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SHRINKPROOFING WOOL

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4 Claims. (Cl. 8—128)

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The invention relates to an improved method of shrink-proofing wool, and to the improved product of such treatment.

Heretofore, the only economical methods for shrink-proofing wool by controlled damage processes have involved the use of chlorine or other halogen in various ways. While good shrinkage control will be the result if the method is carefully regulated as to pH, concentration, time of treatment, etc., there are certain disadvantages in its use that have not been overcome. First, the chlorine or other halogen is disagreeable to handle and is injurious to the health of the workmen; secondly, it is highly corrosive; thirdly, there are side reactions taking place in its use that damage the wool and yet do not aid shrink-proofing, and which involve the formation of chloramines: fourth, the problem of tailing is a big one because of the high reactivity of the chlorine with wool; fifth, chlorine treatment is somewhat expensive; and lastly, uniform penetration of the chlorine or chlorinating agent cannot be expected because the halogen has such a strong affinity for wool that complete exhaustion of the bath occurs rapidly.

The actual shrink-proofing of wool with chlorine or other halogen according to one theory is not caused by a direct union of halogen with the wool molecule, but because the halogen is a very strong oxidizing agent the cystine linkages of the wool molecule are oxidized and broken, which changes the expanding, contracting and frictional characteristics of the fiber.

It is known that dilute solutions of potassium permanganate ($KMnO_4$) will reduce only slightly the felting characteristics of wool and as early as 1907 it was proposed by Kammerer to treat wool with permanganic acid, which is a much stronger oxidizing agent than $KMnO_4$, and effect shrink-proofing. This method and any method involving the use of the permanganate ion at or below 100° C. does not produce a wool possessing satisfactory characteristics. The reasons for this are that the reactions are mainly only surface reactions and do not penetrate to any considerable extent within the fiber. Any real penetration can only be achieved at this or lower temperatures by sacrificing the natural feel or handle of the wool. An objectionable scroop results and the fiber is stiff and useless. Further, different grades of wool display different degrees of shrink-proofing because of variations in the thickness of the varnish-like covering on the cuticle as revealed by the electron microscope.

It is an object of the present invention to improve the method of shrink-proofing wool by subjecting the wool to a treatment that can be controlled easily and that produces a wool which retains its natural feel and strength without appreciable loss of weight.

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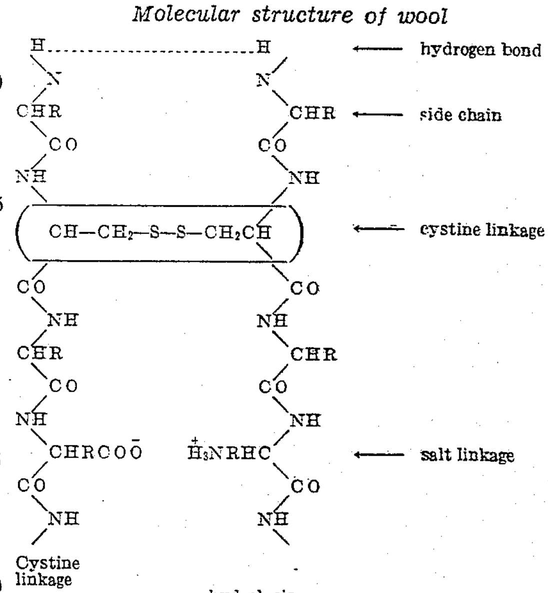
Further, it is an object of this invention to produce a more level dyeing wool. I have discovered that speedy penetration of the wool fiber by a solution of potassium permanganate or other suitable oxidizing agent can be effected by subjecting wool to superatmospheric temperatures and pressures in an autoclave in very dilute solutions of $KMnO_4$, with or without the aid of buffers, as for instance $MgSO_4$.

