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[54] **PERACID TREATMENT OF KERATINOUS FIBERS**
9 Claims, No Drawings

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[50] Field of Search 8/111, 101, 142; 252/104; 26/18.5

[56] References Cited
UNITED STATES PATENTS

1,966,915	7/1934	Baier	252/104 X
3,144,300	8/1964	Cosnard	8/111 X
3,528,115	9/1970	Lawes	8/111

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ABSTRACT: Keratinous fibers, e.g., wool, are treated with organic solutions of organic peracids such as peracetic acid to effect shrinkproofing and also bleaching.

PERACID TREATMENT OF KERATINOUS FIBERS

BACKGROUND TO THE INVENTION

Fabrics containing keratinous fibers, notably wool, exhibit a notorious tendency to shrink when water-washed. Shrinkage is especially severe when the washing is with warm or hot water and is accompanied with agitation. Repeated washings cause further shrinking (fiber tangling) until finally the fabric becomes a thick felt. Often shrinkage of woolen cloth to an area which is but 50 percent (or even less) of the original area occurs.

Shrinkproofing of wool or other keratinous fibers is thus a recognized desideratum. Treatments for such purposes have been proposed. These generally entail coating the scales on the fiber to prevent tangling or chemically oxidizing the fiber surface to remove the scales and thereby prevent permanent fiber entanglement, the prime cause of shrinking and felting. One chemical treatment uses aqueous potassium permanganate. Others rely upon sodium hypochlorite. Each suffer from shortcomings; the permanganate deposits discoloring amounts of manganese dioxide, the hypochlorite like other chlorine-containing oxidizing agents causing yellowing of the wool due to chlorination.

Also, these chemical treatments are performed in aqueous media. They require extended contact periods, e.g., upwards of 60 minutes, with low concentrations of oxidizing agent when performed at ambient temperatures. Although the contact period can be reduced by increasing the concentration of oxidizing agent, increasing the oxidizing agent's concentration gives rise to excessive fiber degradation (loss of strength, felting and distortion). Chemical shrinkproofing processes of this nature, for these and other reasons, leave considerable room for improvement.

In addition it is necessary to dispose of the spent treating baths. Pollution considerations become of considerable import.

THE INVENTION

This invention concerns a new chemical process for treating keratinous fibers and fabrics which avoids many of the shortcomings of prior shrinkproofing techniques. According to this invention, shrinkproofing of wool or other keratinous material is accomplished using an organic solvent solution of peracid, such as a solution of peracetic acid in methylchloroform or like halogenated hydrocarbon solvent. It has been found, quite interestingly, that highly effective shrinkproofing of woolens is obtained by virtue of this invention using shorter contact periods than had heretofore been considered practical and under oxidizing conditions which do not cause undue or intolerable fiber degradation. That is, the present process attains shrinkproofing without resorting to excessively high (and deleterious) concentrations of oxidizing agent. It further offers the advantage of being readily performed continuously. Because, among other things, it circumvents the need for water in the treating bath, and uses reclaimable oxidizing media, problems of water disposal are thrust aside.

"Keratinous" materials, such as fibers, fabrics or goods as used herein encompasses generally the proteinaceous hair of any animal. This includes wool, the hair of a sheep, which is the widest used keratinous material, as well as hair from the goat and camel families. This invention is applicable to the treatment of materials which contain such keratinous materials along or in admixture with other natural and synthetic fibers. Usually, the treatment is applied to woven (or knit) goods, but fibers in any form, such as raw hair, yarn or unwoven fabric may be treated.

Shrinkproofing is accomplished pursuant to this invention by immersing (or otherwise contacting) the wool or like keratinous material in a liquid-treating bath of organic peracid, exemplified by peracetic acid, in organic solvent, especially one of the widely used chlorinated hydrocarbon cleaning solvents, such as methylchloroform, trichloroethylene and perchloroethylene. A variety of conditions and the bath composition contribute to realizing the maximum benefits from this new means for shrinkproofing with peracids.

It has been found that percarboxylic acids such as peracetic acid are unusually effective in shrinkproofing woolens when applied to the wool under substantially anhydrous conditions in the form of a dilute organic solution. Shrinkproofing according to this invention uses as the treating media an organic solution of the peracid, the solvent of the bath ideally being a chlorinated hydrocarbon cleaning solvent, to wit, methylchloroform. The bath should be substantially free of any separate (organic immiscible), distinct aqueous phase to insure that substantially anhydrous conditions prevail.

