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SHRINKPROOFING WOOL WITH SUBSTITUTED POLYMERS OF ETHYLENE

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1

This invention relates to a method for the treatment of keratinous textile fibers and especially wool in the form of woolen fabric or garments and the like, whereby it may be rendered substantially non-shrinkable without any appreciable or detrimental alteration of its desirable characteristics.

Keratinous fibers tend to shrink and/or felt during washing thereby destroying to a large extent their commercial value. In the description of this invention the term "felt" is to be understood to refer to that property of such fibers which causes them to close upon each other in washing, or other treatment in aqueous liquor in which the wool material is repeatedly squeezed and rubbed, so that the keratinous material becomes denser and more compact. This property of felting is primarily responsible for shrinkage which woolen yarns and fabrics suffer when washed. The initial superior physical properties of newly spun fibers that felt are retained by the process of this invention.

An object of the present invention is to improve the physical characteristics of wool. Another object is the treatment of wool and similar keratine-containing fibers to reduce their tendency to felt on mechanical working and during laundering. A further object is the reduction in the tendency of wool to shrink on laundering. Yet another object is the provision of wool-containing fibers of reduced tendency to shrink on laundering, which fibers retain their natural water repellency, resiliency when wet, and softness. Other objects and advantages of the invention will hereinafter appear.

According to the present invention, the tendency of keratinous fibers as raw filaments, yarn, knit, woven goods or mixed goods to felt and shrink on laundering in aqueous liquors is reduced by treating the fibers with a high molecular weight substituted hydrocarbon polymer or like addition agent and if desired a fixative. This treatment is carried out by bringing the addition agent and fixative (if one is used) in contact with the fibers and subjecting the treated fiber to a curing operation which firmly holds the addition agent and fixative, if any, on the fibers. As a result of this treatment the felting and shrinking of the wool is remarkably inhibited, it being possible to decrease these undesirable properties from a normal of 50% to 5% or less. Moreover, materials containing wool which have already been partially felted may have their further felting tendencies inhibited by the process herein described.

It is believed, although this does not limit the

2

invention, that the action of the addition agent and the fixative is mainly confined to the surface of the fiber and that any substantial extension of this action to the interior of the fiber does not occur. The term "quality" is understood to refer to the properties of wool such as tensile strength, softness of handle, color and durability which have to be taken into account in assessing the value and usefulness of wool material. In general the quality is reduced if the wool suffers loss of weight and is made weaker, harsher, yellower and less durable.

The material treated by the process of the invention retains its improved quality and resistance to shrinking even after repeated washing. The addition agent appears to be the principal substance applied that inhibits the shrinking, felting and like undesirable properties of wool and like materials. These agents should be present to the extent of from not less than about 1% to not more than about 25% based on the weight of the keratinous material. The fixative, when one is used, appears to act as a cross-linking agent between the molecules of the addition agent and possibly the wool, and it should be present to the extent of from 0.01% to 10%, based on the weight of the impregnant solution.

The treatment with the high molecular weight substituted hydrocarbon and the fixative may conveniently be carried out as follows: The substituted high molecular weight hydrocarbon polymer or other addition agent and a suitable solvent therefor, are tumbled at room temperature to give a solution of polymer concentration in the range of 1 to 20%, preferably 1 to 5% of the addition agent. To 150 parts of the resulting solution there is added 0.005 to 0.5% of a fixative. A standard wool swatch 7'' x 7'' is immersed in the solution for 5 minutes. The swatch is then run through a set of rubber or metal squeeze rolls five time, rewetting the swatch in the solution after each of the first four times. The swatch, after the fifth passage through the roller, is rolled in a paper towel and weighed until the wet weight corresponds to the amount of polymer desired on the swatch.

The thus impregnated swatch is cured by securing it to a wooden frame without stretching and placing in a circulating air oven at the desired temperature for the desired period of time. The cured swatch is washed by placing in a one-quart friction-top paint can with 15 solid rubber balls, about ½ inch in diameter and 100 parts of soap solution containing about 0.2% by weight of soap flakes and 0.1% by weight of sodium car-

bonate in distilled water. The temperature at the start is 50° C. The can and contents are placed on a vibrating apparatus imparting a vigorous motion to the rubber balls, e. g., a conventional paint-conditioner, and shaken for 15 minutes. The swatch is rinsed with warm water, measured wet and recharged to the container along with a fresh batch of soap solution for a second 15 minute wash. The swatch is again rinsed, measured, air dried and re-measured. The percent area of shrinkage is equal to 100 minus the percent remeasured area over the original area.

The table illustrates the effectiveness of a number of addition agents which inhibit the shrinking of wool when the wool is treated with the agent in the presence of the fixative described. The agents of the table, containing both chlorine and sulfur dioxide, were chlorosulfonated in accord with the process described in the later mentioned Patent 2,212,786.

