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2,980,557

NON-FELTING WOOL AND METHODS FOR PREPARING THE SAME

Kermit S. La Fleur, Union, S.C., and Edwin J. Greene, Charlotte, N.C., assignors to Deering Milliken Research Corporation, Pendleton, S.C., a corporation of Delaware

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This invention relates to methods for improving the characteristics of wool which has been made non-felting by a halogenation procedure and to wool materials prepared by such means.

It is well known in the art that fabrics made from wool can be rendered shrink resistant by halogenation of the woolen fibers and wool has been halogenated for this purpose for many years. The customary procedure comprises simply immersing a wool fabric into an aqueous solution of a halogenating agent for a period of time sufficient to give a modification of the epithelial scales of the individual fibers. Unfortunately, however, such a process results in chemical degradation of the wool fibers to a measurable extent as is evidenced by increased alkali solubility, decreased flex-abrasion resistance, and a harsh hand in the treated fabrics.

In the past, many efforts have been made to eliminate the undesirable effects of wool halogenation and to this end there have been employed a wide variety of halogenating agents including the free halogens, organic and inorganic hypohalites, and N-halogenated organic compounds such as N-chloroamides, N-chloroimides, and in particular the N-chlorohydantoins. Other suggestions have included employing solvents other than water such as various ethers or adding to the halogenation bath various substances such as urea and other nitrogen compounds. It has further been suggested that the wool, while in an acid condition, be halogenated with an alkaline bath and various other arrangements of pH control. While some of these measures do in fact lessen to a material extent the amount of undesirable damage to wool resulting from a halogenation procedure, even under optimum conditions there is still obtained a measurable degradation of the wool fibers as a result of halogenation.

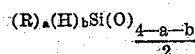
It has now been found that improved characteristics can be imparted to halogenated wools by treating the same with a polymerizable material selected from the group consisting of silicone compounds and carboxylic acid-metal, Werner type complexes of a class, in each instance, to be subsequently defined in greater detail. The application of only a small percent of one of these materials to wools in which the scale structure of the fibers has been modified by halogenation results in the wools having an improved hand, improved abrasion resistance, and decreased alkali solubility.

The class of woolen materials suitable for use in this invention includes fabrics composed of at least largely of wool fibers which have had their scale structure so modified by halogenation that the fabrics can suitably be washed by conventional procedures without excessive felting shrinkage. In more specific terms, a fabric suitable for use in the process of this invention should have the woolen fibers therein halogenated to such an extent that the fabric's potential area felting shrinkage is less than about 10%. When woolen fabrics have been halogenated sufficiently to obtain a fabric characterized by such a low degree of felting shrinkage, the scale structure of the wool fibers has been largely destroyed and the fabric inherently possesses a stiff boardy hand, a relatively high alkali solubility, and a relatively low abrasion resistance. This is generally true regardless of what particular procedure of halogenation is employed and

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even under the most advantageous conditions, a degree of halogenation sufficient to give a wool fabric a satisfactory felting shrinkage for commercial use as a washable woolen generally results in the fabric having an alkali solubility at least 10% greater and a flex abrasion resistance at least 25% less than before halogenation. By the procedure of this invention both the flex abrasion resistance and the alkali solubility can be restored to a value at least approaching that before halogenation.

Silicone compounds suitable for use in this invention include members of the class generally referred to as silicone resins. These compounds are polymers in which silicon atoms are bonded together by oxygen linkages and can be represented by the following empirical formula:

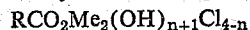


wherein R usually represents a methyl group but can represent other hydrogen groups having not more than about 6 carbon atoms, "a" represents a number of from about 1.0 to 2.0, "b" represents a number of from about 0.25 to 1.25 and "a" + "b" is equal to from about 1.0 to 2.25. Particularly suitable for use in the new process of this invention are the methylhydrogenpolysiloxane resins which are readily capable of undergoing further polymerization on heating in the presence of a catalyst. The methylhydrogenpolysiloxanes can be represented by the above formula wherein R is methyl, "a" is equal to 1.0 to 1.5, "b" equals 0.75 to 1.25 and "a" + "b" is equal to 2.0 to 2.25. Many such compounds are commercially available.

