PROCESS FOR PREVENTING SHRINKAGE AND FELTING OF WOOL

John D. Floyd, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Nov. 13, 1957, Ser. No. 696,672

2 Claims. (Cl. 117—141)

This application relates to a process for preventing shrinkage and felting of wool.

It is well known in the textile trade that both woven and knitted woolen fabrics shrink excessively on laundering. This shrinkage varies with the type of weave in the fabric and, in some cases, may run as high as 60\% of the original dimensions. Woolen fabrics shrink by two methods; by the so-called relaxation or consolidation phenomenon, and by felting. The former is due to the relaxation of tensions introduced during the knitting or weaving operation and is common to all hydrophilic fibers. The latter is due to the unique physical and mechanical properties of the wool fiber. The physical property which brings about felting is the scaled surface of the fiber which gives it a low coefficient of friction in one direction. This means that when a fabric is subjected to mechanical action, the individual fibers migrate in one direction making for a more dense structure, thereby reducing the linear dimensions. This dense structure is consolidated by the higher resilience of the fibers which is related to their curling or spiraling tendency.

Various treatments such as chlorination treatments, oxidative treatments, alkali treatments and resin treatments have been used to reduce the felting shrinkage of wool. None of these treatments, however, has been entirely satisfactory. Thus, chlorination treatments require close control of conditions to prevent general loss of desirable wool-like character of the fabric made therefrom and reduction of wear qualities. Moreover, chlorination treatments generally result in weakening the fabric and also impart a harsh feel thereto. Oxidative treatments as with peroxo compounds and permanganate, are likewise difficult to carry out in a manner such as to achieve adequate resistance to shrinkage without undue fiber damage. Alkali treatments, as with caustic or potash from dry solvents are disadvantageous from the cost standpoint due to the necessity for solvent-recovery systems and other special equipment. Resin treatments, such as with methylated methylenealine and methylated nylon, cause a loss in the subjective properties of the fabric. Such treatments, moreover, require a high-temperature cure and a high add-on level to obtain acceptable shrink resistance. This high additive level causes more or less permanent fabric stiffening and, in addition, increases the cost.

The principal object of the present invention is the provision of an improved process for preventing shrinkage and felting of wool.

Another object of the invention is the provision of a durable treatment to prevent shrinkage in woolen fabrics without detriment to the desirable physical properties of the fabrics.

A further object of the invention is the provision of a process for making a shrink-resistant wool fabric without the use of oxidizing, reducing, strongly acid or strongly basic chemicals, all of which are detrimental to the physical properties of the fabric.

In accordance with the invention, the above and other objects are accomplished by treating a wool fabric with certain water-soluble cationic thermosetting polyamide-epichlorhydrin resins to be described more fully hereinafter. It has been found that treatment with such resins is highly effective for the dimensional stabilization of woolen fabrics. The treatment, moreover, does not add harshness or stiffness to the fabric and does not significantly yellow or otherwise change the color of the fabric.

In carrying out the process of the invention, an aqueous solution of the cationic resin is applied to the fabric in any suitable manner as by dipping, spraying, padding or the like. Any desired or convenient concentration of the aqueous resin solution may be utilized for such application; however, it has been found that concentrations from about 1\% to about 10\% are quite satisfactory. These, therefore, are preferred. The concentration and time of treatment should be such that the fabric absorbs from 0.5% to 10% by weight, based on the dry weight of fabric, of the cationic resin. Less than 0.5% will not produce the desired resistance to shrinkage and felting, and more than 10% offers no particular advantage and, hence, will normally not be used.

After treatment with the cationic resin, the fabric is dried preferably at about 65° C. for about 5 minutes in an air-circulating oven. The oven temperature is then raised to about 100° C. and the treated fabric given a 5-minute cure at this temperature. This short, low-temperature cure cycle can easily be handled by ordinary textile processing equipment. While the described temperatures and times are quite advantageous, it will be appreciated that the invention is not limited thereto and that drying and curing may be effected at higher or lower temperatures, i.e., from about 40° C. to about 150° C. with a corresponding decrease or increase in the duration of treatment.

A particular advantage of the invention is that the treatment may be carried out, under acid, neutral or alkaline conditions, i.e., at pH's from about 3 to about 10. The preferred pH range is from about 5 to about 8.

The cationic thermosetting polyamide-epichlorhydrin resins contemplated for use herein comprise a water-soluble polymeric reaction product of epichlorhydrin and a polyamide derived from a polyalkylene polyamine and a C₆-C₈ saturated aliphatic dicarboxylic acid. It has been found that resins of this type are uniquely effective for preventing shrinkage of wool fabrics without adversely affecting other desirable physical properties of the fabric.