The wool under pressure is rapidly hydrolyzed at the cystine linkage as follows:

Molecular structure of wool



$$R{-}S{-}S{-}R_1 \xrightarrow{\text{hydrolysis}} R{-}SH + HOS{-}R_1$$

$$R{-}SOH \longrightarrow H_2S + {-}CHO$$

H_2S produced acts as a reducing agent and also splits the cystine linkage

$$R{-}S{-}S{-}R_1 \xrightarrow{H_2S} RSH + HSR$$

As $KMnO_4$ is also present, the H_2S is oxidized

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + SH_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 \xrightarrow{O_2} H_2SO_4$$

H_2S is a very feeble acid and the H_2S, H_2SO_3 and H_2SO_4 all react within the fiber and at the surface with $KMnO_4$ to produce permanganic acid. Permanganic acid is a powerful oxidizing compound but is only produced where $KMnO_4$ comes in contact with wool, thereby producing a smooth, non-harsh wool. No H_2S is detectable on the wool after pressure treatment in this manner, which is not the case with pressure alone in the absence of oxygen or oxidizing compounds.

The hydrolyzed cystine group is oxidized as follows:

$$HMnO_4+R{-}Sh \rightarrow RSO_3H$$

There is also a breaking of the cystine linkage by oxidation

$$-CH_2-S-S-CH_2- \xrightarrow{HMnO_4} -CH_2SO_3H + HO_3SCH_2-$$

$KMnO_4$ also does this but is not as predominant as the $HMnO_4$ at the fiber surface and within the fiber

$$-CH_2-S-S-CH_2- \xrightarrow{KMnO_4} -CH_2SO_3H + HO_3SCH_2-$$

A permanent set is also imparted to the wool fiber by heat and as follows:

The hydrolyzed cystine groups are joined by oxidation

$$R-SH + R_1SH \xrightarrow{\text{oxidation}} R-S-R_1$$

Also at elevated temperatures the disulfide bonds of keratin are disrupted. The thiosulfonic acids thus formed react with free amino groups in the keratin to build R—S—NH—R' linkages, thus imparting a permanent set to the wool.

Condensation between an amino group of a basic side chain and an —SH group formed by hydrolysis of —S—S— linkages also occurs.

The hydrolysis of —S—S— yields

—SH+—SOH,

the —SOH going to H_2S+—CHO, condensation of —CHO with NH_2 yields NH—CH—.

All the above phenomena are accompanied by a disarrangement of the surface layers of the cuticle and under the cuticle and a reduction in the differential friction effect, rendering the fiber resistant to felting.

The increased luster and strength is due to the fact that the scaly covering fuses into a more compact and regular surface. The resulting wool has no loss in strength and has a soft and desirable feel.

Further, the method bleaches the wool and gives a product of superior and more level dyeing characteristics. In other words, the method combines the usual bleaching treatment with a shrink-proofing treatment.

After the pressure treatment, the brown manganese hydrate is removed with $NaHSO_3$ followed by Na_2CO_3 and washing.

Advantages of the process are as follows:

1. It is not injurious to health of operators as are the halogens and H_2O_2.
2. The process does not require large concentrations of chemicals.
3. The process can be performed in a short time.
4. The process results in very even treatment by penetrating the fiber.
5. It is not necessary to control the pH because the process is carried out under essentially neutral conditio[illegible].
6. It is no[illegible]y to over treat.
7. One ca[illegible]ach as well as shrink-proof.
8. The pr[illegible]uct is soft and lofty handle.
9. The process is very economical.
10. Excess acids produced are neutralized by KOH present from $KMnO_4$.

The following specific examples are illustrative of the manner in which the treatment may be carried into effect:

Example 1

Virgin wool 60–64's grade yarn was treated with a solution of 250 mg. $KMnO_4$ to two liters of water (.0125%) in an autoclave at 15 lbs. superatmospheric pressure for five minutes. This was followed by a treatment with a dilute solution of $NaHSO_3$ to remove manganese hydrate and then to a dilute solution of Na_2CO_3. The treated wool was completely shrink-proofed. Untreated wool shrank 25%.

Example 2

Virgin wool yarn 70's grade was treated with a solution of 100 mg. $KMnO_4$ in two liters of water (.005%) in an autoclave at 15 lbs. superatmospheric pressure for five minutes. This wool was completely shrink-proofed. Untreated wool shrank 40%.