The carboxylic acid metal complexes suitable for use in this invention are of the type disclosed, for example, in U.S. Patents No. 2,273,040, No. 2,662,835, and No. 2,693,458. Such compounds are Werner type complexes of long chain carboxylic acids with a tri-valent metal such as chromium, aluminum, or molybdenum. Complexes of this type are generally available in the form of chlorides and as such are relatively stable in aqueous or alcoholic solution. Upon dilution of the solution, raising the pH or by mild heating, the chloride compound is partially or totally hydrolyzed to give a basic complex which polymerizes by the formation of metal-oxygen-metal linkages to give an insoluble material. The complexes suitable for use in this invention, when in the form of chlorides, can be represented by the formula:



and the basic complexes before polymerization can suitably be represented by the following empirical formula:



wherein Me represents metal, R represents an aliphatic group, and n represents a number from 2 to 4. The metal in these formulas may be chromium, aluminum, or molybdenum, as previously mentioned, and the aliphatic radical may be any hydrocarbon, fluorocarbon, or hydrofluorocarbon radical having from about 8 to 20 carbon atoms.

While the exact reason or reasons for the success of the new process of this invention are not fully understood, it would appear that the above described type of polymeric compounds have the unique ability to act as both plasticizers and anti-swelling agents for wool fibers. The plasticizing of the wool fibers would explain the improved hand and improved abrasion resistance while the anti-swelling action would possibly explain the improved alkali solubility of the halogenated wool fibers. This is only theory, however, and applicants do not wish to be limited thereby.

The amount of polymerizable material that should be applied to the wool will vary somewhat depending upon

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the particular nature of the material and upon the wool to be treated but as a general rule at least about 0.2% of the polymerizable material should be applied since smaller amounts may not give the desired results. On the other hand, there is generally little advantage in applying more than about 4% of the polymerizable material and larger quantities may actually lessen the effectiveness of the process. The preferred range is generally from about 0.5% to 2%.

The polymerizable material may be applied to the wool fabric in any manner which results in the desired quantity thereof being deposited on the wool fibers. One convenient method of application comprises padding the wool through an aqueous solution or emulsion of such a concentration as to result in there being deposited on the wool the desired quantity of material. A second procedure which is satisfactory in many instances comprises exhausting the polymerizable material onto the wool fabric. In the case of carboxylic acid-chromic complexes, it has been found that halogenated wool is substantive for these materials to a certain extent and if the wetted wool is immersed in an aqueous solution of the complex there can be deposited on the wool, by varying the time of immersion, any desired quantity of the complex. Exhaustion techniques are, however, more satisfactory when applying silicone materials since these materials are applied from emulsions and all that need be done is to add to the aqueous emulsion a material that is incompatible with the emulsifying agent so that the emulsion is thereby destroyed and the polymerizable material is deposited on the wool. Such procedures are extremely convenient when applying the methylhydrogenpolysiloxane resins since the emulsion can be destroyed by adding a heavy metal salt capable of reacting with the emulsifying agent to give a suitable catalyst for the further polymerization of the silicone material. After the polymerizable material has been deposited on the wool, the wool should be dried at an elevated temperature, for instance, at a temperature of from about 200° F. to 300° F., to result in the curing of the polymerizable material.

The invention will now be illustrated by the following specific examples in which all parts are by weight unless otherwise indicated:

EXAMPLE I

A fabric composed of 87% wool and 13% nylon is carbonized after fulling, scouring, and dyeing. Following dry milling, the fabric is chlorinated in a bath containing 0.5% available chlorine, passed into a cold antichlor bath containing 1% sodium bisulfite, neutralized with sodium bicarbonate and rinsed. The fabric is then padded through a bath containing 1% of stearatochromic chloride under such conditions as to give a wet pick up of about 100% and is then dried, cured at a temperature of 200° F. to 220° F. for ten minutes, and conditioned overnight before testing.

A fabric sample processed according to the above procedure, as well as chlorinated and unchlorinated control samples were given a total of five 15 minute washes at 140° F. and the area felting shrinkage of each sample was determined after each wash. The results of these tests are given in Table I.

Table I

Number of washes.....	Percent area felting shrinkage after indicated number of washes				
	1	2	3	4	5
Fabric Sample:					
Not chlorinated.....	26	34	41	47	49
Chlorinated.....	-4	-7	-7	-6	-4
Chlorinated and treated.....	-3	-5	-5	-5	-5

(Negative values indicate area gain.)

