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ANTISHRINKING TREATMENT OF ANIMAL FIBERS

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This invention relates to a method of treating fabrics or other textile materials consisting wholly or partly of wool, to reduce the natural tendency to shrink when washed in aqueous liquors.

Wool goods are usually treated to render them unshrinkable with an acidified solution of a hypochlorite at a pH varying from 1 to 5 according to the nature of the acid, and the quantity employed. Under these conditions, the wool fibre has such a strong affinity for the halogen, that complete exhaustion of the bath takes place within a few minutes. This procedure cannot be expected to give uniform penetration of the chlorinating agent, especially where highly twisted yarns or thick fabrics are under treatment, and it generally results in the surface fibres being over treated, while those in the centre of the yarn or fabric remain appreciably unaffected. If the hyprochlorite solution is used at an alkaline pH, we find that the rate of reaction with the wool is much slower, owing to the fact that as the pH rises above 7, its chlorinating properties rapidly diminish, until at pH 8 it acts almost exclusively as an oxidising agent. Under the latter condition, however, although the wool still gradually absorbs and reacts with the halogen, no appreciable degree of non-felting is produced. These facts are responsible for the general view that wool can only be rendered unshrinkable by direct chlorination or bromination, and that the oxidising properties of the halogens are incidental, and should be eliminated as far as possible. As will be indicated later in this specification we have found it possible to obtain resistance to shrinkage by the use of halogen compounds acting under oxidising conditions, and by this method to retain the natural properties of the animal fibres whilst giving improved appearance and handle of the treated goods.

It is an object of the invention to provide an improved method whereby the materials may be subjected to an even treatment which is easily controlled, and thereby rendered shrink-resistant without the fibre being impoverished and without substantial loss of protein matter, so that the desirable natural properties of the wool, such as fullness of handle, resilience, etc. are retained and the weight loss during the treatment is extremely low.

Another object of the invention is to provide a treatment which gives such uniform results that levelling in subsequent dyeing operations is facilitated.

Our process is applicable to wool materials containing cellulosic fibres, such as cotton or rayon, since the latter are substantially unchanged by the treatment.

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It is known that cold dilute aqueous solutions of alkaline hypochlorites, hypobromites, and also nitrogen-chloro compounds such as nitrogen trichloride, monochloramine, sodium-p-toluene sulphonchloramide, sodium o-dichlorobenzene sulphonchloramide, which may be prepared by the action of chlorine or hypochlorites on solutions or suspensions of ammonia, primary or secondary aliphatic bases, acid amides or sulphonamides, or the salts of the same, have little action in reducing the shrinkability of animal fibres. They therefore cannot successfully be used to give a sufficiently reduced tendency to shrink to enable the fabrics to be termed "shrink-resistant." Also, dilute aqueous solutions of permanganate compounds are known to react with animal fibres, producing modification of molecular structure, but only slight decrease in shrinking properties.

The term nitrogen chloro compounds used in this specification is intended to cover only nitro chloro compounds in which the chlorine atom is directly attached to the nitrogen atom and wherein the chlorine is available chlorine.

We have found that by combining the oxidising action of permanganate compounds with the action of one or more of the halogen containing compounds mentioned above, either in one bath or in separate baths, subject to the precautions given below and under suitable conditions as to pH of the solutions, the anti-shrinking effect on the animal fibre is greatly enhanced, and we are thus able to achieve such effect while still retaining all the attractive properties of woollen fabrics or yarns, even giving with low quality wools an improved appearance, handle and loftiness. Where the nitrogen chloro compounds are used, use them in a separate bath as indicated below and do not combine them in the same bath with the permanganate.

Our invention consists in a method of treating animal fibres, either alone or mixed with other fibres to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating such materials with a dilute aqueous solution of a permanganate compound, and either with an aqueous solution or suspension of a nitrogen-chloro compound as hereinbefore defined, or with a dilute aqueous solution or suspension of an alkali metal or alkaline earth metal hypochlorite or hypobromite. The solutions are used under suitable pH conditions as indicated

below. The oxidising agent has the effect of making the animal fibres more susceptible to attack by the halogen-containing agent, with which they react to give materials having a high degree of unshrinkability.