In the preparation of these cationic thermosetting resins, the dicarboxylic acid is first reacted with the polyalkylene polyamines under conditions such as to produce a water-soluble polyamide containing the recurring groups

\[ \text{—NH(C₃H₆H₂NHN)ₓ—CORCO—} \]

where n and x are each 2 or more and R is the divalent hydrocarbon radical of the dicarboxylic acid. This water-soluble polyamide is then reacted with epichlorhydrin to form the water-soluble cationic thermosetting resin.

The dicarboxylic acids contemplated for use in preparing these resins are the C₆-C₈ saturated aliphatic dicarboxylic acids such as succinic, glutaric, adipic and the like. The saturated dicarboxylic acids having from 4 to 8 carbon atoms in the molecule are preferred. Blends of two or more of the saturated dicarboxylic acids may also be used.

A variety of polyalkylene polyamines including polyethylene polyamines, polypropylene polyamines, polyvin-
tylene polyamines and so on may be employed of which the polyethylene polyamines represent an economically preferred class. More specifically, the polyalkylene polyamines contemplated for use may be represented as polyamines in which the nitrogen atoms are linked together by groups of the formula \(-C\text{H}_2\text{N}-\) where \(n\) is a small integer greater than unity and the number of such groups in the molecule ranges from two up to about eight. The nitrogen atoms may be attached to adjacent carbon atoms in the group \(-C\text{H}_2\text{N}-\) or to carbon atoms further apart, but not to the same carbon atom. This invention contemplates not only the use of such polyamines as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine and the like, which can be readily synthesized from various crude polyamine materials. For example, the mixture of polyethylene polyamines obtained by the reaction of ammonia and ethylene dichloride, refined only to the extent of removal of chlorides, water, excess ammonia and ethylenediamine, is a very satisfactory starting material. The terms polyamines employed in the claims, therefore, refers to and includes any of the polyalkylene polyamines referred to above or to a mixture of such polyalkylene polyamines.

It is desirable, in some cases, to increase the spacing of secondary amino groups on the polyamine molecule in order to change the reactivity of the polyamide-epichlorohydrin complex. This can be accomplished by substituting a diamine such as ethylenediamine, propylenediamine, hexamethylenediamine and the like for a portion of the polyalkylene polyamine. For this purpose, up to about 80% of the polyalkylene polyamine may be replaced by a molecularly equivalent amount of the diamine. Usually, a replacement of about 50% or less will serve the purpose.

The temperatures employed for carrying out the reaction between the dicarboxylic acid and the polyalkylene polyamine may vary from about 110° C. to about 250° C. or higher at atmospheric pressure. For most purposes, however, temperatures between about 160° C. and 210° C. have been found satisfactory and are preferred. Where reduced pressures are employed, somewhat lower temperatures may be utilized. The time of reaction depends on the temperatures and pressures utilized and will ordinarily vary from about \(\frac{1}{2}\) hour to 2 hours, although shorter or longer reaction times may be utilized depending on reaction conditions. In any event, the reaction is desirably continued to substantial completion for best results.

In carrying out the reaction, it is preferred to use an amount of dicarboxylic acid sufficient to react substantially with the secondary amino groups of the polyalkylene polyamine but insufficient to react with the secondary amine groups to any substantial extent. This will usually require a mole ratio of polyalkylene polyamine to dicarboxylic acid of about 0.9:1 to about 1.2:1. However, mole ratios of from about 0.8:1 to about 1.4:1 may be used with quite satisfactory results. Mole ratios outside of these ranges are generally unsatisfactory. Thus, mole ratios below about 0.8:1 result in a gelled product or one having a pronounced tendency to gel while mole ratios above 1.4:1 result in low molecular weight polyamides. Such products when reacted with epichlorohydrin do not produce resins having the desired efficiency for use herein.

In converting the polyamide, formed as described, to a cationic thermosetting resin, it is reacted with epichlorohydrin at a temperature from about 45° C. to about 100° C. and preferably between about 45° C. and 70° C. until the viscosity of a 20% solids solution at 25° C. has reached about C or higher on the Gardner-Holdt scale. This reaction is preferably carried out in aqueous solution to moderate the reaction. pH adjustment is usually not necessary. However, since the pH decreases during the polymerization phase of the reaction it may be desirable, in some cases, to add alkali to combine with at least some of the acid formed.

When the desired viscosity is reached, sufficient water is then added to adjust the solids content of the resin solution to the desired amount, i.e., about 10% more or less, the product cooled to about 25° C. and then stabilized by adding sufficient acid to reduce the pH at least to about 6 and preferably to about 5. Any suitable acid, such as phosphoric, sulfuric, nitric, formic, phosphonic and acetic acid may be used to stabilize the product. However, hydrochloric acid is preferred.