Colourists, 61, 286 (1945). The examples which follow illustrate generally this alternate procedure. Untreated wool subjected to this type of hand-milling shows a shrinkage of 45–55%.

Example 15.—Wool was dipped in a 5% trichloroethylene solution of chlorosulfonated polymer of ethylene so as to obtain about 6% by weight impregnation.

A batch of the wool so treated was baked at 150° C. for 3 minutes, after which its relaxation shrinkage (i. e. shrinkage resulting merely from wetting followed by drying) was 4.5%. The batch had very good color. After a hand-milling treatment, the total shrinkage was only 12.5%, showing a fair degree of shrinkproofing by the action of chlorosulfonated polymer of ethylene alone.

Another batch of wool impregnated as above was air-dried, then dipped in an ether solution of triethylene-tetramine, washed three times with ether, air-dried and finally baked at 110° C. for 20 minutes. There was no relaxation shrinkage.

Table

Agent Used	Substitution		Fixative		Curing		Toluene Solution, Percent X	Dispersion	Agent on Wool, Percent	Area Shrinkage, Percent
	Percent Cl	Percent SO_2	Kind	Percent X	Time, Min.	Temp., ° C.				
1. Polyisobutylene Vistanex B-40	27.7	3.75	N	0.1	5	150	10		10	10
2. Hydrogenated Rubber (smoked sheet).	27.	1.39	M	0.075	5	150	5		5	9
3. Hydrogenated Rubber (smoked sheet).	27.	1.39	M	0.02	5	150	2		2	5
4. Polymer of ethylene (MW 18,000–19,000).	27.7	1.5	M	0.05	2	150	4		4	8
5. Polymer of ethylene (MW 18,000–19,000).	27.7	1.5	-------	0.05	2	150	5		5	9
6. Polymer of ethylene (MW 18,000–19,000).	27.7	1.5	-------	0.05	2	150	7½		7½	5
7. Polymer of ethylene (MW 18,000–19,000).	28.4	3.8	M	0.02	5	150	2		2	12
8. Polymer of ethylene (MW 18,000–19,000).	26.	4.5	M	0.05	3	150	5		5	5
9. Polymer of ethylene (MW 18,000–19,000).	26.	4.5	M	0.01	5	150	2		2	6
10. Polymer of ethylene (MW 18,000–19,000).	27.7	1.5	N	0.1	10	150	----------	22.2% total solids.	6.8	14
11. Polymer of ethylene (MW 18,000–19,000).	27.7	1.5	N	0.1	5	150	----------	22.8% total solids.	9.6	10
12. Polymer of ethylene (MW 10,000–11,000).	30.5	2.2	M	0.075	5	150	5		5	12
13. Polymer of ethylene (MW 10,000–11,000).	29.3	6.4	M	0.02	5	150	3		3	9
14. Polymer of ethylene (MW 18,000–19,000).	32.9	0	M	0.2	5	150	5		5	10

N=Hexamethylenediamine.
M=3-Methoxyhexamethylenediamine.
X=By weight of solution.

The wool in the examples described in the table shows, when untreated, a shrinkage of approximately 60% after the first 15 minute wash. Subsequent washings increase this shrinkage. The table illustrates the advantages of the invention with chlorosulfonated polyisobutylene, hydrogenated rubber and polymers of ethylene. Using polyisobutylene that has been chlorosulfonated, Example 1 illustrates that about 10% of the agent on the wool is a pre-requisite to a 10% shrinkage while with chlorosulfonated hydrogenated rubber, Examples 2 and 3, 2% gives a shrinkage of 5% which is not improved by increasing the percent of the agent to 5%. With chlorosulfonated ethylene polymers there should be present about 2% of the agent and preferably between 4 and 5% as indicated in Examples 9, 4 and 5 respectively. An alternate method of treating wool, and other keratinous fibers, may be carried out by impregnating the wool with the substituted hydrocarbon polymer and thereafter air drying and curing with heat followed by, if desired, after treatment with a fixative. Also, a hand-milling may be used similar to that described by Chamberlain and Menkart in Jour. Soc. Dyers and

After hand-milling the total shrinkage was 11%. After dry cleaning with acetone and trichloroethylene, there was 3% more shrinkage, and only 2% additional after a second hand-milling treatment.

The chlorosulfonated polymer of ethylene used in this example was prepared from a relatively low molecular weight polymer of ethylene having a viscosity of 30 poises at 125° C. It contained 9.5% sulfur and 27.0% chlorine.

Example 16.—Wool was dipped in a 5% trichloroethylene solution of the same chlorosulfonated polymer of ethylene as that of Example 15, the solution containing also a small amount of a dispersing agent consisting of a sulfonic acid salt of a long chain hydrocarbon. There was about 7–8% impregnation of the fabric.

