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(54) Method for the treatment of wool.

(57) A method for the treatment of wool so as to impart shrink resistance comprising, in any order, the steps of:-

i) treating the wool with a proteolytic enzyme, and

ii) subjecting the wool to either or both of an oxidative treatment and treatment with a polymer, with the proviso that when the oxidative treatment is used alone it comprises a wet chlorination process.

The method may be operated either as essentially a batch process or as a process involving a combination of continuous and batch treatments.

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METHOD FOR THE TREATMENT OF WOOL

This invention relates to a method for the treatment of wool so as to impart shrink resistance. The method involves subjecting the wool to an attack by a proteolytic enzyme, together with an oxidative treatment and/or a polymer treatment.

Many ways of rendering wool shrink resistant are known. These typically involve subjecting the wool to an oxidative treatment alone or, more commonly nowadays, followed by a polymer treatment.

Various oxidative treatments for use in imparting shrink resistance to wool are well known. One such method, for example, involves treating the wool with permonosulphuric acid. Chlorinating oxidative treatments can also be employed and these typically make use of chlorine gas or chlorinating agents such as hypochlorite and sodium dichloroisocyanurate. British Patent No. 569,730 describes a batch shrink-proofing treatment involving hypochlorite and potassium permanganate (the Dylan ZB process). British Patent No. 1,073,441 refers to continuous treatments of wool using combinations of permonosulphuric acid and either hypochlorite or dichloroisocyanurate. British Patent No. 2,044,310 describes a treatment with an aqueous solution of permanganate and hypochlorite (the Dylan Fullwash process).

Oxidative treatments used alone will produce a degree of shrink-resistance in the wool. However, the level attained is generally not sufficient to satisfy the modern requirements and IWS standards for shrink resistance. The use of larger amounts of chlorinating agents, for example, in an effort to improve the shrink resistance, has a tendency to cause yellowing and degradation of the wool fibres. This is particularly so in the case of batch treatments, especially of loose wool or wool top, where there is great difficulty in achieving level treatments due to the relatively poor liquor circulation available. The portion of untreated wool fibres thus resulting will produce extensive and undesirable felting shrinkage. It is further generally accepted that once a batch of wool is treated in an unlevel manner the untreated and partly treated fibres cannot be satisfactorily retreated, subsequent attempts at retreatment resulting in further attack on those fibres which have already received the greatest degree of treatment.

Two-step shrink-proofing processes for wool, involving an oxidative treatment of the aforementioned type followed by a polymer treatment, have over the years become very popular and today represent the major type of process used throughout the world. Various two-step shrink-proofing processes in which wool is usually treated first with an oxidative chlorinating agent and subsequently with a pre-formed synthetic polymer have been developed and are well known. A wide variety of polymers can be used in aqueous solution or dispersion, including polyamide-epichlorohydrin resins and polyacrylates. A review of work in this field by J.Lewis appears in Wool Science Review, May 1978, pages 23-42. British Patent Nos. 1,074,731 and 1,340,859 and U.S. Patent Nos. 2,926,154 and 2,961,347 describe two-step shrink-proofing processes and resins or polymers suitable for use therein.

The CSIRO chlorine/Hercosett procedure is considered to be the first commercially acceptable polymer process for the continuous treatment of wool tops. This process comprises the acid chlorination of wool slivers or tops, followed by the application of a cationic polyamide-epichlorohydrin resin (e.g. Hercosett 125; Hercules Chemical Company). Kroy Unshrinkable Wools Ltd. developed a method of chlorinating wool by means of a vertical deep immersion and this often serves as a pretreatment for the subsequent application of shrink-proofing resins,

These conventional two-step processes confer good levels of shrink resistance but, despite achieving considerable commercial success, they do have some disadvantages. In particular, they are generally only suitable for continuous treatments of wool top. There is therefore a need for an improved batch treatment and particularly one which gives a more level treatment.

During the 1940s and early 1950s there was considerable interest in the use of enzymes in processes for making wool shrink resistant. One of the causes of shrinkage is the felting or matting together of the fibres which occurs when wool in any form is submitted to repeated alternate compression and relaxation. The theory was that since the ability of wool to felt is largely dependent on the surface structure of the fibres, it should be possible to reduce the tendency of wool to shrink by means of treatment with enzymes which will attack and degrade the surface of the fibres. Because the enzymes have very large molecules, they cannot penetrate into a wool fibre even if it is wet and swollen. The enzymes are adsorbed on the surface of the fibre, to which their action is restricted, and they bring about surface degradation of the fibre at relatively low temperatures. Wool was found to be attacked by proteolytic enzymes much more slowly than some other proteins and it was thought that the disulphide cross-linkages in wool retard the action of the enzyme. It was then discovered that the activity of the enzymes was greatly increased by the presence of a reducing agent such as sodium bisulphite. The bisulphite reduces and so breaks down some of the disulphide cross-linkages so that the enzyme can gain access to the surface of the wool fibres and so carry

out its proteolytic action. The bisulphite also reduces the enzyme itself to a more active form.

