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TEXTILE TREATMENT

Paul Arthur, Jr., and Max Theodore Goebel, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the improvement of wool and more particularly to reduction of its shrinking tendency.

Woolen textiles are characterized by their tendency to felt when subjected to mechanical working. This felting tendency is essential in the finishing of some woolen goods to give a dense surface, and in the manufacture of felt for paper machine blankets, and the like. However, since it causes shrinking during laundering, it is a serious disadvantage in many wool applications. Considerable attention has therefore been given to reducing or eliminating shrinkage due to felting. For some applications, including knit goods, baby clothing, underwear, and socks, it is desirable to have the material substantially completely shrinkproof. For overcoats, suits, dresses, blankets, jackets, and other articles which are laundered less frequently the wool need be only partially shrinkproof to be satisfactory in practice. Previous shrinkproofing methods, including treatment with chlorine, hypochlorites, sulfuryl chloride, and the like, have not been entirely satisfactory. Chlorination is difficult to control and produces harshness and discoloration. Sulfuryl chloride is less objectionable from the standpoint of harshening effect, but it is inconvenient to use because of its strongly acidic nature, which necessitates the use of special acid-resistant equipment in carrying out the treatment. Also, when, as previously proposed, agents are used to treat union fabrics consisting of both wool and cotton, the acid-sensitive cellulosic fibers are weakened as is shown by a marked decrease in the tensile strength of the fabric.

This invention has as an object the improvement of the physical characteristics of wool by reducing its tendency to shrink on laundering. Another object is the production of a shrinkproof wool free from harshness and discoloration. A further object is the preparation of the product by a convenient process which may be carried out in inexpensive and readily available equipment. A still further object is a process suitable for use on mixed wool-cotton material. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a textile comprising wool is treated with a dispersion, preferably a solution, comprising an organic compound having at least one thiol (SH) group attached to a carbon itself attached to three other atoms by single bonds, in which compound any atom beta to the thiol group, i. e., attached to the carbon in turn attached to the thiol group, has at least two

valences attached to members of the group consisting of carbon and hydrogen, and an acid-binding agent, i. e., an acid neutralizing agent, e. g., a hydroxide, phosphate, bicarbonate, carbonate or alcoholate of an alkali or alkaline earth metal, a strong quaternary ammonium base, or a tertiary aliphatic amine.

In carrying out the invention, wool or a wool-containing textile is immersed in a dispersion of the thiol compound in a suitable solvent which also contains an acid-binding agent such as sodium hydroxide. It is most convenient to use solvents in which both the thiol compounds and the alkali are readily soluble, such as the alcohols or water. Ethyl alcohol is very highly satisfactory, and methanol, isopropanol, butanol, etc., may also be used. Water is satisfactory as a solvent in the case of the lower mercaptans, such as ethyl mercaptan, but is not as useful for higher mercaptans, such as cyclohexanthiol, because of the lower solubility of these substances.

The treatment is most conveniently carried out at room temperature, and may be continued most advantageously for about one hour. After treatment, the excess solution is removed by rinsing the fabric in water or in other solvent. It is also possible to use wringers or centrifuges to remove the excess solution.

The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight unless otherwise specified. There are of course many forms of the invention other than these specific embodiments.

Example I

One part of wool flannel is immersed at 25° C. for one hour in 10.2 parts of a 1.7% solution of cyclohexanethiol which also contains 0.53% of sodium hydroxide in 95% by volume ethyl alcohol denatured with 0.5% by volume of benzene. The treated fabric is then rinsed in water and dried. This treatment completely removes the shrinking tendency of the wool.

In determining the shrinkproofness of the treated wool, it has been found convenient to use a uniform testing procedure, referred to hereinafter as the laundering test. In this test a small sample of wool fabric treated according to a process of this invention and a similar sample of untreated fabric are measured to determine their respective areas and then each is passed a definite number of times (usually 150) through a rubber-roll wringer, dipping after each pass into a solution containing 0.25% of a detergent, e. g., "Ivory Soap" or sulfated oleyl alcohol and 0.1% sodium carbonate at 25° C. Other dilute

alkaline soap solutions can be used in this test. After laundering, the samples are dried and again measured. The area losses sustained by the samples are then determined and the per cent shrinkproofness is calculated from the following formula:

$$\frac{100 \times (\text{area loss of untreated fabric} - \text{area loss of treated fabric})}{(\text{area loss of untreated fabric})}$$

Percent shrinkproofness, i. e., percent reduction of tendency to shrink

The per cent shrinkproofness given in the following examples was determined by this method. The laundering test is also a convenient method of following the shrinkproofing treatment since a small sample may be taken from the textile material which is immersed in the mercaptan dispersion at the end of a period judged to be suitable for obtaining the desired effect and tested in the above manner to determine the per cent shrinkproofness. If the material has not yet been treated to the desired degree, the process may be continued until another test indicates that the desired degree of shrinkproofness has been achieved.

