of oiling agents, the results do not overcome the tactile deficiencies, namely the slippery, sticky feel which is unlike that of animal hair fibers.

In accordance with the present invention there is provided a process for improving the tactile qualities of acrylic fibers which comprises treating said fibers with a liquid medium containing therein a mixture of (A) from 10 to 60 weight percent of a copolymer of (1) 70–92 mole percent of acrylonitrile, (2) 30–8 mole percent of a monomer of a formula selected from $CH_2{=}CR_1COOR_2$ and $CH_2{=}CHOCOR_3$, wherein R_1 is selected from hydrogen and methyl and R_2 and R_3 are individually selected from alkyl of 10 to 18 carbon atoms, and (3) from 0–22 mole percent of another copolymerizable monomer, and (B) from 90 to 40 weight percent of a silicone polymer of the formula:



wherein R_4 is selected from alkyl of 1–3 carbons, alkenyl of 2–3 carbons, and aryl of 1–2 carbocyclic rings; R_5 is selected from hydrogen and R_4; R_6 is selected from hydrogen and



wherein R_7 and R_8 are individually alkyl of 1–3 carbon atoms, R_9 is selected from hydrogen and R_7; and n is an integer such as to provide a polymer of molecular weight in the range of 10,000 and 100,000, the percentages of said (A) and said (B) totaling 100 percent and being based on the total weight of said (A) and said (B) in said medium, said treating being carried out in a manner such as to deposit upon said fibers from about 0.2 to 5.0 percent, by weight, based on the weight of said fibers, of the mixture of (A) and (B), and thereafter removing said medium from said fibers.

The present invention provides acrylic fibers with improved tactile qualities resembling animal hair fibers such as cashmmere and fine wools. The process of the present invention achieves this result without producing stickiness associated with use of prior copolymers alone and the problems associated therewith. The present process also achieves this result without creating problems with respect to crimp formation and stability as are associated with the use of silicone resins alone. The results thus obtained by the process of the present invention are entirely unexpected in view of the difficulties associated with related individual components when applied separately. Further, it is entirely unexpected that the durability of the silicone resin component should be greatly improved by its use in conjunction with the copolymer.

In carrying out the process of the present invention, the copolymer and silicone polymer are admixed in proper amounts in the form of a dispersion or solution of suitable concentration for treatment of the acrylic fiber. Treatment is carried out in suitable manner to provide the proper amount of mixture on the fiber and then the medium used to form the dispersion or solution is removed from the fiber to provide the fiber of improved tactile qualities.

The first essential ingredient of the mixture is a copolymer of (1) 70–92 mole percent of acrylonitrile, (2) 30–8 mole percent of monomer containing a long-chain alkyl group, and (3) 0–22 mole percent of another monomer copolymerizable with said (1) and (2). If the long-chain alkyl monomer content is less than 8 mole percent, the slippery feel is not satisfactory, while if the content exceeds 30 mole percent stickiness develops in the treated fiber and the desired results cannot be achieved. If the content of acrylonitrile is less than 70 mole percent, adherence of the polymer to the fiber diminishes and durability of the imparted tactile qualities to laundering and dry cleaning are reduced to an undesirable level. A content of more than 92 mole percent of acrylonitrile, as indicated above, results in less than the desired extent of slippery feel in the treated fibers. The copolymer may contain up to 22 mole percent of another unsaturated copolymerizable monomer while satisfying the minimum requirements for acrylonitrile and long-chain alkyl monomer but cannot contain the optional monomer at the maximum requirements of acrylonitrile and long-chain alkyl monomer. At intermediate usages of acrylonitrile and/or long-chain alkyl monomer, the amount of optional monomer

used may vary. The optional monomer used, of course, should not interfere with obtaining the effects desired of the copolymer.

Among the long-chain alkyl monomers that may be employed in accordance with the formulas specified above are included acrylic or methacrylic esters of higher alcohols such as undecyl, dodecyl, pentadecyl, octadecyl, and the like, alcohols, and vinyl esters of higher fatty acids such as lauric, palmitic, stearic and the like, acids. If the monomer contains as the alkyl group one having less than 10 carbon atoms, the desired slippery feel cannot be obtained. Since monomers containing more than about 18 carbon atoms are limitedly available commercially and are difficult to copolymerize, the use of such monomers is not practical.

