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PROCESS OF RENDERING WOOL UNSHRINKABLE

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This invention relates to processes of rendering wool unshrinkable.

It is known that wool can be rendered unshrinkable by treatment with elementary chlorine or bromine either in the gaseous state or dissolved in water or organic solvents, e. g. alcohol or carbon tetrachloride, or with an acidulated aqueous solution of hypochlorite. In these known processes the action of the halogen on the wool fibre is so vigorous and quick—in fact it is accomplished in a few seconds only—that it cannot properly be controlled. Consequently, the effect of this treatment is not uniform: while a part of the batch has just reached the desired degree of unshrinkability, another part thereof has already got more than its proper share of halogen and suffered damage by the latter. The feel of the wool so treated is unsatisfactory, and the increase of its color reception properties which, as is known, is brought about by the halogen, is not uniform which leads to the formation of stains when the wool is subsequently dyed. On the other hand it is known that the color reception properties of wool can be improved by treatment with a highly dilute aqueous solution of alkali bromate in the presence of hydrochloric acid and that such treatment does not affect the felting and shrinking properties of the wool.

It has now been found that wool can be made unshrinkable by a well-controllable treatment with an aqueous solution of alkali bromate and hydrochloric acid, if the concentration of bromate in the treating liquor is chosen not below a certain minimum.

When wool is immersed in dilute aqueous acid it absorbs a part thereof which is largely independent of the temperature of the liquor, and is nearly constant even for different specimens of wool. Speakman (Journal of Textile Inst., vol. 22, No. 7, 1941) found that the amount of acid so absorbed is equivalent to about 800 cc. of N/10 acid (i. e. about 0.08 gram-equivalent) per 100 grams of air-dry wool. The character of this absorption is not yet fully recognized. On the one hand the acid disappears for all intents and purposes from the solution and cannot be found back by titration, on the other hand it can be eluted from the wool by intensive washing with much water. It may, therefore, be assumed that it is bound in salt bond to protein and that the bond is liable to be severed by hydrolysis (see also Speakman, l. c.). Where the solution contains several acid anions, e. g. in the case of a mixture of hydrochloric acid and bromate, the total

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amount of anion absorbed by the wool substantially corresponds to the total amount of absorbed hydrogen ion, but the anions are absorbed in a proportion relative to one another substantially equal to their original proportion in the said solution. By elution they are again liberated from the wool substantially in the same proportion.

The shrinkproofing effect obtained by the treatment of wool with hydrochloric acid and bromate according to this invention is due to bromate present in the treating liquor over and above the absorbed quantity. Again the exact nature of the action of the bromate on the wool is not yet recognized but it can be stated with certainty that the effective part of the bromate is irretrievably lost, in contrast to the absorbed portion of bromate which, upon being eluted from the wool, is recovered as bromate.

Accordingly, this invention consists in a process of shrinkproofing wool by treatment with an aqueous liquor containing free hydrochloric acid and water-soluble bromate over and above the amounts of acid and bromate ion liable to be absorbed by the wool, and the treatment is so controlled that an amount of bromate ion of from 6.4 to 16 grams per kilogram of air-dry wool is thereby consumed.

The exact amount of bromate that any particular specimen of wool requires for shrinkproofing has to be ascertained by preliminary tests.

After the treatment with bromate the wool is after-treated with a view to removing any bromate or free halogen left, e. g. by rinsing, washing with dilute ammonia, soaking with an alkali bisulfite solution, and again rinsing.

The hydrochloric acid may be added to the liquor as such or be generated therein from chloride and another acid or an acid salt, e. g. sulfuric acid or a bisulfate.

It is advisable to add to the liquor acid-resisting wetting agents, as known per se, e. g. alkali lauryl sulfate or oleyl sulfate, and protective colloids, e. g. glue, gum or the like.

The shrinkproofing treatment according to this invention may be combined with a milling treatment. In this case the cloth is first immersed in a liquor containing the shrinkproofing agents, and milled therein till the desired degree of thickening has been obtained, then the milling is interrupted and the cloth is left for some time in the liquor without further mechanical agitation, and thereby stabilized in the state of thickening produced by the milling. For the milling

operation, the liquor may contain already the full amount of acid and bromate required for shrinkproofing, or the acid and/or bromate may first be present in less than the full quantity needed for shrinkproofing and the balance be added when the milling is interrupted.

The invention is illustrated by the following examples.

Example 1

1 kg. of wool is treated in 23 litres of a liquor which is kept at 25° C. and contains per litre: 2.1 grams of potassium bromate (corresponding to 1.6 grams of bromate ion), 6 grams of hydrogen chloride (calculated as pure HCl), 5 grams of bone glue and 0.2 gram of sodium lauryl sulfate. By analysis and calculation made on the assumption that hydrochloric acid and bromate ion are absorbed by the wool in the same proportion as originally present in the liquor it can be shown that the absorption of hydrochloric acid is of the order of 29 grams of HCl, and that of bromate ion of the order of 7.7 grams. The rate of disappearance of bromate and acid during the treatment is followed by titration of the acid and bromate contained in samples taken from the liquor at short intervals. After 40 to 60 minutes, an amount of bromate ion of about 8 grams has disappeared over and above the 7.7 grams of absorbed bromate ion mentioned above. When this is the case, the wool is removed from the vat, rinsed with water and introduced into a bath of about 25 litres of water containing 1 gram of ammonia per litre, left therein for about 30 minutes, rinsed and brought into a second bath of about 25 litres of water which contains 1 gram of sodium bisulfite per litre and is kept at 50° C. After about 45 minutes the wool is again rinsed, centrifuged and dried.