Our invention further comprises treating the materials with a dilute aqueous solution of a permanganate compound mixed with a dilute aqueous solution of an alkali metal or alkaline earth metal hypochlorite or hypobromite at a regulated pH value.

Our invention further comprises a process in which the materials are first treated in a dilute aqueous solution of a permanganate compound (e. g., an alkali metal permanganate) at a pH of approximately 5 to approximately 10, and at a temperature not exceeding 60° C., and subsequently treated in a dilute aqueous solution or suspension of a nitrogen-chloro compound of the type such as nitrogen trichloride, monochloramine, p-toluene-sulphonchloramide, etc., at a pH of approximately 1 to approximately 3.

Our invention further comprises a process in which the materials are treated in a dilute aqueous solution of a permanganate compound (e. g., an alkali metal permanganate) at a pH of approximately 5 to approximately 10 and at a temperature not exceeding 60° C. and subsequently treated in an alkaline solution of an alkali metal or alkaline earth metal hypochlorite or hypobromite, with or without the addition of metallic salts such as magnesium sulphate, calcium chloride, calcium acetate, barium chloride, barium acetate and/or zinc sulphate at a pH of approximately 7.5 to approximately 11.

Our invention further comprises treating the materials with a liquor which is alkaline and contains a dilute aqueous solution of an alkali metal or alkaline earth metal hypochlorite or hypobromite, together with a permanganate compound (e. g., an alkali metal permanganate) at a pH of approximately 7.5 to approximately 11.

The oxidising agent has the effect of making the animal fibres more susceptible to attack by the halogen-containing agent, with which they react to give materials having a high degree of unshrinkability. In all cases, only a relatively small concentration of permanganate, e. g., 1 to 2% on the weight of the textile material, is required, and whilst for economic reasons one would employ the lowest concentration which gives the desired results, we have found that higher concentrations such as 5 or 6% have no deleterious effects.

The treatment with permanganate may be carried out in the cold or at varied temperatures, e. g., to 60° C. The treatment with the halogen-containing agent may be carried on until exhaustion of the halogen is obtained, and it is preferably followed by an antichlor treatment.

The solutions used are preferably adjusted to pH values ranging from 5 to 6 for the oxidising pretreatment, from 1 to 2 for the nitrogen-chloro solution, and from 8 to 10 for the hypohalite solution.

It is advantageous to employ the permanganate hypohalite method, with the two reagents combined in one bath, since the mixture gives a stable solution which will react in alkaline solution very slowly with wool or other animal fibre either in the scoured state, or as received directly from the spinning or knitting machine, to give resistance to shrinkage. The rate of this reaction is controlled by the initial pH of the bath, so that where it is advisable to give extremely slow treatment such as with loose wool, or yarn in package form, it is possible by taking an initial pH of 10.0 to obtain an even rate of oxidation taking upwards of one hour for exhaustion of the bath. But where goods are vigorously circulated such as in the treatment of hose or garments in a rotary or paddle machine, results which are still even are more rapidly obtained by lowering the initial pH of the bath to approximately pH 7.5, when a regular rate of exhaustion taking upwards of 30 minutes is obtained.

It is found that an addition of a metallic salt to the oxidising bath aids the reaction, without appreciably affecting the rate of exhaustion at a given pH, and in particular magnesium sulphate, calcium chloride, barium chloride, and zinc sulphate, are useful for this purpose since, either alone or in admixture, they also offer a simple method of pH control. As the action proceeds, the pH of the bath usually falls a little owing to the inefficient buffering of the metallic salts, but it is always advisable to maintain alkaline conditions throughout when employing the single bath as above. In all cases where the wool is intended for light shades or for white, it is necessary subsequently to remove the staining due to the permanganate by means of the usual clearing treatment, as with bisulphite or sulphurous acid. Animal fibres so processed are found to be appreciably bleached. By slightly increasing the permanganate above the amount necessary to induce unshrinkability in this alkaline treatment, it is possible to produce an excellent bleach simultaneously with a high degree of unshrinkability.

Resistance to shrinkage is also induced by first subjecting the animal fibres to treatment with a dilute aqueous solution of alkaline hypohalite particularly in the presence of the above metallic salts, and after exhaustion of the bath to give the additional oxidation with permanganate, maintaining alkaline conditions throughout.