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The alkali solubility, abrasion resistance, and hand of a fabric processed as above and after the fabric had been sheared, sponged, and semi-decated, as well as comparative figures for chlorinated and unchlorinated control samples are given in the following table.

Table II

Fabric Sample	Alkali Solubility, percent	Flex Abrasion Resistance		Hand
		Warp	Filling	
Not chlorinated.....	19	902	695	Good.
Chlorinated.....	22	293	439	Poor-Fair.
Chlorinated and treated.....	19	1,029	887	Excellent.

EXAMPLE II

Example I is repeated except that for the stearatochromic chloride used in the preceding example, there is substituted an equal quantity of a myristic acid-aluminum complex available from E. I. du Pont Company under the name of Du Pont Aluminum Complex 101. The results are substantially the same.

EXAMPLE III

Example I is repeated except that an equal amount of a Werner type chromic complex of perfluorocaproic acid is substituted for the stearic acid complex employed in Example I. A pronounced improvement in hand, alkali solubility and flex abrasion resistance is obtained.

EXAMPLE IV

A sample of 100% woolen material is prepared for treatment by dry milling in a conventional manner. The woolen material is then divided into three approximately equal portions and one of the three samples is set aside as a control.

In a suitable tank there is placed 460 gallons of water, 200 pounds of ice and sufficient sodium hypochlorite to give an available chlorine concentration of approximately 0.6%. Sulfuric acid is added to reduce the pH from approximately 12.5 to 10 and there is then added 6 gallons of wetting agent (3 gallons each of Tergitol EH and Tergitol #4). A final check of the solution shows the temperature to be 72° F., a pH of 10, and an available chlorine concentration of 0.64%. Two of the three samples are then passed continuously through the chlorination bath at a linear velocity of 26 yards per minute and immediately thereafter are passed through a pair of squeeze rolls and into a water rinse which results in the goods being in contact with the chlorinating agent for approximately eight seconds. The samples are then neutralized in a dolly washer with sodium bicarbonate solution for five minutes, rinsed 15 minutes, extracted and dried.

One of the chlorinated samples is padded through a 1% solution of a stearic acid-chromic complex sold by E. I. du Pont under the name of (Quilon) to give a pick-up of approximately 100% and is then dried at a temperature of approximately 200° F. The three samples are then given a total of five 15 minute washings at 140° F. after which their shrinkage, hand, and abrasion resistance are tested.

It is found that chlorination alone gives good shrinkage control so that even after five washes at 140° F. the felting shrinkage of the chlorinated sample is acceptable. It is found, however, that the plain chlorinated sample has a thin brittle hand as compared to a soft, full, and mellow hand in the control, the flex abrasion resistance of the chlorinated sample is materially lessened, the tensile strength is slightly lower, and the alkali solubility is measurably increased. The sample of woolen material chlorinated and then treated with the chromic complex is found to have a hand comparable to the unhalogenated control, flex abrasion resistance in excess of the control,

a tensile strength higher than that of the plain chlorinated sample, wrinkle recovery in excess of that of the control and an alkali solubility measurably improved over that of the plain chlorinated sample.

EXAMPLE V

A piece of a woolen fabric containing 87% wool and 13% nylon is carbonized after fulling, scouring, and dyeing. After dry milling the piece is divided into four samples three of which are then chlorinated using the procedure of Example IV except that the chlorination bath is adjusted to contain only 0.5% available chlorine and instead of passing the samples directly into water after chlorination, they are passed into a cold anti-chlor bath containing 1% sodium bisulfite and then neutralized with sodium bicarbonate as above. One of the three chlorinated samples is then padded through a 1% solution of a fatty acid-chromic complex (Quilon), to give a pick-up of approximately 100%, and dried at a temperature of approximately 200° F. The second of the chlorinated samples is passed through a bath containing approximately 1% of an emulsion of a methylhydrogenpolysiloxane resin (Dow Corning No. 1107), a fatty acid salt emulsifying agent and 1% stannous chloride as a catalyst to give a pick-up of approximately 100%. The sample is then dried at a temperature of approximately 250° F.

All samples were given five 15 minute washes at 140° F. The sample chlorinated without other treatment is found to have an increased alkali solubility, greatly decreased flex abrasion resistance, and a poor hand. The sample chlorinated and treated with a fatty acid-chromic complex is found to have an alkali solubility about equal to that of the unchlorinated control and to exceed the control in flex abrasion resistance, hand, and wrinkle recovery. The sample chlorinated and treated with a silicone resin is found to have an alkali solubility only slightly in excess of that of the unchlorinated control, a flex abrasion resistance only slightly less than that of the control and a hand substantially unchanged from that of the control.