Example II

One part of wool crepe is immersed for one hour at 25° C. in 5.5 parts of a 0.89% dispersion of formthional which also contains 0.35% of sodium hydroxide in 95% by volume ethyl alcohol denatured with 0.5% by volume benzene. At the end of the treatment the solution is removed by rinsing the fabric in water. The treated fabric is shrinkproof and free from tendering.

Example III

One part of union fabric having a cotton warp and a wool woof is immersed at 25° C. for one hour in 4.5 parts of a 0.89% dispersion of formthional which also contains 0.35% of sodium hydroxide in 95% by volume ethyl alcohol denatured with 0.5% by volume benzene. The treated fabric is found to be substantially shrinkproof (90.5%) and free from discoloration.

Example IV

One part of wool flannel is immersed for one hour at 25° C. in 6.4 parts of a 1.4% solution of ethanethiol in saturated lime water. The fabric is then wrung dry and rinsed in water. The shrinking tendency of the flannel is greatly decreased (57%).

Example V

One part of wool flannel is immersed at 25° C. for one hour in 7.4 parts of a 1.5% solution of octanethiol-2 which also contains 0.42% sodium hydroxide in 95% by volume ethyl alcohol denatured with 0.5% by volume benzene. The fabric treated in this manner is rinsed in water and dried. The shrinking tendency of the flannel is greatly reduced (54%) by this treatment.

Example VI

One part of wool flannel is immersed for one hour at 25° C. in 7.5 parts of a 1.95% solution of cetanethiol which also contains 0.35% of sodium hydroxide in 95% ethyl alcohol denatured with 0.5% by volume benzene. The excess solution is rinsed from the fabric with solvent and the cloth is dried. A 30% reduction in the shrinking tendency is obtained as a result of this treatment.

Example VII

One part of wool flannel is immersed for seventeen hours at 25° C. in 6.4 parts of a 1.4%

solution of thiosemicarbazide in saturated lime water. A marked reduction (27.5%) in the shrinking tendency of the flannel is effected by this treatment.

In the process of the present invention, there may be used any organic substance which, when in a weakly alkaline solution, contains or yields at least one thiol (—SH) group attached to aliphatic carbon. Because of their higher effectiveness, those substances are greatly preferred in which the thiol groups are attached to aliphatic carbon atoms which are, in turn, attached to other atoms only by single bonds. The following types of substances are included in the preferred class:

(a) Aliphatic mercaptans such as ethyl, methyl, cetyl, n-propyl, isopropyl, n-propylbutyl, sec.-butyl, tert.-butyl, amyl and n-octyl mercaptans, octanethiol-2, etc.

(b) Thioglycols, including mono- and dithioglycols, e. g. pentamethylenedithiol and 2,2'-dimercaptodiethyl ether.

(c) Polythiols, including sym.-neopentanedithiol and thioglycerine.

(d) Alicyclic mercaptans, e. g., cyclohexanethiol, methylcyclohexanethiols, and halogenated cyclohexanethiol.

(e) Heterocyclic mercaptans, e. g., 4-mercaptopyrane, and furfuryl mercaptan.

(f) Aralkyl mercaptans, e. g., beta-phenylethyl mercaptan, in which the thiol group is attached to the aliphatic part of the molecule.

(g) Polymeric mercaptans, e. g., condensation products of aldehydes and hydrogen sulfide, e. g., that described in U. S. 1,991,765. Formthional, the material prepared by saturating a formaldehyde solution with hydrogen sulfide as described in this patent, is particularly preferred because of its great effectiveness and low volatility. Its chemical formula is probably



Other compounds useful in this invention, but much less preferred because of lower effectiveness, include those which enolize under alkaline conditions to yield thiol groups, such as thiosemicarbazide. The N-dialkyl dithiocarbamates may also be used.

The thiol compounds of this invention may contain other groups, such as amide or amine linkages, or also aromatic groups, provided the thiol groups are attached to aliphatic carbon. The thiol and the product of the neutralization thereof by the acid binding agent in the solution are regarded as equivalents. However, the thiophenols, such as beta-thionaphthol, are ineffective and are therefore excluded. All the above thiol compounds can be prepared by well-known methods, and their preparation forms no part of the present invention. The thiol-containing material used as the reagent in the treatment need not be pure, nor does it have to be a chemical individual. Satisfactory results can be obtained by using crude mixtures of mercaptans such as those derived from petroleum fractions or by using mixtures containing polymeric thiols of various molecular weights. A perfect solution is preferable to prevent deposits on the material being treated, but very slightly soluble thiol materials, such as formthional, may be used as suspensions or dispersions, and give the desired degree of shrinkproofing. While any solvent may be employed, it is preferred that a solvent having at least some swelling action on the wool be

employed. Hydroxylated solvents such as alcohol and water are preferred.