The term "alkali hypohalite" as used herein is intended to designate alkali metal and alkaline earth metal hypochlorites and hypobromites.

The advantages of the processes of the present invention in comparison with the usual acid hypochlorite chlorinating processes are:

1. The animal fibres are subjected to an even anti-shrink treatment which is readily controlled, and shows low loss of protein matter.

2. The treated wool develops an improved soft handle and lustre, and retains its loftiness and resiliency even on repeated washing.

3. A bleaching treatment may be given simultaneously with the anti-shrink process.

4. The process has less effect on the colours of dyed wool.

5. The treated wool is more uniform and subsequent dyeing processes are facilitated.

6. The process can be carried out in almost any type of machine, i. e., wood, stainless steel, etc.

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

Example 1.—100 parts by weight of wool are treated for 1 hour at 40° C. with a solution of 2.5 parts potassium permanganate in 2500 parts of water, corrected to pH 5.0.

After giving one cold rinse, the wool is transferred to a solution of monochloramine prepared as follows: 3 parts of chlorine as sodium hypochlorite in 2500 parts of water, to which mixture is added 3 parts of ammonium chloride, followed

by sufficient hydrochloric acid to bring the pH to 1.5. After 20 minutes circulation in this liquor, the wool is cleared of discolouration due to the permanganate compounds by addition of sodium bisulphite to the same bath.

Example 2.—100 parts of scoured Botany yarn in the hank are treated with 2 parts of potassium permanganate in 2500 parts of water previously corrected to pH 5 with sulphuric acid. After exhaustion of the bath the wool is given one rinse and then steeped in a 1 g./litre solution of sodium sesquicarbonate until definitely alkaline. It is then entered into a cold solution containing 3 parts of chlorine as sodium hypochlorite to which has been added 10 parts of calcium chloride. After processing until complete exhaustion of the chlorine is obtained, anti-chlor treatment with bisulphite and acid is given.

Example 3.—100 parts of all wool army half hose are treated in the grease (or after scouring and milling) with 2,500 parts of water containing:

	Parts
Potassium permanganate	2
Chlorine as sodium hypochlorite	4
Calcium chloride	7
Zinc sulphate	3
Sulphonated fatty alcohol or suitable wetting agent	½

This oxidising mixture gives a pH of 8.2, and the cold treatment in a paddle or rotary machine is continued until complete exhaustion is obtained. Acidified bisulphite solution is then added to the same bath to remove the discolouration due to the permanganate.

Example 4.—100 parts of 24/2 wool yarn in cheese form are treated in the grease with 2500 parts of water containing 1½ parts potassium permanganate, 2½ parts of chlorine as sodium hypochlorite, 10 parts calcium chloride and ½ part sulphonated fatty alcohol. This mixture gives a pH of approximately 11, and the cold treatment is continued in a pressure dyeing machine until exhaustion of the bath is obtained. Acidified bisulphite solution is then added and processing continued until the discolouration of the permanganate is removed.

Example 5.—100 parts of 12/4 Botany yarn in the grease are treated with 2500 parts of water containing:

	Parts
Chlorine as sodium hypochlorite	3
Calcium chloride	10
Sulphonated fatty alcohol or suitable wetting agent	½

Treatment is continued in the cold until almost complete exhaustion of the halogen is obtained. A well diluted solution containing 2 parts potassium permanganate is then added, and the treatment is continued until it is fully absorbed by the wool. Acidified bisulphite solution is then added to remove the discolouration due to the permanganate.

Example 6.—100 parts of unscoured 12/3 wool yarn in the hank form is treated with 2500 parts of water containing:

	Parts
Potassium permanganate	2
Bromine as sodium hypobromite	3
Calcium chloride	10
Sulphonated fatty alcohol or suitable wetting agent	½

The solution of sodium hypobromite is conveniently prepared by circulating in the cold 3 parts of bromine in 1½ parts of caustic soda contained in 400 parts of water, until complete solution is obtained.

The above oxidising mixture gives a pH of about 11, and the treatment is continued until exhaustion is obtained. Acidified bisulphite is then added to the same bath to remove the discolouration due to the permanganate.