As the optional monomers that may be employed in preparing the copolymer, there are included acid monomers such as acrylic, methacrylic, itaconic, and the like, acids, as well as salts, alkyl, and aryl esters thereof; sulfonic acid monomers such as allylsulfonic, methallylsulfonic, styrenesulfonic, and the like, acids and their salts; neutral monomers such as acrylamide, styrene, vinyl chloride, methacrylonitrile, and the like; basic monomers such as vinyl pyridine, dimethylaminoethyl methacrylate, and the like; and crosslinkable monomers such as N-methylolacrylamide, glycidyl methacrylate, and the like.

The copolymer is prepared by any of the conventional polymerization techniques, such as solution, suspension, or emulsion polymerization technique, to provide the polymeric product. Use of emulsion polymerization is preferred because the product thus obtained is directly useful in treating the acrylic fiber, requiring generally only dilution. Other procedures generally require additional steps such as solvent removal and/or re-dispersion.

The silicone polymer, the second essential ingredient of the mixture, is represented by the general formula given above. Examples of suitable silicone polymers are dimethyl polysiloxane, methyl hydrogen polysiloxane, and the like. Usage of the silicone polymer in admixture with the copolymer must be in the range of 40 to 90 percent, by weight, based on the total weight of silicone polymer and the copolymer. If the amount of silicone polymer is less than that specified, the mixture tends to produce stickiness to the acrylic fiber and poor tactile qualities. If the amount of silicone polymer is greater than that specified, crimp processability and stability are poor and durability of tactile qualities is unsatisfactory.

The acrylic fiber is treated with the mixture of copolymer and silicone polymer in a manner so as to coat or impregnate the fiber with from about 0.2 to 5.0 percent, by weight of the mixture based on the weight of the fiber. For treating purposes, a liquid medium is employed. The mixture may form a solution in a suitable solvent or may form a dispersion in other liquid media. The treatment may be by dipping, padding, spraying, or other technique for obtaining uniform treatment. If a solvent is employed to dissolve the mixture, it must be inert with respect to the acrylic fiber. The amount of liquid medium employed will depend upon the method of treatment selected and the combination of amount of medium and treatment method should be properly selected so as to provide the required amount of mixture on the fiber. If less than 0.2 percent of mixture is used in the fiber treatment effected, the tactile qualities will be undesirable. If more than 5.0 percent of mixture is used in the fiber treatment, the excess will be wasteful since maximum tactile qualities appear at or below the 5 percent level. High usages can also interfere with other fiber qualities and processability.

The treatment can be effected on acrylic fiber in the form of raw fiber, partly-finished or finished goods. However, when the treatment is effected on the fiber while it is in the swollen wet-gel state as it emerges from the wet-spinning process, the mixture is retained in the fiber in a highly durable manner while imparting the desirable tactile qualities.

After treatment is effected, the liquid medium employed in the treatment is removed. This is conveniently effected by subjecting the fiber to elevated temperatures, although evaporation of the medium will generally occur at ambient conditions. The drying conditions may be influenced by the state which the fiber is in when treatment is effected. If the fiber is treated in the wet-gel state, it is preferred to effect drying at temperatures above 90°C. so as to collapse the fiber in conjunction with removal of treating medium. Conventional collapsing temperatures are employed. When the fiber is treated in other forms, temperatures above about 70°C. are useful to expedite medium removal, particularly water.

The invention is more fully illustrated by the examples which follow, wherein all parts and percentages are by weight unless otherwise specifically designated.

EXAMPLES 1 – 6

Using the following recipe, a copolymer was prepared by emulsion polymerization:

Octadecylacrylate	11.4 parts
Acrylonitrile	4.9 parts
Emulsifying agent	2.0 parts
Potassium persulfate	0.16 part
Sodium metabisulfate	0.16 part
Demineralized water	82.0 parts

The emulsifying agent was nonionic and a polyethylene oxide modified nonylphenol. The copolymerization was carried out under a nitrogen blanket for 4 hours at 40°C. The copolymer obtained contained 27 mole percent of octadecylacrylate.

A dimethyl polysiloxane, of viscosity 8,000 centipoises was separately emulsified in water using the same emulsifying agent used above.

The silicone and copolymer emulsions were then mixed in various proportions for different examples to provide specific ratios of silicone polymer to copolymer in the treatments effected.

The fiber treated was in the wet gel state and was obtained by wet-spinning a terpolymer of 91 percent acrylonitrile, 8.7 percent methyl acrylate, and 0.3 percent sodium allyl sulfonate. The treatment with the mixture was carried out so as to deposit 1 percent of the mixtures of copolymer and silicone polymer prepared in separate examples. The fiber after treatment was heated under dry conditions for 15 minutes at 105°C. and was then relaxed in a steam atmosphere at 127°C. for 10 minutes. The fiber was then subjected to mechanical crimping.