A wide range of acid-binding agents may be used including the alkali metal hydroxides, carbonates, bicarbonates, phosphates, and alcohols, the corresponding alkaline earth compounds, e. g., barium, calcium, and strontium hydroxides, and the strong quaternary ammonium bases, e. g., tetramethyl ammonium hydroxide. For economic reasons, it is preferred to use the cheap alkali metal or alkaline earth acid-binding agents rather than the organic compounds.

The solvent, wool to liquor ratio, temperature, and length of treatment are interdependent variables. Thus it is possible to obtain satisfactory shrinkproofing within a shorter period of time by increasing the temperature and concentration of the treating agents. In most cases, it is preferred to adjust conditions so that a period of one-half to two hours may be used to obtain satisfactory shrinkproofing treatments. A longer period of immersion is undesirable because of operating costs and some danger of lowering the tensile strength of the fiber.

The concentration of acid-binding agent is important in obtaining the best results as is shown by the following table of treatments in which the wool is immersed one hour in 5.2 parts by weight of a 1.7% solution of cyclohexane thiol in 95% by volume benzene-denatured ethyl alcohol containing varying percentages of sodium hydroxide.

Table I

Weight percent of sodium hydroxide	Percent of shrinkproofing
0.034	13
0.105	30
0.340	67.5
0.530	79.5

If formthional is used as the shrinkproofing agent, the optimum concentration of the acid-binding agent is very nearly the same as in the case of cyclohexane thiol as is shown by the following table. The values were obtained on testing wool flannel (1 part) which has been immersed for 75 minutes at 25° C. in 7.5 parts of 0.85% dispersions of formthional, which also contained various percentages of sodium hydroxide, in 95% by volume ethyl alcohol denatured with 0.5% by volume benzene.

Table II

Weight percent of sodium hydroxide	Percent of shrinkproofing
0.05	23.7
0.25	67.4
1.2	76.3
2.4	71.1
5.8	Completely shrinkproof

It should be noted from the above table that it is permissible to use widely varying percentages of the acid-binding agent without seriously affecting the process. Of course, it will be obvious to one skilled in the art of wool finishing that abnormally excessive treating periods or acid-binding agent concentrations should be avoided.

It is preferred to use acid-binding agent concentrations within the range of 0.2-2% by weight based on the total weight of solution employed. Higher acid-binding agent concentrations cause a slightly less soft feel in the product, but are still useful, particularly when the wool is treated

for periods of time shorter than two hours. Thus, as is shown in Table II, satisfactory shrinkproofing effects have been obtained by using formthional and 5.8 percent of sodium hydroxide in alcohol for a 75 minute period. Even higher acid-binding agent concentrations are inconvenient to prepare in alcohol solvents and cause some loss of tensile strength. For these reasons they are not preferred. Acid-binding agent concentrations of 0.01-0.2% by weight are useful where substantially complete shrinkproofing is not essential. In any case the acid-binding agent concentration should be below that which would cause any substantial injury to the wool at the temperature and for the time employed.

The process of the present invention is applicable to any textile comprising wool, or a mixture of wool with other textile materials whether in the form of fabric, yarns, or threads. Other finishing treatments can be applied before or after the shrinkproofing treatment. Such finishes include the application of waterproofing agents, dyes, metallic salts, lubricants, or starch preparations.

To obtain best results, it is preferred to operate this invention at substantially room temperature, i. e., 15-35° C. although temperatures up to 50° C. may be employed.

Because of the widely different characteristics of the various kinds of wool, it is obvious to one skilled in the art of wool treatment that account should be taken of these variations in carrying out any modification of the fibers. The effectiveness of the shrinkproofing treatment for a specific woolen fabric is contingent on the correct balance of a number of factors, including the choice of reagent, solvent, and acid-binding agent, the ratio of wool to thiol dispersions, the concentration of the reagents and the temperature and duration of the treatment. However, a few simple trials by one skilled in the art will serve to indicate optimum treating conditions in any given case. It will be noted that the treatment durations and temperatures used in the examples are those most suited to large-scale applications.

Wool, shrinkproofed by the processes of this invention, is well suited for finishing treatments with other chemicals. Useful modifications of the wool may be obtained through after-treatment with aldehydes, ketones, ketenes, acyl alkyl ketenes, urea-aldehyde reaction products, acylating agents, oxidizing agents, alkylating agents, metallic salts, and the like.