In the polyamide-epichlorohydrin reaction, it is preferred to use sufficient epichlorohydrin to convert all secondary amine groups to tertiary amine groups. However, more or less may be added to reduce or increase reaction rates. In general, satisfactory results may be obtained utilizing from about 0.5 moles to about 1.8 moles of epichlorohydrin for each secondary amine group of the polyamide. It is preferred to utilize from about 1.0 mole to about 1.5 moles for each secondary amine group of the polyamide.

The following examples will serve to illustrate the invention. In these examples the cationic water-soluble thermosetting polyamide-epichlorohydrin resin utilized was prepared as follows: Two hundred twenty-five grams (2.18 moles) of diethylenetriamine and 100 grams of water were placed in a 2-liter flask equipped with a mechanical stirrer, thermometer and condenser. To this was added 290 grams (2.0 moles) of adipic acid. After the acid had dissolved in the amine, the solution was heated to 185–200° C. and held there for \(\frac{1}{2}\) hour. Then vacuum was applied to the flask during the period required for the contents of the flask to cool to 140° C. following which 430 grams of H_2O was added. The polyamide solution contained 52.3% solids and had an acid number of 2.1. To 60 grams of this polyamide solution in a round-bottom flask was added 225 grams of H_2O. This solution was heated to 50° C. and 12.5 grams of epichlorohydrin was added dropwise over a period of 11 minutes. The contents of the flask was then heated to 60–70° C. until it had attained a Gardner viscosity of >E. Then 150 grams of H_2O was added to the product, and it was cooled to 25° C. Eleven ml of 3.7% HCl was then added to adjust the pH to 5.8. The product contained 9.0% solids and had a Gardner viscosity of C-D.

Example 1

A sample of scoured, carbonized and bleached wool flannel cloth was treated in the following manner with a 5% aqueous solution of the cationic thermosetting resin prepared as described above. The dry fabric was padded, double ended, through a room-temperature solution of the resin on a 10-inch laboratory wetter. The wet pick-up was found to be 113% (5.6% resin solids based on the dry weight of the cloth). The treated fabric was air-dried and cured for 5 minutes at 150° C. after which it was washed for 45 minutes in a 130° F., 0.1% neutral soap wash. After air-drying, the total shrinkage of the fabric was 9.1%. This compared to 50% shrinkage for an untreated sample. It should be noted that these values represent total shrinkage, i.e., relaxation shrinkage plus felting shrinkage. The hand and color of the fabric after washing were not impaired by the foregoing treatment.

Example 2

The treated sample from Example 1 was given a second wash as described in Example 1, followed by \(\frac{1}{2}\)-hour room temperature dry-cleaning cycle, followed by a third wash cycle. The additional shrinkage after these treatments was found to be nil.

Example 3

A sample of woolen fabric was treated as in Example 1.
with a 5.1% aqueous solution of the cationic resin prepared as above described and cured for 5 minutes at 100° C. The wet pick-up was 100% (5.1% resin solids based on dry weight of the fabric). It was washed and dried as previously described. The total shrinkage was found to be 6.1%.

Example 4

A sample of woolen fabric was treated with a 3.13% aqueous solution of the cationic resin prepared as described above and treated as in Example 3. The wet pick-up was 100% (3.13% resin solids based on dry weight of the fabric). After washing, its total shrinkage was 3.1%. This sample was given four additional launderings. The increased shrinkage due to the extended laundering was 4.8%, or a total of 7.9% after five launderings.

The following example gives comparative results obtained with well-known resins used commercially for shrinkproofing wool fabrics. In this example, samples of woolen fabric similar to those treated in Examples 3 and 4 were treated with different commercial resins in accordance with the following procedure. The commercial resin was padded onto the fabric from a cold aqueous solution containing the ammonium sulfate catalyst (5% on resin solids). The fabric was dried 5 minutes and cured 5 minutes at 150° C. The results are shown in the following table.

