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METHOD OF REDUCING SHRINKAGE OF WOOL

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This invention relates to the improvement of wool and other keratinous textile fibers, and more particularly to reduction of the shrinking tendency of such fibers.

A number of keratinous (see Lloyd and Shore, Chemistry of the Proteins, 1938, page 88) textile fibers, of which wool is the most important, 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 felts for hats, 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 as completely shrinkproof as is possible. For overcoats, suits, dresses, blankets, jackets, and other articles which are laundered less frequently, the shrinking tendency of the wool need be only partially and not completely eliminated to be satisfactory in practice.

Methods previously proposed for reducing the shrinking tendency of wool include treatment with halogens, hypohalites, sulfuryl chloride and the like. However, chlorination procedures result in damage to the wool which is manifested in decreased strength, increased harshness, a slimy feel when wet, discoloration, and loss of the natural water repellency of the wool. Another disadvantage of halogenation is that "tailing" effects occur, due to the rapid reaction of the halogen with the wool first entering the bath, which exhausts the reagents before all of the fabric is treated.

The use of sulfuryl chloride does not discolor and weaken the wool to the same extent as does halogenation, but the wool so treated is somewhat harsh and has lost its natural water repellency.

This invention has as an object the improvement of the physical characteristics of keratinous textile fibers. A further object is the treatment of wool and similar keratin-containing fibers to reduce their tendency to felt on mechanical working. A still further object is reduction of the tendency of wool to shrink on laundering. Another object is the preparation of keratin-containing fibers of reduced tendency to shrink on laundering, which retain their natural water repellency, resiliency when wet, and softness. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a keratin-containing animal fiber, e. g., wool, is subjected to the action of an alpha-halogenated ether wherein the radicals attached to the ether oxygen contain each not more than six carbon atoms.

The shrinking tendency of wool can be reduced or completely eliminated by treating the wool with alpha-halogenated ethers in which the halogen or halogens are attached to an aliphatic carbon atom or carbon atoms and in which each organic radical separated from the remainder of the molecule by ether oxygen contains not more than six carbon atoms. More than one halogen atom may be attached to either or both of the carbon atoms linked by the ether oxygen atom and the compound may contain more than one alpha-halogen ether grouping.

Halomethyl ethers, e. g., chloromethyl ethers, that is, compounds of the structure $ROCH_2Cl$, may be readily prepared by reacting the corresponding alcohols of the formula ROH with formaldehyde and hydrogen halide, e. g., hydrogen chloride. Dichloromethyl ether,

$$ClCH_2OCH_2Cl$$

which has proven particularly valuable in the practice of this invention and is therefore particularly preferred, may be prepared by the reaction of formaldehyde with hydrochloric acid in the presence of concentrated sulfuric acid. 2,3-dichlorodioxan, which is also particularly suited to the practice of the invention and therefore particularly preferred, exemplifies the many halogenated ethers which may readily be prepared by the reaction of free halogen with the corresponding ether. All of these methods are well known to the art.

The treatment with halogenated ethers may conveniently be carried out as follows: The wool, after preconditioning at a suitable humidity, is immersed in a vessel containing a solution of the halogenated ether. The solvent used should, of course, be an inert solvent, i. e., one which does not itself readily react with the halogenated ether under the conditions of the treatment. Hydrocarbons such as xylene, toluene, naphtha, and chlorinated hydrocarbons such as trichloroethylene and carbon tetrachloride, are suitable. Ethers, including dioxan and 1,2-dimethoxyethane, are also useful as solvents. Particularly good results are obtained when ketones such as methyl ethyl ketone and methyl amyl ketone are employed as the solvents. The concentration of the halogenated ether in the solution, the dura-

tion of the treatment, and the amount of solution used in proportion to the amount of wool to be treated, may be varied considerably. After treatment, the wool is removed from the solution, freed from excess liquid by any convenient method such as centrifuging or squeezing, and dried. A final washing with water, soap solution, or a weak solution of ammonia may follow.

It has been found that impregnation of the textile material with an amide such as urea before treatment yields particularly soft and white wool. A weight of urea equivalent to 2–6% of the weight of the fibers may be used.

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 with an alphahalogenated ether 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:

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

Per cent shrinkproofness, i. e., per cent reduction of tendency to shrink.

The percent 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 alpha-halogenated ether solution 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.