Processes for making wool shrink resistant comprising an oxidative pretreatment followed by treatment with an enzyme are described by Phillips and Middlebrook in The Journal of the Society of Dyers and Colourists, May 1941, Volume 57, No. 5, pages 137-144 and by A.N. Davidson and R. Preston, in J. Text. Inst. Proc., 1956, Volume 47, pages 685-707. British Patent Nos. 513,919 and 804,781 relate to such processes. A general review of the work in this field appears in Wool Shrinkage by R.W. Moncrieff (1953), pages 322-332. The enzymes used were trypsin, pepsin and most commonly papain.

Several shrink resist processes using papain were developed to a commercial scale :-

a) In the first of these processes, papain and sodium bisulphite were used in an aqueous solution adjusted to pH 6 to 7 with sodium carbonate. In order to obtain optimum results it was considered necessary for the papain solution to contain at least 1%, generally from 1 to 2%, of its weight of sodium bisulphite. The treatment time for wool in this solution was generally from 10 to 60 minutes. The main disadvantage of the process was that the papain attacks the wool irregularly, particularly attacking weathered fibres and the tips of fibres more than other areas. Any shrink resist process which gives an irregular product is clearly not well suited for industrial use.

b) In an attempt to make all of the wool fibres equally susceptible to the action of papain, a process was then devised in which the wool was first bleached with hydrogen peroxide - this was known as the Perzyme Process. In a two-stage operation, the wool was firstly bleached at pH 10.5 with hydrogen peroxide for a time (up to 1 to 2 hours in some cases) and then treated with a mixture of papain and sodium bisulphite. The disadvantages of the process were that the wool suffers a weight loss of from 1 to 3% during the treatment, it is slow and is not so easily applied to wool tops as to yarns and fabrics. In addition, there was a tendency for the handle of the wool to suffer.

c) In a variation of the Perzyme Process, organic peracids were used in place of hydrogen peroxide as the pretreatment reagent. Solutions of peracetic acid, sodium peracetate, potassium persulphate, permonosulphuric acid and performic acid were tried. Suitable conditions for the shrink resist treatment of botany wool (64s) were found to be treatment in a solution of peracetic acid (0.08%) at 15°C for 30 minutes followed by treatment with a mixture of papain and sodium bisulphite. The bisulphite is used as a 0.5 to 1% solution.

d) The Chlorzyme Process consisted of dry chlorination of the wool followed by treatment with papain and bisulphite. The generally preferred procedure was to dry chlorinate wool containing 7 to 9% of moisture, neutralising the hydrochloric acid which is formed on the wool during the chlorination with dilute sodium sesquicarbonate. The papain treatment was then carried out at a liquor:wool ratio of 15:1, the solution containing 0.025% papain and about 0.25% sodium bisulphite to act as an accelerator and being adjusted to pH 5. The treatment was performed at 50 to 65°C and took about 2 hours. The main disadvantage of this process was that it gave wool with an unnatural lustrous, almost glossy, appearance. In addition, there are severe disadvantages and practical problems associated with the treating of wool by dry chlorination

While these processes achieved some limited commercial success during the 1940s and 1950s, the standards set for shrink resistance at that time were much lower than those demanded today. These early enzyme processes, when operated using the combinations of materials and treatment conditions described in the literature and summarised above, do not achieve the levels of shrink resistance needed to satisfy the modern standards and requirements for IWS washable wool labelling. For this reason, none of the processes are in commercial operation today. Furthermore, the present inventors are not aware of any shrink resist processes having been developed subsequently and which include an enzyme treatment of the wool.

The present invention seeks to provide a method for the treatment of wool involving the use of an enzyme and which achieves levels of shrink resistance sufficient to meet the standards that are required today.

According to the present invention there is provided a method for the treatment of wool so as to impart shrink resistance comprising, in any order, the steps of:-

i) treating the wool with a proteolytic enzyme, and

ii) subjecting the wool to either or both of an oxidative treatment and treatment with a polymer, with the proviso that when the oxidative treatment is used alone it comprises a wet chlorination process.

With regard to the enzyme treatment which characterises the method of this invention, it is envisaged that any proteolytic enzyme may be used and this could be of either vegetable origin, such as papain, or of bacterial origin, such as an alkaline proteinase. Examples of suitable enzymes include Scintillase (a papain-based enzyme preparation), Proteinase 200L (Bacterial Neutral), Proteinase AP (Fungal Acid), Panazyme Conc. (Fungal Neutral) and Proteinase T (Thermostable Bacterial Neutral). A particularly preferred enzyme

is Proteinase D (IUB number 3.4.21.14) and which is a bacterial alkaline proteinase produced by Bacillus licheniformis.

The enzyme treatment is preferably carried out in a fresh bath containing 0.05 to 30% o.w.w. (preferably 10 to 20% o.w.w) solids of a mixture of sodium bisulphite and sodium sulphite balanced to achieve the optimum pH for the enzyme. Other conventional buffering systems are known and could, of course, be used instead. At the preferred liquor ratio, 15% o.w.w. corresponds to about 0.5% sodium bisulphite. The optimum pH will obviously vary according to the enzyme employed, but is typically pH 6.5 to 7.0. In the same way, the temperature is adjusted according to the enzyme employed but is typically 60 to 65°C for optimum results. Time of treatment may vary widely, but is typically from 5 to 120 minutes (most preferably from 10 to 60 minutes). The level of enzyme used may vary from 0.01 to 1.0% (most preferably from 0.02 to 0.5%). All of these percentages are on the weight of the wool. It is to be understood, however, that the precise conditions adopted for the enzyme treatment may be varied according to the particular circumstances.