The relationship between properties of the fiber obtained and the ratios of copolymer and silicone polymer used in the treatment is given in Table I which fol-

lows. Dry cleaning was carried out using perchloroethylene and conventional dry cleaning soaps at a fiber:liquor ratio of 1:50 at 25°C. for 15 minutes, followed by two rinses.

TABLE I

	Example Number					
	1	2	3	4	5	6
Mixture Ratio Copolymer (%)	100	80	60	40	20	0
Silicone Polymer (%)	0	20	40	60	80	100
Fiber Agglutinations	Numerous	Moderate	None	None	None	None
Crimp Processability	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Unsatisfactory
Tactile Qualities after Dry Cleaning	Slippery and Highly Sticky	Slippery and Moderately Sticky	Slippery, not Sticky	Very Slippery, Not Sticky	Very Slippery, Not Sticky	Neither Slippery nor Sticky
	Comparative Examples			Examples of the Invention		Comparative Example

As is apparent from Table I, when the copolymer was employed alone as treating agent or was employed with insufficient quantity of silicone polymer, the treated fiber exhibited agglutinations. In such cases, although the treated fiber possessed a slippery feel, such feel was accompanied by an undesirable sticky feel and the fiber did not possess the tactile qualities of animal hair fibers. When the silicone polymer was used without copolymer, as initially prepared, it possessed no stickness but was too slippery to be properly crimped. After dry cleaning, however, the slippery feel was completely absent, indicating the lack of durability of the treatment.

When the copolymer and silicone polymer were employed as treatment in the ratios specified by the present invention, no fiber agglutinations occurred, crimping was readily effected, the tactile qualities of animal hair fibers were imparted, and the imparted tactile properties were durable.

When the above fibers were subjected to spinning, those of Examples 1 and 2 were unsatisfactorily opened during carding and formed yarns with numerous neps. The fiber of Example 6 was not spun satisfactorily because of its inability to intertwine properly. The fibers of Examples 3, 4 and 5 were all satisfactorily spun without difficulties.

EXAMPLES 7 – 11

In this series of examples, five copolymers were prepared in which the mole percent of octadecylacrylate in the copolymer was varied. The polymerizations were carried out following the procedure of Example 1 in all essential details except that the total charge of octadecylacrylate and acrylonitrile was 10 parts, the water charge was 88 parts, and the redox catalyst was 0.1 part of each component in this series. The emulsions obtained were mixed with a silicone polymer emulsion as in Example 1 to provide mixtures containing copolymer and silicone polymer in respective amounts of 20 and 80 percent, based on the total amount of silicone polymer and copolymer in the emulsions. The wet-gel fiber used in Example 1 was treated with the mixtures prepared as in Example 1 to provide the five fiber samples. The relationship between mole ratio of octadecylacrylate in the copolymer and fiber properties is shown in Table II, which follows. Dry cleaning was carried out as in Example 1.

TABLE II

	Example Number				
	7	8	9	10	11
Mole % of Octadecyl acrylate in copolymer	40	27	20	14	7
Agglutinations of fiber	← Completely Absent →				
Tactile Qualities, Initial	No stickiness	satisfactory touch	slippery		slippery touch unsatisfactory
Tactile Qualities, Dry Cleaned	Unsatisfactory Slippery touch	No stickiness, satisfactory slippery touch			No slippery touch evident
	Comparative Example	Examples of this invention			Comparative Example

As is apparent from Table II, when the amount of octadecyl acrylate in the copolymer exceeded 30 mole percent, the durability of tactile qualities imparted to the treated fiber was unsatifactory. When the amount of octadecyl acrylate in the copolymer was below 8 mole percent, the tactile properties imparted to the fiber initially or after dry cleaning were unsatisfactory.

EXAMPLES 12 – 17

The copolymer prepared as in Example 10 above was employed to provide a series of mixtures wherein the amount of silicone polymer in the mixture was varied. The mixtures were then employed to treat the wet-gel fiber employed in Example 1 following the procedure of Example 1.

The treated fibers thus obtained were subjected to test to determine fiber-against-fiber frictional coefficients in accordance with conventional procedures. These results as well as sensory evaluations of the tactile qualities are given in Table III, which follows.