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

Example I

Wool flannel which has been conditioned overnight in a chamber maintained at 100° F. and 86% relative humidity is immersed at 140° F. for one hour in a 2% solution, by volume of dichloromethyl ether in the hydrocarbon solvent having a typical boiling point range from 300–400° F., which is known to the trade as Stoddard solvent. Five parts by weight of solution are used per part of wool. The sample is then freed from excess solution by wringing, rinsed and dried. The product is 75% shrinkproof, as determined by the laundering test and has a very desirable soft feel. The treated wool is wetted only with difficulty, resembling in this respect the untreated wool.

Example II

Wool flannel which has been conditioned in a chamber maintained at 100° F. and 86% relative humidity is treated at 140° F. for an hour with a 4% solution by volume of dichloromethyl ether in Stoddard solvent. The wool is freed from the excess solution as in Example I. The treated wool is completely shrinkproof, as determined by the laundering test, and retains the natural resiliency, soft feel, and water resistance of the untreated wool.

Example III

Wool flannel is soaked in a 4% solution of urea in water and then wrung until it contains only its own weight of the solution. The fabric is then conditioned overnight in a chamber maintained at 90° F. and 86% relative humidity, and then immersed for one hour at 140° F. in 5 parts by weight of a 3.8% solution of dichloromethyl ether in Stoddard solvent. The product is completely shrinkproof and retains the natural resiliency and water resistance of the untreated wool. It has a particularly soft feel and excellent whiteness.

Example IV

Wool flannel which has been conditioned in a chamber maintained at 110° F. and 80% relative humidity is treated at 210° F. for 2 minutes with 7.5 parts by weight of a 2% solution by volume of dichloromethyl ether in Stoddard solvent (A. S. T. M. vol. 38, part 1, 1938). The excess treating solution is removed from the sample and the wool is rinsed in water. The shrinking tendency of the treated wool is reduced 33 per cent, as determined by the laundering test.

Example V

Wool flannel which has been conditioned at 110° F. in an atmosphere of 80% relative humidity is treated at 140° F. for one hour with 7.5 parts by weight of a 2% solution by volume of ethyleneglycol bis-chloromethyl ether in Stoddard solvent. The treated wool is about 60 per cent shrinkproof and has a lofty handle. The water repellency is substantially the same as that of the untreated wool.

Example VI

Wool flannel which has been conditioned overnight in a chamber maintained at 77° F. and 50% relative humidity is treated at 122° F. for two hours with 10 parts by weight of a 5.4% solution by volume of trimethylene glycol bis-chloromethyl ether in Stoddard solvent. The shrinking tendency of the treated wool is reduced 33 per cent.

Example VII

Wool flannel which has been conditioned overnight in a chamber maintained at 110° F. and 80% relative humidity is treated at 140° F. for one hour with 7.5 parts by weight of a 5.4% solution by volume of 1,3-bis-chloromethoxy-2,2-dimethylpropane in Stoddard solvent. The treated wool is about 65 per cent shrinkproof and retains the lofty handle and natural water repellency of the untreated wool.

Example VIII

Wool flannel which has been conditioned in a chamber maintained at 110° F. and 80% relative humidity is treated for one hour at 140° F. with 7.5 parts by weight of 5.4% solution by volume of n-butyl chloromethyl ether in Stoddard solvent. The shrinking tendency of the treated

wool is reduced 52 per cent. The flannel has an extremely soft feel.

Example IX

Wool flannel which has been conditioned in a chamber maintained at 80° F. and 80% relative humidity is treated for one hour at 140° F. with 5 parts by weight of a 2% solution by volume of 2,3-dichlorodioxan in Stoddard solvent. The shrinking tendency of the treated wool is reduced 60 per cent. The flannel retains the natural water repellency and soft feel of the untreated wool.

Example X

Wool flannel which has been conditioned overnight in a chamber maintained at 92° F. and 86% relative humidity is treated for one hour at 140° F. with 6 parts by weight of a 3% solution by volume of the bis-bromomethyl ether of ethylene glycol in Stoddard solvent. The excess solution is removed from the sample which is then rinsed first in dilute ammonia solution and then in water. The treated wool retains the water repellency and softness of the untreated wool and is about 89 per cent shrinkproof.

While normal, air-dried wool, which contains about 6% moisture, for example, wool which has been stored at 77° F. at a relative humidity of about 15%, may be used, and some effect is obtained even with bone-dry wool, it is preferred, in order to obtain more pronounced effects, to treat wool which contains about 12 to 28% moisture, for example, wool which has been conditioned at 50–100% relative humidity at 77–100° F., because more complete removal of the shrinking tendency is thereby obtained. The effect can thus be varied by controlling the moisture content of the wool to be treated. The conditioning treatment may be varied somewhat with the different types of wool to get the best results. It is, of course, possible to otbain the same percentage of moisture in the wool under different sets of relative humidity-temperature conditions. Although the wool to be treated may contain 6 to 28% moisture or more, it is particularly preferred to employ wool which contains about 17–24% moisture.