The treatment of the wool with the enzyme may be carried out either before or after the oxidative treatment or before or after the polymer treatment. If the process includes both an oxidative treatment and the application of a polymer, the enzyme treatment may be performed before, after or between these treatments. Most preferably, the enzyme treatment takes place after the oxidative treatment and before any polymer treatment of the wool. For example, the enzyme treatment could be combined with the sulphite/bisulphite antichlor or cleaning treatments which would conventionally follow the oxidative treatment. However, the possibility of treating the wool with enzyme after a polymer treatment is considered to be a significant advantage of the method of this invention since it provides a means for recovering or salvaging wool which has been ineffectively treated by conventional two-stage oxidation-resin treatments and where recovery to Superwash standards may otherwise be difficult or impossible.

As previously mentioned, the oxidative treatment of the wool is a conventional procedure and a number of suitable treatments are well known. Most preferably, however, a chlorinating oxidative treatment is employed. When the oxidative treatment is used alone, i.e. without any subsequent polymer treatment,it is necessarily a wet chlorination process. The wet chlorination may comprise any treatment known from the prior art, such as the use of dichloroisocyanuric acid (DCCA), DCCA plus permonosulphuric acid (the Dylan XB2 and XC2 processes), and hypochlorite either alone or together with other materials such as potassium permanganate (e.g. the Dylan Fullwash and Dylan ZB processes). The use of the Dylan ZB process is particularly preferred.

The oxidative treatment,when present,is carried out in a conventional manner and the suitable conditions, such as pH, time and temperature for the treatment, are well known and will not be repeated here in detail. The oxidative treatment will normally be applied at any level between 0.25 and 4% of the oxidising species (active chlorine or equivalent) by weight on the weight of the dry wool, either alone or in admixture. It is to be understood, however, that since according to the method of this invention the oxidative treatment is combined with an enzyme treatment, and optionally also with a polymer treatment, reduced amounts of the oxidising system can in some cases be used while still attaining very acceptable levels of shrink resistance in the final product. This potential for reducing the severity of the oxidative treatment has the advantage that it can also result in a lessening of the adverse side effects which are associated with some of these processes (i.e. weight loss and/or yellowing of the wool, unsatisfactory rate of strike on dyeing and effects on dye shade and fastness in pre-dyed material). In addition, there would also be an environmental benefit in reducing the amount of chlorine-containing by-products that are released into the environment where they can persist for undesirably long periods of time.

With regard to the polymer treatment, when included in the method of this invention, any of the polymers conventionally applied to oxidised wool may be used. These include, for example, the polymers described in our own European Patent Application Nos. 0129322 and 0260017, the Hercosett polymers, silicone polymers and the Dylan Ultrasoft polymers. The only real restriction is that the polymer chosen should be suited to the further processing to which the wool will be subjected. As is well known, for example, certain silicones may not be suitable on wool which has to be subsequently spun into yarn because of the undesirable effects that this type of polymer system can have on the spinning operation.

The application of the polymer to the wool will normally be carried out in the conventional manner, using the amounts and conditions appropriate for the particular polymer system and which are well known in the art and need not be repeated here in detail. It is to be understood, however, that having regard to the combined effectiveness of any oxidative pretreatment and the enzyme treatment, the minimum amounts of the various polymers that it is normally considered necessary to apply in order to achieve acceptable levels of shrink resistance may be substantially reduced. The Hercosett polymers and Polymer PKS (of our European Patent Application No. 0260017), for example, are conventionally applied at 2% solids. Using the

method of this invention, acceptable standards of shrink resistance can still be achieved with the application to the wool of perhaps as little as 50% of these amounts. This potential for reduction in the amount of polymer applied has obvious cost advantages. In addition, the application of many polymer systems in conventional amounts can produce a marked deterioration in the handle of the wool and the consequent need to use softeners.

A particularly preferred sequence of treatments according to the method of this invention is the Dylan ZB oxidation treatment, followed by treatment of the wool with the enzyme Proteinase D and then application of Polymer PKS. The resulting product has very good shrink resistance and is exceptionally soft. Indeed the handle of the wool, following the oxidative and enzyme treatments, is in some instances actually further improved by the Polymer PKS application. This improvement in softness is unexpected since any polymer treatment would normally be expected to have at best no effect on the handle or, more probably, a detrimental effect.

The method may be operated either as essentially a batch process or as a process involving a combination of continuous (oxidation, polymer application) and batch treatments (enzyme application). The wool may be in any suitable form from loose wool to finished garments, dyed or undyed, including top, slivers, roving, yarn or carded web, provided of course that suitable mechanical means are available to facilitate handling and treatment of wool in these forms. When performed at the same time as the enzyme treatment, the oxidative treatment could occur in batch processing machinery. However, the wool could of course still be treated by more conventional continuous processes as a separate operation. This would be necessary, for example, when processing wool top using the Fullwash or chlorine gas treatments.