Example 7.—100 parts of scoured 12/4 Botany yarn is treated with 2 parts of permanganate in 2500 parts of water corrected to pH 5 with sulphuric acid, for 1 hour in the cold. It is then lifted and re-entered into a fresh bath containing 5 parts of sodium p-toluene-sulphonchloramide in 2500 parts of water, corrected to pH2 with hydrochloric acid. This treatment is continued in the cold for about 20 minutes, or until complete exhaustion of the chloramine, after which the discolouration due to the permanganate is removed by addition of bisulphite to the same liquor.

The expression "to reduce the natural tendency to shrink when washed in aqueous liquors," and similar expressions used herein, are intended to designate either neutral or alkaline liquors which have a natural tendency to cause shrinkage in wool.

What we claim is:

1. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating such materials with a dilute aqueous solution of an alkali metal permanganate at a pH of not less than about 5 and with a dilute aqueous solution containing a substance selected from the group consisting of alkali hypohalite at a pH of at least 7.5 and a nitrogen-chloro compound in which the chlorine atom is directly attached to the nitrogen atom and in which the chlorine is present as available chlorine having a pH of about 1 to 3.

2. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a dilute aqueous solution of an alkali metal permanganate mixed with a dilute aqueous solution containing an alkali hypohalite at a pH of approximately 7.5 to approximately 11.

3. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a dilute aqueous solution of an alkali metal permanganate at a pH of 5 to 10 and at a temperature not exceeding 60° C., and subsequently treating them with a dilute aqueous solution containing a nitrogen-chloro compound at a pH of 1 to 3.

4. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a dilute aqueous solution of an alkali metal permanganate at a pH of 5 to 10 and at a temperature not exceeding 60° C., and subsequently treating them with a dilute aqueous solution containing an alkali hypohalite at a pH of approximately 7.5 to approximately 11.

5. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating

the textile materials with a dilute aqueous solution of an alkali metal permanganate at a pH of not less than about 5 and with a dilute aqueous solution containing an alkali hypohalite at a pH of at least 7.5 and a metal salt selected from the group consisting of magnesium sulphate, calcium chloride, calcium acetate, barium chloride, barium acetate, and zinc sulphate.

6. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a dilute aqueous solution containing an alkali hypohalite at a pH of 7.5 to approximately 11 and subsequently treating them with a dilute aqueous solution of an alkali metal permanganate at a pH over 7.

7. A method as claimed in claim 1, in which the permanganate compound is potassium permanganate.

8. Textile materials containing wool, which have had the natural tendency to shrink when washed in aqueous liquors reduced by treatment with a dilute aqueous solution of an alkali metal permanganate at a pH of not less than about 5 and with a dilute aqueous solution containing a substance selected from the group consisting of alkali hypochlorite at a pH of at least 7.5 and a nitrogen-chloro compound in which the chlorine atom is directly attached to the nitrogen atom and in which the chlorine is present as available chlorine having a pH of about 1 to 3.

9. A method as claimed in claim 1, in which the concentration of an alkali metal permanganate is less than 6% on the weight of the textile material.

10. A liquor for treating textile materials containing wool in order to reduce the natural tendency to shrink when washed in aqueous liquors, said liquor containing an alkali metal permanganate, an alkali hypohalite and a metal salt selected from the group consisting of magnesium sulphate, calcium chloride, calcium acetate, barium chloride, barium acetate, zinc sulphate having a pH of approximately 7.5 to approximately 11.

11. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a single bath containing a dilute aqueous solution of an alkali metal permanganate and a dilute aqueous solution of an alkali metal hypochlorite at a pH of approximately 7.5 to approximately 11 until a permanent resistance to shrinkage against alkaline liquors occurs.

12. A method of treating fabrics and other textile materials consisting at least in part of wool, to reduce the natural tendency to shrink when washed in aqueous liquors, comprising treating the textile materials with a single bath containing a dilute aqueous solution of an alkali metal permanganate and a dilute aqueous solution of an alkali metal hypochlorite at a pH of approximately 7.5 to approximately 11 until a permanent resistance to shrinkage against alkaline liquors occurs, and thereafter removing any discoloration due to the permanganate.

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