As indicated in the above examples, the wool is treated with the alpha-halogenated ether per se, i. e., the ether as such and not in combination. Treatment of wool with the alpha-halogenated ethers in combination with other materials reactive therewith, e. g., tertiary bases, does not attain the results of this invention as is further disclosed in Examples A, B, and C below. For this reason, applicant describes his treating agent as an alpha-halogenated ether wherein the radicals bounded by ether oxygen atoms are each of not more than six carbon atoms and this ether is used per se, i. e., as such and not in combination with any material reactive therewith to any substantial extent.

Example A

Wool (5.5 parts) conditioned at 78% relative humidity was treated with a solution of 1.5 parts of the bis-pyridinium salt of dichloromethyl ether in 35 parts of water at 60° C. for one hour. The reduction in shrinkage was only 8%.

Example B

Wool (5.5 parts) conditioned at 78% relative humidity was treated with a solution of 1.3 parts of the pyridinium salt of n-butyl chloromethyl ether in 53 parts of water at 60° C. for one hour. The reduction in shrinkage was 8%.

Example C

Wool (5 parts) conditioned at about 8% relative humidity was treated with a solution of 1 part of dichloromethyl ether and 0.6 part of hexamethylenimine in 27 parts of Stoddard solvent at 60° C. for one hour. The shrinkage reduction was only 5.5%.

Any keratin-containing animal fiber, e. g., wool, alpaca, vicuna, angora rabbit hair, goat hair, and camel hair may be reduced in shrinking tendency according to this invention. The material which is to be processed may be a fabric, or may be in another form, for example, in the form of fibers, yarn, or threads.

The treatment may take place either before or after dyeing, or, if a suitable solvent is used, it may take place in the dyeing bath. Other finishing treatments can be applied before or after the shrinkproofing treatment. The duration and the temperature of the treatment are mutually interdependent. Thus, it is possible to vary the temperature within wide limits and obtain a satisfactory product. At the same time, the duration of the treatment may be correspondingly regulated. In general, it is preferred to treat the wool at 130–150° F. for one to two hours. However, if the temperature is raised to 210° F. a period of two minutes is sufficient to obtain a good effect. Treatment at room temperature or below requires such extended treatment to obtain satisfactory effects that it is not ordinarily practiced. Treatment at temperatures above 210° F. is ordinarily of no particular further advantage.

The reagent may be applied either in the liquid phase, when the compound is a liquid under the conditions of the treatment, or the wool may be treated with the vapor of the compound at normal or reduced pressures, either pure or admixed with non-reactive gas. In general, it has been found preferable to apply the halogenated ethers from an inert solvent, i. e., diluent. From a commercial standpoint, it is often preferable to use a low concentration of the reagent in the solvent, e. g., below 10%. It is particularly preferred to use a concentration of 2–5%. Among the solvents which are suited for the application of the reagent are hydrocarbons or hydrocarbon mixtures such as hexane, octane, xylene, benzene, benzine, and naphtha; chlorinated hydrocarbons such as carbon tetrachloride, trichloroethylene, and perchloroethylene; ethers, including dioxan; ketones, and other inert solvents. The solvent may be recovered after each treatment, or series of treatments, for example by distillation, or it may be reused after replenishing the active agent.

From a commercial standpoint, dichlorodimethyl ether and dichlorodioxan are preferred, but any other alphahalogenated ether, including thioethers, wherein any organic radical separated from the rest of the molecule by ether oxygen or thioether sulfur, i. e., each carbon chain attached to the ether oxygen or thioether sulfur contains not more than six carbon atoms may be employed to accomplish the object of this invention. There is no limitation on other groups present in the compound except that none should be present which would react with the halogenated ether, such as an amino group. For example, the compounds may contain one or more aromatic nuclei which may also contain halogen substitutes.

Aryl halogens are not necessary in increasing the resistance of the wool to shrinkage. Ethers in which the halogen atom is substituted on a saturated carbon atom are much preferred over

ethers in which the halogen atom is substituted on an unsaturated carbon atom. Oxygen ethers are preferred to thioethers because of lower cost and freedom from residual odor.