The method of this invention also renders more feasible the successful treatment of wool in forms previously considered very difficult. This especially relates to loose wool, wool top or yarn in hanks treated in a batch process. Conventional oxidative treatments do not give very level results in such processes, thus giving rise to a very low effectiveness of treatment. Because of the nature of the action of the enzyme used in the present invention, it seems to be capable of covering up or "levelling" these differences, thus rendering such processes more commercially applicable. The same effect cannot be obtained using conventional oxidation treatments alone as further attack tends to take place on the most oxidised parts of the fibres, thereby worsening the problem or even degrading the wool.

The present invention will now be illustrated by the following Examples.

Examples 1 to 10 relate to prior art shrink-resist treatments of wool involving the use of enzymes. In Examples 1 to 4, knitted swatches are treated under conditions quoted in British Patent No. 513,919 and The Journal of the Society of Dyers and Colourists, 57, 137 (1941). Examples 5 and 6 are similar to Examples 3 and 4, respectively, but a popular modern bleaching recipe is used in the hydrogen peroxide pretreatment. In Examples 7 and 8, knitted swatches are treated under conditions quoted in British Patent No. 804,781 and J.Text. Inst. Proc., 47, 691-703 (1956) in which enzyme is used after a pretreatment with peracetic acid. In Examples 9 and 10, the enzyme is used following a pretreatment with permonosulphuric acid. However, 2% active permonosulphuric acid o.w.w. was actually applied instead of the 0.3% o.w.w. referred to in the literature. As will be seen below, none of the treatments of Examples 1 to 10 achieves a machine washable level of shrink resistance which would be commercially acceptable by today's standards-(as laid down by the International Wool Secretariat).

Examples 11 to 16 refer to treatments according to the present invention. Example 11 involves the use of a conventional Dylan ZB pretreatment. In Example 12, the process is consolidated by combining the clearing/antichlor stage with the application of enzyme and this makes the whole process quicker and simpler. Example 16 demonstrates the use of the enzyme treatment of this invention in shrink-resist recovery work, i.e. following a conventional shrink-resist process in which the necessary level of shrink resistance has not been achieved.

Measurement of Shrink Resistance

The shrink resistance conferred by the various treatments was measured by washing according to the test method TM31 of the International Wool Secretariat using 5A wash cycles in a Wascator machine. It should be noted that a maximum of a 10% area shrinkage after 2 x 5A wash cycles is the minimum acceptable standard for knitted outerwear and 5 x 5A wash cycles the minimum acceptable standard for knitted underwear.

Applications to Knitted Swatches

Knitted swatches were prepared from 2/24's Worsted count wool yarn spun from 70's quality dry combed top and knitted to a cover factor of 1.29 direct tex. The swatches were scoured at a 30:1 liquor to wool ratio using 1% o.w.w. Dylachem Millscour (non-ionic scouring agent, Precision Processes (Textiles) Ltd.) and 3% sodium bicarbonate o.w.w. at 45°C for 20 minutes. After scouring swatches were thoroughly rinsed.

In the following examples liquor volume to wool weight ratio was 30:1 throughout, unless otherwise stated.

Example 1

A knitted swatch was stirred in a water bath containing 30% sodium bisulphite o.w.w. and 0.75% Scintillase 240 D (purified papain vegetable proteinase enzyme, ABM-Sturge) o.w.w. at a pH of 6.8 and temperature of 65°C for 60 minutes. The swatch was rinsed, hydroextracted and flat dried at 80°C.

Example 2

As for Example 1 but 0.75% Proteinase D (bacterial alkaline proteinase, ABM-Sturge) o.w.w. was used instead of Scintillase 240 D.

Example 3

A knitted swatch was stirred in a water bath containing 4 volume hydrogen peroxide at pH 10.5 (obtained with 2 gl^{-1} sodium silicate and sodium hydroxide) and temperature 50°C for 60 minutes. After thoroughly rinsing the swatch was treated with enzyme as in Example 1, but at a temperature of 50°C.

Example 4

A knitted swatch was treated with hydrogen peroxide as in Example 3. After thoroughly rinsing the swatch was treated with enzyme as in Example 2, but at a temperature of 50°C.

Example 5

A knitted swatch was stirred in a water bath containing 4 volume hydrogen peroxide at pH 8.5 to 9.0 (obtained with 2 gl^{-1} sodium tetrapyrophosphate) and temperature 50°C for 60 minutes. After thoroughly rinsing the swatch was treated with enzyme as in Example 1 but at 50°C.

Example 6

A knitted swatch was treated with hydrogen peroxide as in Example 5. After thoroughly rinsing the swatch was treated with enzyme as in Example 2 but at 50°C.

Example 7

Two knitted swatches were stirred in a water bath containing 6% (2.4% active) peracetic acid (40% strength) o.w.w. for 30 minutes at 15°C. Then the temperature was raised to 50°C and stirring continued until the peractic acid had fully exhausted onto the wool. After thoroughly rinsing, one of the swatches was stirred in a water bath containing 30% sodium bisulphite o.w.w. and 0.3% Scintillase 240 D o.w.w. at a pH of 6.8 and temperature of 50°C for 60 minutes. The swatch was rinsed, hydroextracted and flat dried at 80°C.