Example 2

1 kg. of wool is treated for about one hour in 23 litres of a liquor which is kept at 25° C. and contains per litre: 3.6 grams of $KBrO_3$ (corresponding to about 2.8 grams of bromate ion), 13.5 grams of NaCl (corresponding to about 8.4 grams of HCl), 27 grams of potassium bisulfate and 0.2 gram of a wetting agent. For the rest, the treatment is carried out as described in Example 1.

Example 3

The treatment and composition of the liquor are the same as described in Example 1, except that the temperature of the liquor is 35° C. and the amount of HCl 3 grams. Duration of the treatment: 60 to 80 minutes.

Example 4

Composition of the liquor: 23 litres containing per litre: 5.25 grams of potassium bromate (corresponding to 4 grams of bromate ion), 8 grams of HCl, 5 grams of glue and 0.2 gram of wetting agent. Temperature 12° C., duration 45 minutes, otherwise as described in Example 1.

Example 5

1 kg. of wool is treated at 60° C. in 23 litres of a liquor which contains per litre: 0.65 gram of bromate ion (in the form of potassium bromate), 3 grams of hydrogen chloride and 0.2 gram of sodium lauryl sulfate. After about 90 minutes, the consumption of bromate ion amounts to about 9 grams. The wool is then removed from the liquor and further treated as described in Example 1.

Example 6

1 kg. of wool is treated at 60° C. in 50 litres of a liquor which contains per litre: 0.5 gram of bromate ion (in the form of potassium bromate), 2.25 grams of hydrogen chloride and 0.2 gram of sodium lauryl sulfate. After about 60 minutes, the consumption of bromate ion amounts to about 9.5 grams. The wool is then removed from the liquor and further treated as described in Example 1.

Example 7

1 kg. of wool is treated at 65° C. in 60 litres of a liquor which contains per litre: 0.4 gram of bromate ion (in the form of potassium bromate), 1.85 grams of hydrogen chloride and 0.2 gram of sodium lauryl sulfate. After about 70 minutes, the consumption of bromate ion amounts to 8.5 grams. The wool is then removed from the liquor and further treated as described in Example 1.

Example 8

1 kg. of wool is immersed in a fulling mill in 23 litres of a liquor containing per litre: 6 grams of hydrogen chloride (calculated as pure HCl) and 0.8 gram of bromate ion (in the form of potassium bromate) and milled at 25° C. till the desired degree of thickening has been obtained. Then the milling is interrupted, a further 0.8 gram of bromate ion (as potassium bromate) per litre is added and the cloth is left in the liquor without mechanical agitation for about 35 minutes, and further treated as described in Example 1.

We claim:

1. The process of shrinkproofing wool, which comprises immersing the wool in an aqueous liquor containing hydrochloric acid and water-soluble bromate in excess over the amount of acid and bromate absorbable in the wool, which absorbable amount corresponds to about 0.08 gram-equivalents per 100 grams of air-dry wool, the excess of bromate (expressed as bromate ion) being not less than 1.5%, and that of hydrochloric acid (expressed as HCl) being comprised between 6 and 20%, both calculated on the weight of air-dry wool; leaving the wool in the liquor until bromate ion has disappeared therefrom in an amount of about 0.65 to 1.6 grams per 100 grams of air-dry wool; withdrawing the wool from the liquor and removing excess treating liquor from the wool.

2. A process as claimed in claim 1 wherein a wetting agent is added to the treating liquor.

3. A process as claimed in claim 1 wherein a protective colloid is added to the treating liquor.

4. The method of treating woollen cloth by a combined milling and shrinkproofing process comprising immersing the cloth in a fulling mill in an aqueous liquor containing hydrochloric acid and water-soluble bromate in excess over the amount of acid and bromate absorbable in the wool, which absorbable amount corresponds to about 0.08 gram-equivalents per 100 grams of air-dry wool, the excess of bromate (expressed as bromate ion) being not less than 1.5%, and that of hydrochloric acid (expressed as HCl) being comprised between 6 and 20%, both calculated on the weight of air-dry wool; milling the cloth until the desired degree of thickening has been obtained, interrupting the milling and further leaving the cloth in the liquor until bromate ion has disappeared therefrom in an amount of about 0.65 to 1.6 grams per 100 grams of air-dry wool; withdrawing

the cloth from the liquor and removing excess treating liquor from the cloth.

5. The method of treating woollen cloth by a combined milling and shrinkproofing process comprising immersing the cloth in a fulling mill in an aqueous liquor containing hydrochloric acid and water-soluble bromate in at least the amount thereof absorbable in the wool, which absorbable amount corresponds to about 0.08 gram-equivalents per 100 grams of air-dry wool, and at least hydrochloric acid in excess over said absorbable amount, the excess amount of the acid (expressed as HCl) being comprised between 6 and 20% by weight of air-dry wool; milling the cloth until the desired degree of thickening has been obtained, interrupting the milling, adding to the liquor so much further water-soluble bromate that the liquor contains a total excess of bromate ion, over and above the aforesaid absorbable amount, of not less than 1.5% by weight of air-dry wool; leaving the wool in the liquor until bromate ion has disappeared therefrom in an amount of about 0.65 to 1.6 grams per 100 grams of air-dry wool; withdrawing the cloth from the liquor, and removing excess treating liquor from the cloth.

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