As intended herein, in describing the percarboxylic acid bath, substantially anhydrous bath conditions characterize a condition in which the bath does not contain (i.e., is free from) a distinct organic immiscible aqueous phase. Small amounts of water, typically water dissolved in the organic solvents may however be present without departing from the necessary substantially anhydrous conditions. Many of the useful organic solvents dissolve minor quantities of water (in the parts per million range); at this level and state this water is no problem and can be tolerated. Substantially anhydrous conditions also include those wherein the wool contains moisture. That is, it is not essential to the performance of this invention that the wool be dried free of absorbed water prior to contact with the bath. When the relative humidity of the wool undergoing treatment is below 100 percent, the wool will pick up dissolved water, i.e., have a dehydrating effect on the treating bath. Thus, wool containing absorbed water is treated with percarboxylic acids pursuant to this invention.

The solvent component of the treating bath can be one or more of many organics in which the peroxycarboxylic acid is adequately soluble. Particularly appropriate are the halogenated hydrocarbon cleaning solvents such as the normally liquid, substantially water-immiscible chlorinated hydrocarbons, methylchloroform, trichloroethylene, perchloroethylene, carbon tetrachloride, methylene dichloride, ethylene dichloride (1,2 -dichloroethane) and chloroform. Of these the two carbon chlorocarbons (perchloroethylene, trichloroethylene and methylchloroform) are especially noteworthy. Other fluorinated or chlorofluoro counterparts of these chlorinated solvents include 1,1,2-trifluoro 1,2,2-trichloroethane, difluoromethane, trifluoroethylene; chloro-fluoro hydrocarbon cleaning solvents such as trichlorofluoromethane, 1,1,2,2-tetrafluoro 1,2-dichloroethane, as well as other halogenated cleaning solvent containing two or more different halogen atoms. Drycleaning solvents including hydrocarbon solvents, notably the petroleum drycleaning solvents such as the Stoddards Solvents are operable but being hazardous because of flammability are not preferable.

Effective treatment of woolens or other keratinous materials with peroxycarboxylic acids is possible with baths comprised of other organic solvents. Any solvent for the peroxycarboxylic acid which is basically inert chemically (as to the peracid and woolen) and in which the percarboxylic acid dissolves is of use. Preference is for those boiling normally above ambient temperatures (e.g., 25° or 30° C.) but below about 120° C. or 135° C. since recovery by their vaporization (and drying of treated woolens) is easier with solvents boiling at these moderate temperatures.

With percarboxylic acids which are not especially soluble in the hereinbefore mentioned chlorinated solvents, this lack of adequate solubility can be overcome by use of a cosolvent, i.e., an organic solvent such as an alcohol or ketone which is miscible with the chlorinated solvent and in which the peracid is more soluble. Simple alkanols such as methanol, ethanol, n-propanol, isoproponal and the butyl alcohols are typical of cosolvents useful for this purpose. Also suitable in this regard are the ketones such as acetone, methyl ethyl ketone and other lower ketones.

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Typically, woolen fiber (unw
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ganic solution of percarboxylic
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proofing, usually of at least about
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contact periods (i.e., up to 10 to 15
particularly suited to performance co

Peracid concentration in the treati
time of initial immersion should be su
active oxygen content of at least about
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is provided for example, by including fr
peracetic acid by weight of the bath (per
about 1.5 percent peracetic acid. Althoug
active oxygen concentrations effec
economics usually dictate use of the lesser c

After an effective period of contact with

the woolen material is withdrawn and further treated. Re
ing the residue of bath composition is conventional. A
water wash followed by air drying is effective. Washin
rinsing can be accomplished with an organic sol
(preferably those used in the treating bath). If the solvent c
tent is appreciable, air drying or vacuum drying to vapori
and evolve the solvent coupled with the recovery of the vapo
is advisable.

The following examples illustrate the manner in which thi
invention may be practiced.

TABLE 3

Fabric style	Percent shrinkage					
	Relaxation shrinkage		Felting shrinkage		Total shrinkage	
	Length	Width	Length	Width	Length	Width
Untreated 100% woolen	7.0	2.5	9.5	8.5	16.5	11.0
Treated 100% woolen	1.0	0	+1.0	+2.0	0	+2.0
Untreated 50% woolen, 50% worsted	1.4	6.5	9.3	11.2	10.7	17.7
Treated 50% woolen, 50% worsted	0.5	0.5	0.6	0	1.1	0.5

NOTE.—+ indicates stretch or elongation.