Example 8

As for Example 7 but 0.3% Proteinase D o.w.w. was used instead of Scintillase 240 D.

Example 9

Two knitted swatches were stirred in a bath containing 2% active permonosulphuric acid at ambient temperature and a pH of 3. After exhausting the permonosulphuric acid onto the wool 5% sodium sulphite (anhydrous) was added to the bath, to neutralise any residual unreacted permonosulphuric acid and to develop any potential shrink resistance, and stirring continued for 20 minutes. After thoroughly rinsing one of the swatches was treated with 0.3% Scintillase 240 D o.w.w. at a pH of 6.8 and temperature of 50°C for 60 minutes. The swatch was hydroextracted and flat dried at 80°C.

Example 10

As for Example 9 however 0.3% Proteinase D o.w.w. was used instead of Scintillase 240 D.

Effectiveness of treatments applied in Examples 1 to 10 was measured by washing test method TM31. Results were as follows:-

	Test Method TM31 % Area Shrinkage after:-	
Application	5A	2 x 5A
1. Untreated scoured swatch	-54.0	-
2. Example 1 0.75% Scintillase 240 D	-42.4	-
3. Example 2 0.75% Proteinase D	-45.1	-
4. Example 3 Hydrogen Peroxide (pH 10.5) followed by 0.75% Scintillase 240 D	-39.7	-
5. Example 4 Hydrogen Peroxide (pH 10.5) followed by 0.75% Proteinase D	-37.0	-
6. Example 5 Hydrogen Peroxide (pH 8.5) followed by 0.75% Scintillase 240 D	-37.6	-

	Application	Test Method TM31 % Area Shrinkage after:- 5A	2 x A
7.	Example 6		
	Hydrogen Peroxide (pH 8.5) followed by 0.75% Proteinase D	-39.5	-
8.	Example 7		
	2.4% Peracetic acid	-48.3	-
	2.4% Peracetic acid followed by 0.3% Scintillase 240 D	-11.7	-36.6
9.	Example 8		
	2.4% Peracetic acid	-50.2	-
	2.4% Peracetic acid followed by 0.3% Proteinase D	-37.6	-
10.	Example 9		
	2.0% Permonosulphuric acid	-38.8	-55.9
	2.0% Permonosulphuric acid followed by 0.3% Scintillase 240 D	-19.0	-39.1
11.	Example 10		
	2.0% Permonosulphuric acid	-38.8	-55.9
	2.0% Permonosulphuric acid followed by 0.3% Proteinase D	-26.5	-44.8

Example 11

a). A combination of 2% active chlorine o.w.w from sodium hypochlorite and 2% potassium permanganate o.w.w. was applied to stirred knitted swatches in a water bath containing 5% calcium chloride o.w.w. and 0.5 ml l^{-1} Dylan Fullwet (original process disclosed in British Patent No. 569,730 - known

commercially as the Dylan ZB process). After equilibriating the swatches in the calcium chloride and Dylan Fullwet, the sodium hypochlorite and potassium permanganate (predissolved in water) is added to the bath, (pH approximately 8.5 at this stage). After 25 minutes the oxidising agents had exhausted onto the wool (pH dropped to approximately 7.5). A fresh bath was prepared and the manganese dioxide formed on the surface of the wool (brown colour) was cleared and any residual oxidising agent removed by treating with 8.5% sodium bisulphite and 3% formic acid (90% strength) for 25 minutes. Swatches were then rinsed and hydroextracted. One swatch was flat dried at 80°C.

b). One of the swatches from treatment a) was stirred in a water bath at pH 8.0 for 5 minutes to wet out and equilibriate. pH of 8.0 was maintained throughout the application. 8% (2% solids) o.w.w. of Polymer PKS (cationic water soluble polyamide, Precision Processes (Textiles) Ltd.) was drip fed into the bath over 10 minutes. After a further 5 minutes the temperature was raised to 40°C and stirring continued until the polymer had exhausted onto the swatches (tested for exhaustion by removing a 50 ml aliquot of the liquor from the bath and adding 1 ml of Dylachem Indicator 25 - an indicator for cationic polymers sold by Precision Processes (Textiles) Ltd. A turbid result indicates polymer is still in bath. A clear result indicates the polymer has exhausted). The swatch was then hydroextracted and flat dried at 80°C.

c). Two of the swatches from treatment a) were stirred in a water bath containing 15% sodium bisulphite o.w.w. and 0.3% Proteinase D o.w.w. at a pH of 6.8 and temperature of 65°C for 60 minutes. Then the swatches were rinsed. One swatch was hydroextracted and flat dried at 80°C. The other swatch was further treated with 8% Polymer PKS as in Example 11b).