### Table

**Shrinkproofing of wool fabric with commercial resins**

<table>
<thead>
<tr>
<th>Type of Resin</th>
<th>Concentration, Weight Percent</th>
<th>Catalyst</th>
<th>Curing Conditions after 1-30 min. Neutral Wash</th>
<th>Percent Shrinkage after 1-30 min. Neutral Wash</th>
<th>Condition of Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine-formaldehyde Resin</td>
<td>6.45</td>
<td>Ammonium Sulfate...</td>
<td>5</td>
<td>7.6</td>
<td>Harsh, stiff, discolored.</td>
</tr>
<tr>
<td>Methylated melamineformaldehyde Resin (Type 1)</td>
<td>6.30</td>
<td>Ammonium Sulfate...</td>
<td>5</td>
<td>13.7</td>
<td>Harsh and stiff.</td>
</tr>
<tr>
<td>Methylated melamineformaldehyde Resin (Type 2)</td>
<td>6.25</td>
<td>Ammonium Sulfate...</td>
<td>5</td>
<td>29.6</td>
<td>Slightly stiff.</td>
</tr>
<tr>
<td>Methylated melamineformaldehyde Resin (Type 3)</td>
<td>6.15</td>
<td>Ammonium Sulfate...</td>
<td>5</td>
<td>41.3</td>
<td>Soft.</td>
</tr>
<tr>
<td>Methylated melamineformaldehyde Resin (Type 5)</td>
<td>6.07</td>
<td>Ammonium Sulfate...</td>
<td>5</td>
<td>51.1</td>
<td>Slightly stiff.</td>
</tr>
</tbody>
</table>

It will be seen from the examples that woolen fabrics treated in accordance with the process of the invention are dimensionally stabilized through at least five one-half hour wash cycles. A particular advantage of the invention is the fact that the treated fabric, after washing, is desirable soft, whereas commercial resins such as those illustrated in Example 5, lend a harsh, stiff hand to the fabric and/or provide substantially less dimensional stability in the fabric. The fact that the resins herein disclosed lend a durable soft hand to the fabric is unexpected since the resins themselves form rather brittle films.

Other advantages flowing from the use of the type of resin herein disclosed in comparison with commercial resins is that it is effective at low concentrations, cures independently of pH and at lower temperatures, ca. 100° C., requires no catalyst and does not significantly yellow or otherwise change the color of the fabric.

The term “wool fabric” as used herein includes any animal hair fabric such as sheep wool, mohair, cashmere, camel hair, alpaca wool, vicuna wool, llama wool, yak wool, and horsehair. The term also includes fabrics which are 100% animal hair and fabrics which are blends of animal hair with natural and/or synthetic fibers such as cotton, polyacrylonitrile fiber, polyethylene terephthalate fibers, polystyrene fibers and so on.

While specific embodiments of the invention have been illustrated and described herein, it will be understood that changes and variations may be made without departing from the scope of the invention as defined in the claims which follow.

What I claim and desire to protect by Letters Patent is:

1. A process of treating wool fabrics to prevent shrinkage thereof during washing which comprises treating the fabric with from about 0.5% to about 10% by weight, based on the weight of the fabric, of a cationic water-soluble thermosetting resin obtained by reacting a polyalkylene polyamine having two primary amine groups and at least one secondary amine group with a C₈-C₁₀ saturated aliphatic dicarboxylic acid in a mole ratio of from about 0.8 to about 1.4 of the former to about 1.0 of the latter to form a long-chain polyamide having secondary amine groups, and then reacting the polyamide with epichlorohydrin in a mole ratio of epichlorohydrin to secondary amine groups of said polyamide of from about 0.5:1 to about 1.8:1, and thereafter heating the treated fabric at a temperature from about 40° C. to about 150° C. to cure the resin.

2. A process according to claim 1 wherein the cationic thermosetting resin is obtained by (1) reacting the C₈-C₁₀ saturated aliphatic dicarboxylic acid with the polyalkylene polyamine at a temperature from about 110° C. to about 250° C. to form the polyamidine and (2) reacting the polyamidine with epichlorohydrin at a temperature from about 45° C. to about 100° C. to form the water-soluble cationic thermosetting resin.

3. A process according to claim 1 wherein the cationic thermosetting resin is obtained by (1) reacting a C₈-C₁₀ saturated aliphatic dicarboxylic acid with the polyalkylene polyamine at a temperature from about 160° C. to about 210° C. to form the polyamidine and (2) reacting the polyamidine with epichlorohydrin at a temperature from about 45° C. to about 70° C. to form the water-soluble cationic thermosetting resin.

4. A wool fabric having improved resistance to shrinkage, said fabric containing from about 0.5% to about 10% by weight, based on the weight of the fabric, of a cured cationic thermosetting resin obtained by reacting a polyalkylene polyamine having two primary amine groups and at least one secondary amine group with a C₈-C₁₀ saturated aliphatic dicarboxylic acid in a mole ratio of from about 0.8 to about 1.4 of the former to about 1.0 of the latter to form a long-chain polyamide having secondary amine groups, and then reacting the polyamide with epichlorohydrin in a mole ratio of epichlorohydrin to secondary amine groups of said polyamide of from about 0.5:1 to about 1.8:1.

### References Cited in the file of this patent

**UNITED STATES PATENTS**

- 2,468,086 Latham et al. .......... Apr. 26, 1949
- 2,595,935 Daniel et al. .......... May 6, 1952

**OTHER REFERENCES**