Example 3

70's grade yarn was treated with a solution of 250 mg. $KMnO_4$ to two liters of water (.0125%) in an autoclave at 10 lbs. superatmospheric pressure for five minutes. The wool was completely shrink-proofed. Untreated wool shrank 40%.

Example 4

70's grade yarn was treated with a solution of 250 mg. $KMnO_4$ to two liters of water (.0125%) in an autoclave at 5 lbs. superatmospheric pressure for five minutes. The wool shrank about 4% because of the lower pressure used but still was fairly well shrink-proofed. Seven minutes at 5 lbs. produced a completely shrink-proofed wool. Untreated wool shrank 40%.

Example 5

Woolen socks 60's–64's grade was treated in .05% $KMnO_4$ solution for ten minutes at 15 lbs. superatmospheric pressure in an autoclave. This was followed by treatment with a dilute 5% solution of $NaHSO_3$ and then with Na_2CO_3 to neutralize the acidity and the treated goods were then washed thoroughly. Untreated socks shrank 30% after thirty launderings, and treated socks exhibited no felting shrinkage. This was a strong anti-shrinking treatment.

The yarns treated in the above examples were dried and cut into four inch lengths and the tips cemented with cellulose acetate and shaken in a .5% $Na_2CO_3.10\ H_2O$ solution for fifteen minutes. The shaker made 276 completed (back and forth) strokes per minute. In shrink-proofing enough $KMnO_4$ should ordinarily be used so that the bath has a permanganate color at the end of treatment. This insures an oxidation reaction throughout.

In shrink-proofing wool it is sometimes desirable to use a pre-treatment of soaking the wool in dilute $KMnO_4$ solutions which may have a concentration of .1% or less which may be at atmospheric pressure, and at a temperature below 100° C. or even as low as room temperature, and to then introduce the wool into dilute $KMnO_4$-pressure baths.

The presence of re-worked or bleached wool, which may have been damaged in prior treatment, may become a disturbing factor.

When working with larger concentrations of $KMnO_4$, shorter pressure times and/or lower pressure may be used. Larger concentrations may be desirable where considerable bleach is also desired. However, I prefer lower concentrations of $KMnO_4$ with the lower limit in the neighborhood of .001% and the upper limit to be determined by the damage done to the wool. This upper limit may be around 0.1% except for short times of treatment.

A combination of unshrinkable wool with untreated fibers of all types permits the production of two-tone effects as well as novelty or blister effects and differently dyed fabrics.

While in the above description potassium permanganate has been referred to as the preferred oxidizing agent, other oxidizing agents may be substituted for the permanganate either in whole or in part, without departing from the spirit of the invention considered in its broadest aspects, although, as previously set forth, potassium permanganate is preferred. Where other oxidizing agents are employed the quantity employed should be such as to be the equivalent of the proportions of permanganate herein set forth.

In some instances it has been found desirable to give the wool a preliminary treatment with an oxidizing agent other than $KMnO_4$, such as an alkaline or acid permanganate, oxygen, ozone, hydrogen-peroxide, organic peroxides, halogenated organic compounds, $K_2Cr_2O_7$, and the like, with or without catalysts, followed by a treatment with potassium permanganate. These and other oxidizing agents used either singly or in combination may be used in addition to or in place of the permanganate in the main treating step.

I claim:

1. A process of shrink-proofing wool which comprises treating the wool for a short period of time in a closed chamber under superatmospheric

pressure conditions and at a temperature above 100° C. with an alkali metal permanganate in aqueous solution, the strength of the permanganate employed being within the range of .001 to .1%.

2. A process as set forth in claim 1 wherein the wool is treated for a period of from 5 to 10 minutes.

3. A process as set forth in claim 1 wherein the superatmospheric pressure employed is approximately within the range of 5 to 15 pounds per square inch.

4. A process as set forth in claim 1 wherein the wool is treated for a period approximately within the range of 5 to 10 minutes at superatmospheric pressures substantially within the range of 5 to 15 pounds per square inch.

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