Effectiveness of treatments applied in Example 11 was measured by washing test method TM31. Results as follows:-

Application	Test Method TM31 % Area Shrinkage after:-			
	2 x 5A	3 x 5A	4 x 5A	5 x 5A
1. Example 11a)				
2% available chlorine/2% $KMnO_4$ at pH 8.5	-31.5	-	-	-
2. Example 11b)				
2% available chlorine/2% $KMnO_4$ followed by 8% PKS	-25.5	-	-	-
3. Example 11c)				
(i) 2% available chlorine/2% $KMnO_4$ followed by 0.3% Proteinase D	-6.3	-9.6	-14.2	-
(ii)2% available chlorine/2% $KMnO_4$ followed by 0.3% Proteinase D then 8% Polymer PKS.	+10.5	+11.0	+7.6	+4.2

Example 12

a). A combination of 2% active chlorine o.w.w. from sodium hypochlorite and 2% potassium permanganate o.w.w. was applied to seven knitted swatches as in Example 11a). However only one swatch was cleared with 8.5% sodium bisulphite/3% formic acid, rinsed, hydroextracted and dried.

b). (i) Three of the swatches from treatment a) which had not been cleared were stirred in a fresh bath containing 0.3% Proteinase D o.w.w., 6% sodium bisulphite o.w.w. at a pH of 6.8 and temperature of 65°C for 60 minutes. The swatches were then rinsed and hydroextracted. One swatch was flat dried at 80°C.

(ii) One of the swatches from (i) was treated with 8% Polymer PKS as in Example 11b).

iii) One of the swatches from (i) was stirred in a water bath at pH 6.5. 1% Catalyst B (catalyst for Resin B, Precision Processes (Textiles) Ltd.) o.w.w. prediluted with water (approximately 1 part Catalyst B to 50 parts water) was drip fed over a period of 5 minutes. After a further 5 minutes, Resin B (reactive silicone based polymer emulsion, Precision Processes (Textiles) Ltd.) prediluted with water (approximately 3 parts Resin B to 100 parts water) was drip fed over a period of 10 minutes. After a furthr 5 minutes the temperature of the

bath was raised to 35°C and stirring continued until the polymer system had exhausted onto the wool (as indicated by a completely clear bath - the polymer system is turbid in water). The swatch was hydroextracted and flat dried at 80°C.

c). (i) The three remaining swatches from treatment a) which had not been cleared were treated as in Example b) (i) but 15% sodium bisulphite o.w.w. was used instead of 6% sodium bisulphite o.w.w.

(ii) One of the swatches from c) (i) was treated with 8% Polymer PKS as in Example 11b).

(iii) One of the swatches from c) (i) was treated with 1% Catalyst B and 3% Ultrasoft B as in Example 12b) (iii).

Whiteness of swatches after 12c) treatments were acceptable when compared with conventional clearing treatment from 12a). However swatches from 12b) were yellower than 12a) due to the use of less sodium bisulphite and the higher pH of the treatment.

Effectiveness of treatments applied in Example 12 was measured by washing test method TM31. Results as follows:-

Application	Test Method TM31 % Area Shrinkage after:-									
	5A	2 x 5A	3 x 5A	4 x 5A	5 x 5A	6 x 5A	7 x 5A	8 x 5A	9 x 5A	10 x 5A
1. Example 12a)										
2% available chlorine/2% $KMnO_4$ at pH 8.5. (Coventional clear with 8.5% sodium bisulphite/3% formic acid)	-10.4	-32.4	-	-	-	-	-	-	-	-
2. Example 12b)										
(i) 2% chlorine/2% $KMnO_4$ no clear. 0.3% Proteinase D and 6% sodium bisulphite.	- 2.3	- 7.6	-17.9	-	-	-	-	-	-	-
(ii) as for (i) then 8% Polymer PKS	- 2.0	- 2.7	- 4.4	- 8.1	-12.4	-19.1	-	-	-	-
(iii) as for (i) then 1% Catalyst B and 3% Resin B	- 2.2	- 1.5	- 1.7	- 4.5	- 4.8	- 7.5	- 9.3	-11.2	-	-
3. Example 12c)										
(i) 2% chlorine/2% $KMnO_4$ no clear. 0.3% Proteinase D and 15% sodium bisulphite.	- 0.9	- 2.2	- 5.5	-13.6	-	-	-	-	-	-
(ii) as for (i) then 8% Polymer PKS	- 2.0	- 1.1	- 2.7	- 4.7	- 5.0	- 7.0	- 6.6	- 7.2	- 8.9	-10.2
(iii) as for (i) then 1% Catalyst B and 3% Resin B	- 2.7	- 1.5	- 4.4	- 4.3	- 4.9	- 6.5	- 2.2	- 3.7	- 5.7	- 5.5

Example 13

a). (i) Eight knitted swatches were stirred in a water bath at a pH of 3.5 (using formic acid). 3.0% sodium dichloroisocyanurate (DCC) o.w.w. prediluted with water (3 parts to 300 ml of water) was drip fed over 20 minutes. After exhausting the DCC onto the wool 6% sodium sulphite was added as antichlor and stirring continued for a further 20 minutes. Swatches were rinsed and hydroextracted. One swatch was flat dried at 80°C.