EXAMPLE VI

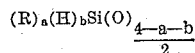
A sample of woolen material composed of 60% wool and 40% rayon is divided into two swatches. Swatch number 1 is employed as a control. Swatch number 2 is treated in an aqueous halogenation bath employing 30 parts by weight of bath for each part by weight of wool material. The bath during treatment is held at a temperature of 70-75° F. and initially contains 1% by weight of HCl, 1% sodium chloride, and 0.2% of wetting agent (Tergitol #4), the percentages in each instance being based on solution weight. There is then added to the bath 7-10% of 1,3-dichloro-5, 5-dimethylhydantoin (on weight of wool) and the wool material is passed through the bath for 1 hour. The material is then rinsed by overflow for 15 minutes, treated with 5% sodium acetate (on cloth weight) for 15 minutes and then again rinsed by overflow for 15 minutes. The material while still wet is then padded through a 1% solution of a fatty acid-chromic complex (Quilon) and dried. The chlorinated sample has an alkali solubility only slightly in excess of that of the control sample, good flex abrasion resistance, and an excellent hand.

The procedure when employing other polymerizable materials is substantially identical to that illustrated in the above examples.

Having thus described our invention, what we desire to claim and secure by Letters Patent is:

1. A washable fabric with an area felting shrinkage of less than 10% which is composed largely of wool fibers having their scale structure destroyed by halogenation to such an extent that they are substantially non-felting, said fibers having deposited thereon from about 0.2% to 4%, by weight of the wool, of a water-insoluble

polymer of a member selected from the group consisting of silicones capable of being represented by the formula:



wherein R represents a hydrocarbon radical having not more than about six carbon atoms, "a" is a number from 1.0 to 2.0, "b" is a number from 0.25 to 1.25 and "a" + "b" is equal to 1.0 to 2.25; and carboxylic acid-metal Werner type complexes capable of being represented by the formula:



wherein R is a radical selected from the group consisting of hydrocarbon, fluorocarbon, and hydrofluorocarbon radicals having from 8 to 20 carbon atoms, Me represents a metal selected from the group consisting of chromium, aluminum, and molybdenum, and n is an integer from 2 to 4.

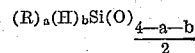
2. A fabric according to claim 1 wherein said polymer is a methylhydrogenpolysiloxane polymer.

3. A fabric according to claim 1 wherein said polymer is a polymer of stearatochromic chloride.

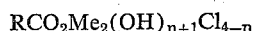
4. A fabric according to claim 1 wherein said polymer is a polymer of myristato aluminum chloride.

5. A fabric according to claim 1 wherein said polymer is a polymer of perfluorocaprato chromic chloride.

6. A method for improving the properties of a fabric formed largely of wool fibers which has been subjected to a degree of halogenation sufficient to reduce its potential felting shrinkage below about 10% and which has a harsh hand, an objectionably high alkali solubility, and an undesirably low flex abrasion resistance, which method comprises applying to said fabric from about 0.2% to 4%, by weight of the wool, of a polymerizable material which is a member selected from the group consisting of silicones capable of being represented by the formula:



wherein R represent a hydrocarbon radical having not more than about six carbon atoms, "a" is a number from 1.0 to 2.0, "b" is a number from 0.25 to 1.25 and "a" + "b" is equal to 1.0 to 2.25; and carboxylic acid-metal, Werner type chloride complexes of the formula:



wherein R is a radical selected from the group consisting of hydrocarbon, fluorocarbon, and hydrofluorocarbon radicals having from 8 to 20 carbon atoms, Me represents a metal selected from the group consisting of chromium, aluminum, and molybdenum, and n is an integer from 2 to 4, and basic complexes derived from said chloride complexes by hydrolysis, and thereafter heating said fabric to cure said material to a state such that it is not readily water dispersible.

7. A method according to claim 6 wherein said material is a methylhydrogenpolysiloxane polymer.

8. A method according to claim 6 wherein said material is stearato chromic chloride.

9. A method according to claim 6 wherein said material is myristato aluminum chloride.

10. A method according to claim 6 wherein said material is perfluorocaprato chromic chloride.

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