Reflectance values of the untreated and treated wool fabrics were determined and demonstrate bleaching as well as shrinkproofing is achieved. The results are as follows:

TABLE 4

	Fabric Style	Reflectance (%)[1] Blue	Green
Untreated	100% Woolen	47.5	66.2
Treated	100% Woolen	53.8	71.8
Untreated	50% Woolen 50% Worsted	45.8	64.5
Treated	50% Woolen 50% Worsted	55.9	72.6

[1]Values were determined on fabric surface using a Hunterlab Model D-40 Reflectomter.

EXAMPLE 4

A 72-inch long, 18-inch wide single piece of woolen fabric was passed "single-dip" through a bath of 1.5 liters of a peracetic acid solution in methylchloroform containing 4.1 weight-percent peracetic acid and then padded between a pair of rolls so as to contain an amount of solution equal to twice its dry weight. Then the fabric was cut into 24-inch long strips. One strip was allowed to stand for the specified number of minutes at room temperature (78°F.) and another was steamed for 2 minutes at 212°F. in a rotary dryer. Thereafter, each piece was given three successive 30-second washes with water at 106° F., centrifuged for 45 seconds and air dried. Table 5 lists the conditions and results.

TABLE 5

Treatment while saturated with shrinkproofing solution			Shrinkage resistance, percent		
Time, mins.	Temp., °F.	Type of heating	Total area shrinkage	Relaxation shrinkage	Felting shrinkage
5	78	Room temperature	1.89	0.39	2.28
10	78	do	0.02	+0.38	0.40
2	212	Steam rotary dyer	3.34	+0.37	3.61
5	212	do	6.59	0.02	6.59
10	212	do	1.24	0.77	0.47
Untreated control sample			56.62	7.26	49.36

The peracid bath during treatment may be at any temperature consistent with insuring the bath be liquid and does not tend to lose solvent by undue vaporization. Ambient temperatures are perfectly suitable. Typical bath temperatures are from 50° F. up to the boiling point of the bath's organic solvent at the prevailing pressure. Although it is not necessary to operate other than at atmospheric pressure, shrinkproofing is accomplished under super or subatmospheric pressures.

Treatments employed in connection with known shrinkproofing and bleaching steps can be utilized with the present treatment. For example, prior to immersion in the peracid solution, the wool fiber may be scoured. Thus, prior to being treated to be shrinkproofed, the wool may be scoured by either of the two most widely recognized scouring techniques, the soap-alkali process or the solvent process, or any like scouring process. After being treated with the peracid, the wool is washed, dried, and otherwise treated (spun, dyed, creaseproofed, etc.).

While this invention has been described by reference to certain details of specific embodiments, it is not intended that the claims be construed as limited to such details except to the extent that they are set forth in the claims appended hereto.

I claim:

1. The method of shrinkproofing keratinous fiber which comprises contacting the fiber with a liquid bath of a percarboxylic acid selected from the group consisting of monoperacids and diperacids in an inert organic solvent which bath is substantially free of a distinct aqueous phase immiscible with the organic solvent.

2. The method of claim 1 wherein the acid is an aliphatic carboxylic peracid.

3. The method of claim 2 wherein the acid is peracetic acid.

4. The method of claim 2 wherein the solvent of the bath is a halogenated hydrocarbon cleaning solvent.

5. The method of claim 4 wherein the solvent is selected from the group consisting of methylchloroform, trichloroethylene and perchloroethylene.

6. A method of treating keratinous fiber which comprises immersing the fiber in a substantially anhydrous bath of a percarboxylic acid conforming to the structure $R(COOOH)_x$ wherein x is a whole integer of 1 or 2 and wherein R is principally composed of a carbon chain or carbocyclic ring and hydrogen atoms in an inert organic solvent, the percarboxylic acid content being sufficient to provide said bath with an initial active oxygen content of at least 0.04 weight-percent.

7. The method of claim 6 wherein the keratinous fiber is woven wool.

8. The method of claim 6 wherein the organic solvent content of the bath is composed of chlorinated aliphatic hydrocarbon solvent and a cosolvent selected from the group consisting of alkanols and lower ketones.

9. The method of claim 1 wherein the peracid is peracetic acid, the inert organic solvent is selected from a group consisting of methylchloroform, trichloroethylene and perchloroethylene and wherein the peracid content of the organic bath is initially sufficient to provide an active oxygen content of at least 0.04 weight-percent.

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