(ii) One of the swatches was dyed using a mixture of 3% Lanasol Red 2G o.w.w. and 1% Lanasol Red G o.w.w. at pH 6.0 buffered with sodium acetate and using Albegal B as levelling agent.

b). Two of the swatches from a) (i) were treated with 8% Polymer PKS as in Example 11b). One of the swatches was dyed as in Example 13a) (ii).

c). (i) Four of the swatches from a) (i) were treated with 0.3% Proteinase D as in Example 11c). One of the swatches was dyed as in Example 13a) (ii).

(ii) Two of the swatches from c) (i) were treated with 8% Polymer PKS as in Example 11b). One of the swatches was dyed as in Example 13a) (ii).

Effectiveness of treatments applied in Example 13 was measured by washing test method TM31. Results as follows:-

Application	Test Method TM31 % Area Shrinkage after:-	
	5A	2 x 5A
1. Example 12a)		
(i) 3% DCC, undyed	-32.7	-52.4
(ii)3% DCC, dyed	-24.6	-40.6
2. Example 12b)		
3% DCC, followed by 8% PKS undyed	- 5.5	-13.9
3% DCC, followed by 8% PKS dyed	-10.6	-20.9
3. Example 13c)		
(i) 3% DCC followed by 0.3% Proteinase D, undyed	- 9.7	-22.5
3% DCC followed by 0.3% Proteinase D, dyed	-14.2	-27.5
(ii) 3% DCC followed by 0.3% Proteinase D, then 8% Polymer PKS, undyed	- 2.2	- 1.5
3% DCC followed by 0.3% Proteinase D, then 8% Polymer PKS, dyed	- 2.4	- 2.1

Example 14

In all the previous examples (Examples 1 to 13) treatments were carried out on 2/24's Botany swatches as the substrate. In this example treatments were carried out on 2/16's woollen spun lambswool knitted to a cover factor of 1.12 direct tex. The lambswool swatches were scoured at a 30:1 liquor to wool ratio using 6% Dylachem Millscour XBN (non ionic scouring agent, Precision Processes (Textiles) Ltd.) o.w.w. at 45°C for 10 minutes in the first bath. A second scour was carried out in a fresh bath containing 3% Millscour XBN o.w.w. at 45°C for 15 minutes. Then the swatches were thoroughly rinsed.

a). A combination of 2% active chlorine o.w.w. from sodium hypochlorite and 2% potassium permanganate o.w.w. was applied to four knitted swatches as in Example 11a).

b). One swatch from a) was treated with 8% Polymer PKS as in Example 11b).

c). (i) Two of the swatches from a) were treated with 0.3% Proteinase D as in Example 11c).

(ii) One of the swatches from b) (i) was treated with 8% Polymer PKS according to the procedure given in Example 11b).

d). (i) Two of the lambswool scoured swatches were stirred in a water bath containing 0.3% Proteinase D o.w.w. and 15% sodium bisulphite o.w.w. at pH 6.8 for 60 minutes. After rinsing the swatches a combination of 2% active chlorine o.w.w. from sodium hypochlorite and 2% potassium permanganate o.w.w. was applied as in Example 11a).

(ii) One swatch from d(i) was treated with 8% Polymer PKS as in Example 11b).

Effectiveness of treatments applied in Example 14 was measured by washing test method TM31.

Results as follows:-

Application	Test Method TM31 % Area Shrinkage after:-									
	5A	2 x 5A	3 x 5A	4 x 5A	5 x 5A	6 x 5A	7 x 5A	8 x 5A	9 x 5A	10 x 5A
1. Example 14a)										
2% available chlorine/2% $KMnO_4$	- 1.0	- 7.2	-14.5	-19.6	-	-	-	-	-	-
2. Example 14b)										
(i) 2% available chlorine/2% $KMnO_4$ followed by 8% Polymer PKS	- 0.6	- 4.2	- 7.3	- 9.8	-13.2	-18.2				
3. Example 14c)										
(i) 2% available chlorine/2% $KMnO_4$ followed by 0.3% Proteinase D	+ 3.6	+ 0.9	+ 6.3	+ 4.2	+ 3.5	+ 2.6	- 1.7	+ 0.1	- 0.1	- 0.9
(ii) as for (i) then 8% Polymer PKS	- 0.3	- 0.3	- 1.7	+ 0.9	+ 0.6	+ 0.7	- 4.3	- 1.2	- 2.3	- 3.4
4. Example 14d)										
(i) 0.3% Proteinase D followed by 2% available chlorine/2% $KMnO_4$	+ 5.2	+ 2.1	+ 1.8	+ 1.7	- 0.2	+ 0.2	- 4.8	- 6.2	- 7.2	-
(ii) as for 14d) (i) then 8% Polymer PKS	+ 3.0	- 1.3	+ 0.5	0	- 1.2	- 3.0	- 7.3	- 9.2	-11.6	-
5. Scour only no treatment	-27.4	-	-	-	-	-	-	-	-	-

Example 15

In this example 70's quality dry combed wool top was the substrate.

a). The top was packed in ball form in a loose stock finishing machine. 0.5 ml l^{-1} Dylan Fullwet and 5% calcium chloride o.w.w. was added (liquor volume to wool weight ratio was 15:1) and pumped through the top for 10 minutes. 2% potassium permanganate o.w.w. (predissolved in water) and 2% available chlorine o.w.w. from sodium hypochlorite was added. After 20 minutes the oxidising agents had exhausted onto the wool. A fresh bath was prepared and the wool cleared by treating with 3gl^{-1} of sodium bisulphite and 3 ml l^{-1} of formic acid at 40°C for 15 minutes. The top was rinsed twice. 8% Polymer PKS was applied at pH 8.0.

b). A ball of top was treated with 2% potassium permanganate o.w.w. and 2% available chlorine from sodium hypochlorite o.w.w. as in Example a). However, in this instance the top was treated with 0.3% Proteinase D, 15% sodium bisulphite at pH 6.8 for 60 minutes, rinsed twice then treated with 8% Polymer PKS at pH 8.0.