A batch of the impregnated wool was air-dried, then dipped in a 1% acetone solution of ethylenediamine, air-dried and baked at 100° C. for 15 minutes. The batch had good color and showed 7% relaxation shrinkage. After hand-milling, the total shrinkage was 12.5%.

Example 17.—Batches of wool were dipped in a 5% aqueous solution of the same chlorosulfo-

nated polymer of ethylene as used in Example 15, solubilized by partially reacting the halogen groups with pyridine. Fabric impregnation was about 6–7%.

One such treated batch was dried at 60° C. for 30 minutes, then baked at 150° C. for 8 minutes. The relaxation shrinkage was 6%. After hand-milling, the total shrinkage was 22%.

A second batch was dried at 60° C. for 30 minutes, then dipped in an acetone solution of triethylene-tetramine, air-dried and baked at 150° C. for 8 minutes. Its relaxation shrinkage was 7% and it had good color. After hand-milling, the additional shrinkage was only 5%. An untreated control test fabric had 10% relaxation shrinkage and 45% shrinkage after hand-milling.

Example 18.—A 35% solution of polymer of ethylene sulfonamide in ethyl acetate was diluted to 5% solids by addition of methyl ethyl ketone. Batches of wool were dipped in the solution and air-dried. Fabric impregnation was 8–10%. The color was very good.

One such batch after hand-milling showed only 12% shrinkage.

Another batch was baked at 100° C. for 3 minutes, rinsed in soap solution and in water, then dipped in 1% aqueous formaldehyde for 5 minutes and air dried. The batch was slightly stiffened but retained its good color. After hand-milling, it showed only 4% shrinkage. After dry-cleaning with trichloroethylene followed by a second hand-milling, the additional shrinkage was only 2%.

In a variation of this treatment, the 35% ethyl acetate solution of polymer of ethylene sulfonamide (20 parts) was dispersed in 30 parts of water by rapid stirring in the presence of 0.4 part of a dispersing agent consisting of a fatty acid ester of a polyoxyethylene-sorbitol condensation product. Wool was treated with this dispersion to 7–8% impregnation and air-dried. It had very good color and showed 12% shrinkage after hand-milling.

The polymer used in this example was prepared by partially amidating the sulfochlorination product of a relatively low molecular weight polymer of ethylene (viscosity 125 poises at 125° C.). It contained approximately 28% chlorine, 6.5% sulfur and 3.5% nitrogen.

Example 19.—Batches of wool were dipped in a 5% trichloroethylene solution of chlorosulfonated high molecular weight polymer of ethylene to 11–12% impregnation.

One such batch was air-dried, then dipped in 5% aqueous ammonia for 15 minutes and baked at 100° C. for 15 minutes. The batch was slightly stiff and it had very good color. Its relaxation shrinkage was 3%. After hand-milling, the batch showed no additional shrinkage. After dry-cleaning with trichloroethylene and a second milling, the additional shrinkage was only 4%.

A second batch was air-dried, then dipped in 2% aqueous sodium carbonate for 15 minutes and baked at 100° C. for 15 minutes. The batch was slightly stiff, had very good color and showed a relaxation shrinkage of 3%. After hand-milling, there was only 2% additional shrinkage. After dry-cleaning with trichloroethylene, followed by a second hand-milling, there was only 5.5% shrinkage.

Before the second milling, both of the above batches were given a soiling treatment by immersing them in a dispersion of 0.5 part of lampblack in 400 parts of water and 80 parts of ethanol.

High molecular weight substituted hydrocarbons used to produce the decrease in felting and shrinking of the invention include halogenated and sulphonated high molecular weight hydrocarbons as well as their amidation products. Olefin polymers and copolymers are preferably the basic hydrocarbons from which the halogenated and sulfonated high molecular weight hydrocarbons are prepared. Polymers produced in accord with the process described in U. S. Patent, 2,183,556 of E. W. Fawcett and in U. S. Patent 2,200,429 of Perrin are especially suitable. Other highmolecular weight hydrocarbons may be employed, such, for example, as those produced by the low temperature polymerization of the olefins that give polyisobutylene, polypropylenes and higher molecular weight olefins. Other high molecular weight hydrocarbons may be used, as for example, high molecular weight paraffin wax, gilsonite, Fischer Tropsch wax, rubber, hydrogenated rubber, isomerized rubber, polybutadiene, polystyrene and the synthetic rubbers, e. g. copolymerized butadiene -styrene, etc. The polymers used desirably have a molecular weight in excess of 500, and preferably in excess of 1000.

These and similar high molecular weight hydrocarbon addition agents, as has been stated, are first either treated with chlorine and then with sulfur dioxide or vice versa or simultaneously treated with these reactants to give chlorosulfonated hydrocarbons. The chlorosulfonation and amidation processes described in the McQueen Patent 2,212,786 may be employed or any other suitable process.