Thus, there may be used in the processes of the present invention any alpha-halogenated ether, including thioether, wherein any organic radical separated from the rest of the molecule by ether oxygen or thioether sulfur, i. e., each carbon chain attached to the ether oxygen or thioether sulfur contains not more than six carbon atoms, including the following reagents which are illustrative of compounds useful in practicing this invention:

Chlorodimethyl ether	$ClCH_2OCH_3$
Sym.-dichlorodimethyl ether	$ClCH_2OCH_2Cl$
Unsym.-dichlorodimethyl ether	Cl_2CHOCH_3
Chloromethyl butyl ether	$ClCH_2OC_4H_9$
Bromodimethyl ether	$BrCH_2OCH_3$
Iododimethyl ether	ICH_2OCH_3
Ethylene glycol bis-chloromethyl ether	$ClCH_2OCH_2CH_2OCH_2Cl$
Trimethylene glycol bis-chloromethyl ether	$ClCH_2OCH_2CH_2CH_2OCH_2Cl$
Dibromodiethoxymethane	$C_2H_5OCBr_2OC_2H_5$
Alpha, alpha'-dichlorodiethyl ether	CH_3-CHCl-O-CHCl-CH_3
Alpha, alpha'-dichlorodiethyl sulfide	CH_3-CHCl-S-CHCl-CH_3
Ethylene glycol bis(alpha-chloroamyl) ether	C_4H_9CHCl-O-CH_2CH_2-O-$CHClC_4H_9$
Beta-phenoxyethyl alpha-chloroethyl ether	C_6H_6-O-CH_2CH_2-O-$CHClCH_3$
Beta-phenoxyethyl chloromethylether	C_6H_6-O-CH_2CH_2-O-CH_2Cl

Halogenated cycloaliphatic ethers, including 2,3-dichlorodioxan, may be used.

The ethers may also be defined as of the formula: R—X—R' wherein X is a member of the 6th group of the periodic table having an atomic weight not greater than approximately 32.06 (1935 Table), R and R' are the non-hydroxy residues or portions of alcohols and have a chain of carbon atoms not longer than six atoms and at least one of the radicals contains a halogen on the carbon attached to the ether oxygen or thioether sulfur, i. e., on the alpha carbon. For convenience the term "ether" in the claims includes both oxyethers and thioethers.

Although fluoro-, bromo-, and iodo-ethers may be used, the chloroethers are preferred because they are less expensive, are more stable in storage, and are outstanding in the quality of the products which they produce.

Combinations of halogenated ethers may be used to reduce the shrinking tendency of the wool.

It has not been possible to advance a theory of reaction adequate to explain the shrinkproofing effect of the halogenated ethers. The shrinkproofing is accomplished without destroying the natural soft feel and water repellency of the wool. This shows that the treatment must have a radically different effect on the wool from that of inorganic halogen compounds such as sulfuryl chloride, chlorine, or hypochlorites, organic or inorganic, as these reagents cause wool to become harsh and to wet readily.

Although some of the agents of this invention can be prepared from formaldehyde and hydrochloric acid, the effect is not due to possible hydrolysis to formaldehyde, as is shown by the fact that wool treated with formaldehyde itself is not reduced in its tendency to shrink on laundering, and by the fact that many of the agents, including 2,3-dichlorodioxan, an especially effective agent, do not yield formaldehyde on hydrolysis.

Thus when flannel is treated for 5.5 hours at 77° F. and at a pH of greater than 9 with 16 parts by weight of a 10% solution of formaldehyde in water, then rinsed in water, the shrinking tendency of the wool is not reduced.

When fifty parts by weight of a solution containing 5 grams per liter of a suspension of 4 grams of a 40% aqueous formaldehyde solution with 10 grams of 50% lactic acid and 7.5 grams of "Monopol" oil was applied to wool at 120° F. for 15 minutes and the wool then rinsed in water, there was actually a slight increase in the shrinking tendency of the treated wool.

When flannel is treated for one hour at 122° F. with 11.5 parts by weight of a 0.33% suspension of paraformaldehyde in Stoddard solvent, then rinsed in water, the shrinking tendency of the wool is not altered.

An important advantage of this invention is that it yields a superior product which is neither harshened by the treatment nor made readily susceptible to wetting. The advantages of softer feel and lofty handle are readily apparent in applications of the treated wool to the manufacture of clothing, in particular baby clothing, where the comfort of the wearer is of prime importance. The fact that the wetting characteristics of the wool are unchanged by the treatment is also of extreme importance. Natural wool, after cleaning, degreasing, and scouring is markedly resistant to wetting. When wetted by prolonged contact with moisture, it has the property of taking up considerable water without acquiring a soaked, scroopy, feel.