The treated tops were hydroextracted, dried, gilled and spun to 2/24's worsted count then knitted to a cover factor of 1.29 direct tex.

Effectiveness of treatments applied in Example 15 was measured on the knitted swatches by washing test method TM31. Results were as follows:-

Application	Test Method TM31 % Area Shrinkage after:-
	2 x 5A
1. Example 15	
a). 2% available chlorine/2% $KMnO_4$ followed by 8% Polymer PKS	-30.3
b). 2% available chlorine/2% $KMnO_4$ followed by 0.3% Proteinase D then 8% Polymer PKS	-3.6

Example 16

a). (i) 70's quality dry combed top was treated with chlorine by continuously padding a solution containing 0.5% available chlorine o.w.w. at pH 2.5 onto the wool top and passing continuously through an antichlor bowl containing sodium sulphite, then through two rinse bowls. A portion of the top was dried by passing through a suction drum dryer then gilled, spun to 2/24's worsted count and knitted to a cover factor of 1.29 direct tex.

(ii) After rinsing and before drying a portion of the top treated in a) (i) was passed continuously through a bowl containing Polymer PKS (pH 8.0) so as to give a pick-up of 8% (2% solids) Polymer PKS o.w.w. The top was then dried and converted to knitted fabric as in a) (i).

b). (i) Two knitted swatches from a) (i) were treated with 0.3% Proteinase D as in Example 11c).

(ii) One swatch from b) (i) was treated with 8% Polymer PKS according to Example 11b).

c). A knitted swatch from a) (ii) was treated with 0.3% Proteinase D as in Example 11c).

Effectiveness of treatments applied in Example 16 was measured by washing test method TM31. Results as follows:-

Application	Test Method TM31 % Area Shrinkage after:-
	2 x 5A
1. Example 16a)	
(i) 0.5% available chlorine (*continuous)	-37.8
(ii) 0.5% available chlorine followed by 8% Polymer PKS (continuous)	-16.9
2. Example 16b)	
(i) 0.5% available chlorine (continuous) followed by 0.3% Proteinase D (*batch)	- 7.3
(ii) as for (i) then 8% Polymer PKS (batch)	- 5.7
3. Example 16c)	
0.5% available chlorine (continuous) followed by 8% Polymer PKS (continuous) then 0.3% Proteinase D (batch).	- 8.8

* "Batch" and "continuous" refer to type of treatment system. In this context "continuous" refers to the continuous treatment of top on a backwasher range while "batch" refers to treatment of knitted swatches in a water bath.

Claims

1. A method for the treatment of wool so as to impart shrink resistance comprising, in any order, the steps of:-

i) treating the wool with a proteolytic enzyme, and

ii) subjecting the wool to either or both of an oxidative treatment and treatment with a polymer,

with the proviso that when the oxidative treatment is used alone it comprises a wet chlorination process.

2. A method as claimed in claim 1, wherein the proteolytic enzyme is Proteinase D.

3. A method as claimed in claim 1 or claim 2, wherein the treatment with the proteolytic enzyme is carried out in a bath containing from 0.05 to 30% on weight of the wool of a mixture of sodium bisulphite and sodium sulphite.

4. A method as claimed in claim 3, wherein the bath contains from 10 to 20% on weight of the wool of a

mixture of sodium bisulphite and sodium sulphite.

5. A method as claimed in any of the preceding claims, wherein the proteolytic enzyme is used at a level of from 0.01 to 1.0% of the weight of the wool.

6. A method as claimed in claim 5, wherein the proteolytic enzyme is used at a level of from 0.02 to 0.5% of the weight of the wool.

7. A method as claimed in any of the preceding claims, and which comprises subjecting the wool to both an oxidative treatment and a polymer treatment in addition to the treatment with a proteolytic enzyme.

8. A method as claimed in any of the preceding claims, and which comprises subjecting the wool to an oxidative treatment followed by treatment with a proteolytic enzyme and then treatment with a polymer.

9. A method as claimed in any of the preceding claims,wherein the oxidative treatment comprises the use of hypochlorite and potassium permanganate.

10. A method as claimed in any of the preceding claims, wherein the polymer treatment comprises the use of a polyamide-epichlorohydrin resin.

11. A method as claimed in any of the preceding claims, wherein the polymer treatment comprises the use of Polymer PKS.

12. A method as claimed in any of the preceding claims and which is carried out as a batch treatment.