The fixatives employed are poly-functional organic compounds and may contain polyhydroxy, polymercapto, polyamino or polyamide groups. Specific fixatives which may be used include the polyhydric alcohols such, for example, as ethylene glycol, propylene glycol, diethylene glycol, hexamethylene glycol, octadecandiol and the like; the polyfunctional mercaptan containing compounds such, for example, as ethane dithiol, propane dithiol and the like; the diamino compounds such, for example, as ethylene diamine, propylene diamine, hexamethylene diamine, hexamethylenetetramine, diethylene triamine, triethylene tetramine, N-isobutyl hexamethylene diamine, N-N'-diisobutylhexamethylene diamine, and the like; the carbamates such, for example, as methoxymethoxyethyl carbamate, hydroxypropyl carbamate, N-N'-dialkyl ureas such as N-N'-diisobutyl urea and the like; the diamides such, for example, as hexamethylene diamide and related diamides. Unsymmetrical poly-functional compounds may likewise be employed such as ethanolamines, ethanol mercaptans, ethanol amides and the like. The use of a fixative is particularly desirable with polymers in the lower molecular weight range, e. g., between 1000 and 30,000, while higher molecular weight polymers give satisfactory results even without a fixture, although the use of the latter is preferred in any event.

While the curing of the wool with the high molecular weight substituted hydrocarbon polymers, with or without a fixative, is conducted in most of the examples at a temperature of 150° C. this temperature is not critical for temperatures ranging between 75 and 250° C. may be employed if desired. At the higher temperatures a much shorter curing time should be employed and at the lower temperatures a longer

curing time to effect the same degree of shrinkage and felting inhibitions.

In Examples 1 to 9, 13 and 14 of the table and 15 to 19, the treatment was effected by means of a solution of the addition agent and fixative. This solution may be in any suitable organic solvent for the addition agent which likewise is a solvent for the fixative. Inasmuch as the fixative is employed in only very small percentages it is necessary only that the solvent be effective to that extent. Such solvents as toluene, carbon tetrachloride, benzene, chlorinated aromatic hydrocarbons and tetrachloroethylene, trichloroethylene as well as other suitable solvents may be used if desired.

Examples 10, 11 and 18 (second part) illustrate another method of applying the addition agent and the fixative to the wool, these examples describing the use of aqueous dispersions of chlorosulfonated ethylene polymer. Any suitable method for preparing dispersions of these and the other treating agents may be employed. The dispersions illustrated in Examples 10 and 11 were made in this manner:

The chlorosulfonated polymer of ethylene, to the extent of 20.2% by weight, 9.9% of a fatty acid ester of a polyoxyethylene-sorbitol condensation product and 5% of medium viscosity sodium carboxymethyl cellulose, the latter two being based on the weight of the chlorosulfonated hydrocarbon, were processed in a dispersing mill. To 18.6 parts of the dispersion was added 56.4 parts of distilled water and 0.075 part of hexamethylene diamine. A wool swatch, 7'' x 7'', was impregnated in this bath in the manner described above and the swatch cured as indicated.

Any keratinous containing animal fiber, e. g. wool, alpaca, vicuña, Angora rabbit hair, goat hair, camel hair and the like may be reduced in shrinking tendency by the process of this invention. The material which is to be processed may be in the raw fibrous form or may be in any form, for example, as yarn, thread, knit, woven or mixed goods.

We claim:

1. A keratinous textile fiber which substantially retains its natural resiliency, softness and fibrous quality, containing, based on the weight of keratinous textile fiber, from 2 to 10% by weight of a chlorosulfonated polymer of ethylene and an alpha-omega diamine containing 2 to 6 carbon atoms.

2. A wool fiber which substantially retains its natural resiliency, softness and fibrous quality, containing, based on the weight of wool fiber, from 2 to 10% by weight of a chlorosulfonated polymer of ethylenehexamethylene diamine reaction product.

3. A keratinous textile fiber which retains substantially all of its original resiliency, softness and fibrous character, the surface of which is coated with from 2 to 10% by weight of a chlorosulfonated high molecular weight olefin polymer chemically combined with a fixative of the group consisting of alpha-omega diamines and alpha-omega diamides containing 2 to 6 carbon atoms, based on the weight of the keratinous textile fiber.

4. Wool fibers which retain substantially all of their original resiliency, softness and fibrous character, the individual fibers having a surface coating of from 2 to 10% by weight of a chlorosulfonated polymer of ethylene chemically combined with a fixative of the group consisting of alpha-omega diamines and alpha-omega diamides containing 2 to 6 carbon atoms, based on the weight of the wool fibers.

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