The advantages of this characteristic are obvious in the case of outer garments such as sweaters, suits and overcoats. However, the advantage is also marked in the case of clothes to be worn next to the body as in the case of underwear, socks, and baby clothing. The chief advantage of wool for these uses is that due to its free air spaces, it has a high insulating value and also retains the moisture given off by the body next to the skin thus retarding evaporation and cooling of the body surfaces. When wool is damaged, as in previous shrinkproofing treatments, it takes up body moisture readily, filling up the free air spaces, and also transfers moisture away from the skin, thus permitting more rapid evaporation by air currents. In this way the warmth-retaining characteristics of wool are partly lost. These disadvantages are overcome by the processes of the present invention whereby the shrinking tendency of the wool is reduced without destroying the natural resistance to wetting, so that the natural insulating value of the wool is also retained. It should be pointed

out, however, that the processes of the present invention do not render the wool water-proof or more resistant to wetting than the natural, untreated product. The uses for which wool of reduced shrinking tendency produced according to the present invention is particularly suited include knitted goods, such as socks, sweaters, and mufflers; woven goods such as baby clothing, underwear, suits, overcoats, sports apparel, and blankets; and the yarns or threads from which these are made.

The agents are, in general, readily soluble in common organic solvents so that the wool can be given a uniform treatment by easily prepared solutions. The action, in contrast to chlorination, is slow enough to permit of easy control by varying the duration and temperature of the treatment. Dichloromethyl ether, a preferred agent, is readily prepared from formaldehyde and hydrogen choride.

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 ncluded within the scope of the clams.

What is claimed is:

1. Process for reducing the tendency of a keratinous textile fiber to shrink, which comprises treating said fiber with an alpha-halogenated ether wherein the organic radicals have each not more than six carbon atoms, said ether being employed as such.

2. Process for reducing the tendency of wool to shrink which comprises treating said wool with an alpha-halogenated ether wherein the organic radicals have each not more than six carbon atoms, said ether being employed as such.

3. Process for reducing the tendency of a keratinous textile fiber to shrink, which comprises treating said fiber with an alpha-halogenated oxyether wherein the organic radicals have each not more than six carbon atoms, said ether being employed as such.

4. Process for reducing the tendency of wool to shrink which comprises treating said wool with an alpha-halogenated oxyether wherein the organic radicals have each not more than six carbon atoms, said ether being employed as such.

5. Process for reducing the tendency of wool to shrink which comprises treating said wool with an alpha-chlorinated oxyether wherein the radicals attached to the ether oxygen contain each not more than six carbon atoms, said ether being employed as such.

6. Process for reducing the tendency of wool to shrink which comprises treating said wool with α,α'-dichlorodimethyl ether, said ether being employed as such.

7. Process for reducing the tendency of wool to shrink which comprises treating said wool with 2,3-dichlorodioxan, said ether being employed as such.

8. Process for reducing the tendency of a keratinous textile fiber to shrink which comprises treating said keratinous textile fiber containing from about 12% to about 28% of moisture with an alpha-halogenated oxyether wherein the radicals attached to the ether oxygen contain each not more than six carbon atoms, said ether being employed as such.

9. Process for reducing the tendency of wool to shrink which comprises treating said wool containing from about 12% to about 28% of moisture with an alpha-chlorinated oxyether wherein the radicals separated from the remainder of the molecule by ether oxygen contain each not more than six carbon atoms, said ether being employed as such.

10. Process for reducing the tendency of wool to shrink which comprises treating said wool containing from about 17% to about 24% of moisture with an alpha-chlorinated oxy ether wherein the radicals, separated from the remainder of the molecule by ether oxygen contain each not more than six carbon atoms, in 2–5% concentration in an inert solvent at 130–150° F. for 1–2 hours, said ether being employed as such.

11. Process for reducing the tendency of wool to shrink which comprises treating wool containing from about 17% to about 24% of moisture with a 2-5% solution of α,α'-dichlorodimethyl ether in an inert solvent at 130–150° F. for 1–2 hours, said ether being employed as such.

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CERTIFICATE OF CORRECTION.

Patent No. 2,253,102. August 19, 1941.

JOSEPH FREDERIC WALKER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 41, for "otbain" read --obtain--; and second column, line 2, for "8%" read --80%--; page 5, first column, line 25, for "ncluded" read --included--; 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 28th day of October, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)

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