No satisfactory method has as yet been developed for instrumentally measuring tactile qualities and sensory methods are currently employed. However, the difference between static frictional coefficient (SFC) and kinetic frictional coefficient (KFC), as determined above, is frequently employed as a measure of tactile qualities. It is considered that as the value of SFC minus KFC decreases, preferably to a negative value, the desirable slippery touch increases: when the value of SFC minus KFC is a large positive value, the touch sensed

is of strong frictional resistance.

The sensory tests reported are the average of values obtained by five qualified people using a value of 5 for the highest value of slipperiness and a value of 1 for frictional resistance. An asterisk associated with a sensory value indicates the presence of stickiness.

Dry cleaning was as in Example 1. Washing was carried out using a synthetic detergent at 2 grams per liter and a liquor to fiber ratio of 200 to 1 for 10 minutes at 40°C., followed by water rinsing for 20 minutes at 25°C.

TABLE III

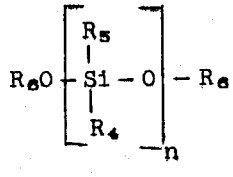
		Example Number					
		12	13	14	15	16	17
Mixture:	(Copolymer (%)	100	80	60	40	20	0
	(Silicone Polymer (%)	0	20	40	60	80	100
SFC - KFC[1]		0.036	0.028	0.013	−0.003	0.003	0.018
Sensory Tests:	Initially	4.8*	4.7*	4.7	4.8	4.7	4.4
	After Washing	4.7*	4.3*	4.3	4.7	4.7	4.0
	After Dry Cleaning	4.3*	4.2*	4.1	4.6	4.6	3.5
		Comparative Examples		Examples of this Invention			Comparative Example

Notes: [1]Kinetic frictional coefficient determined at 500 centimeter per minute, and both coefficients determined on initial treated fiber.
*Sticky touch.

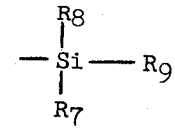
As is apparent from Table III, mixtures of the present invention provide more desirable tactile qualities than mixtures outside the range of the invention, and the differences in frictional coefficients confirms the sensory determinations, with a preferred mixture exhibiting a negative difference in frictional coefficients. The Table also shows that fibers of the invention lack sticky feel and exhibit excellent durability.

I claim:

1. A process for improving the tactile qualities of acrylic fibers which comprises treating said fibers with a liquid medium inert with respect to said fibers containing therein a mixture of (A) from about 10 to 60 weight percent of a copolymer of (1) 70–92 mole percent of acrylonitrile, (2) 30–8 mole percent of a monomer of a formula selected from $CH_2{=}CR_1COOR_2$ and $CH_2{=}CHOCOR_3$, wherein R_1 is selected from hydrogen and methyl and R_2 and R_3 are individually selected from alkyl of 10 to 18 carbon atoms, and (3) from 0–22 mole percent of another copolymerizable monomer, and (B) from 90 to 40 weight percent of a silicone polymer of the formula:



wherein R_4 is selected from alkyl of 1–3 carbon atoms, alkenyl of 2–3 carbon atoms, and aryl of 1–2 carbocyclic rings; R_5 is selected from hydrogen and R_4; R_6 is selected from hydrogen and



wherein R_7 and R_8 are individually alkyl of 1–3 carbon atoms, R_9 is selected from hydrogen and R_7, and n is an integer so as to provide a polymer of molecular weight in the range of 10,000 and 100,000, the percentages of said (A) and said (B) totaling 100 percent and being based on the total weight of said (A) and said (B) in said medium, said treating being carried out in a manner such as to deposit upon said fibers from about 0.2 to 5 percent, by weight, based on the weight of said fibers, of the mixture of (A) and (B), and thereafter removing said medium from said fibers.

2. The process of claim **1** wherein said copolymer consists of 27 mole percent of octadecyl acrylate and 73 mole percent of acrylonitrile.

3. The process of claim **1** wherein said copolymer consists of 14 mole percent of octadecyl acrylate and 86 mole percent of acrylonitrile.

4. The process of claim **1** wherein said silicone polymer is dimethyl polysiloxane.

5. The process of claim **3** wherein said silicone polymer is dimethyl polysiloxane and is present in said mixture in the amount of 60 weight percent.

6. The process of claim **1** wherein said acrylic fiber is treated in wet-gel form.

7. The process of claim **1** wherein said liquid medium is water.

8. The process of claim **1** wherein said treating is carried out so as to deposit upon said fibers 1 percent of said mixture.

9. The process of claim **6** wherein said medium is removed from said fibers by dry heat treatment at 105°C.

10. The process of claim **9** wherein said fibers after removal of said medium are subjected to relaxation in steam at 127°C.

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