The reagents of this invention offer the advantage over those hitherto commercially employed of being less dangerous and much less corrosive, so that it is not necessary to use special acid-resistant apparatus. The reaction is slow enough to permit of easy control by varying the duration of the treatment and the concentration of the reagents. A further advantage of this process over those hitherto employed commercially is that it is suited for application to wool-cotton union fabrics. Procedures previously employed for the shrinkproofing of wool are carried out under somewhat acidic conditions to which the cellulosic components of the textile materials are sensitive. For example, a strip one inch wide of material treated as in Example III is found to have a tensile strength of 80.2 pounds measured in the direction of the warp, consisting of cellulosic fibers. An untreated control has a value of 82.0 pounds under the same testing conditions, indicating that the treatment, described in Example III, has substantially no effect on the

tensile strength of the cotton component of the fabric. On the other hand, the same fabric treated with sulfuryl chloride according to the process described below gives a tensile strength of only 65.2 pounds under the same testing conditions, indicating that serious damage has been caused. The sulfuryl chloride treatment is carried out by immersing a union fabric (7 parts) having a cotton warp and a wool woof at 20° C. for one hour in 27 parts of a 2% by volume solution of the shrinkproofing agent in Stoddard solvent. The fabric is then freed from the excess solution, rinsed first in water, then in 5% aqueous ammonium hydroxide solution, and finally in water. The sample treated according to Example III is 90.5% shrinkproofed whereas that treated with sulfuryl chloride was 76% shrinkproofed.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. A process for reducing the tendency of a textile comprising wool to shrink which comprises treating the same with a dispersion comprising an acid-neutralizing substance and an organic compound containing at least one thiol ($-SH$) group attached to a carbon atom attached to three other atoms by single bonds in which compound the non-thiol portion of the molecule is selected from the class consisting of aliphatic, araliphatic and cycloaliphatic hydrocarbon radicals, aliphatic hydrocarbon radicals containing ether groups and aliphatic hydrocarbon radicals containing thioether groups.

2. A process for reducing the tendency to shrink of a textile comprising wool which comprises treating the same with a solution comprising an acid-neutralizing substance and an organic compound containing at least one thiol ($-SH$) group attached to a carbon atom attached to three other atoms by single bonds in which compounds the non-thiol portion of the molecule is selected from the class consisting of aliphatic, araliphatic and cycloaliphatic hydrocarbon radicals, aliphatic hydrocarbon radicals containing ether groups and aliphatic hydrocarbon radicals containing thioether groups.

3. A process for reducing the tendency of a woolen textile to shrink which comprises treating the same with a solution in an alcohol of an acid-neutralizing substance and an organic compound containing at least one thiol ($-SH$) group at-

tached to a carbon atom attached to three other atoms by single bonds in which compound the non-thiol portion of the molecule is selected from the class consisting of aliphatic, araliphatic and cycloaliphatic hydrocarbon radicals, aliphatic hydrocarbon radicals containing ether groups and aliphatic hydrocarbon radicals containing thioether groups.

4. A process for reducing the tendency of a woolen textile fabric to shrink which comprises treating the same with a solution of an acid-neutralizing substance and an organic compound containing at least one thiol ($-SH$) group attached to a carbon atom attached to three other atoms by single bonds in which compounds the non-thiol portion of the molecule is selected from the class consisting of aliphatic, araliphatic and cycloaliphatic hydrocarbon radicals, aliphatic hydrocarbon radicals containing ether groups and aliphatic hydrocarbon radicals containing thioether groups.

5. A process for reducing the tendency of a woolen textile fabric to shrink which comprises treating the same with a solution, in ethyl alcohol, of an acid-neutralizing substance and formthional.

6. A process for reducing the tendency of a textile comprising wool to shrink which comprises treating the same with a dispersion comprising an acid-neutralizing substance and formthional.

7. A process for reducing the tendency to shrink of a textile comprising wool which comprises treating the same with a solution comprising an acid-neutralizing substance and formthional.

8. A process for reducing the tendency of a woolen textile to shrink which comprises treating the same with a solution in alcohol of an acid-neutralizing substance and formthional.

9. A process for reducing the tendency of a woolen textile fabric to shrink which comprises treating the same with a solution of an acid-neutralizing substance and formthional.

10. A process for reducing the tendency of a union goods comprising wool to shrink which comprises treating the same with a solution, in ethyl alcohol, of an acid-neutralizing substance and formthional.

11. Process of claim 10 wherein the union goods comprises an acid-sensitive textile material having a cellulosic nucleus selected from the class consisting of cellulose and cellulose acetate.

PAUL ARTHUR, JR.
MAX THEODORE GOEBEL.

CERTIFICATE OF CORRECTION.

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PAUL ARTHUR, JR., ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 15, claim 4, for the word "compounds" read --compound--; line 38, claim 8, before "alcohol" insert --an--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of July, A. D. 1941.

(Seal)

Henry Van Arsedale,
Acting Commissioner of Patents.