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## PROCESS FOR THE CHLORINATION OF WOOL

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This invention relates to improved processes for chlorinating wool.

An object of this invention is to provide a process capable of controlling the character and extent of the physical and chemical change of the wool, thus rendering it the unshrinkable character.

A further object of this invention is to minimize the so-called yellowing of the chlorinated wool.

Another object of this invention is to obtain the improved uniformity in the chlorination of wool.

A still further object of this invention is to protect the wool from the reduction of its softness and touch.

Still another object of this invention is to minimize the alkali and acid solubilities of wool.

Said objects and other objects of this invention have been attained by the process which comprises passing the wool to be treated through an acidic bath having a pH between 1 and 3 for a short time such as 10–50 seconds so that the wool fibers may be made acidic in such a degree as to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool into a chlorinating bath and transferring it therethrough; and pouring a dilute aqueous solution of hypochlorite having a pH between 11 and 6 on said pretreated wool at its position being introduced into the chlorinating bath so that the chlorinating bath having a pH of 1–4 may be established by instantaneous reaction of the poured liquor with the acid liberated from the wool fibers. The preferable quantity of the pouring chlorination liquor is about 10 to 25 times the dry weight of the wool under charging and the preferable quantity of the liquor in the chlorinating bath is about 10–25 times the weight of the wool immersed in the chlorinating bath.

In the well-known conventional processes for the chlorination of wool and more particularly in the Scholler process, is adopted the process which comprises subjecting the wool to be treated, after dipping thereof in an acidic bath for a long period of time such as about 20 minutes, to an intermediate treatment for removing the excess amount of the acid to moderate the acidity in the interior regions of the wool fibers to a degree suitable for the following step; and then subjecting said intermediately treated wool fibers to chlorination by bringing said fibers in contact with an alkaline chlorinating bath containing available chlorine of the combined form such as in calcium or sodium hypochlorite, thus causing the gradual and controllable chlorination of the wool by the reaction of the hypochlorous acid with the acid contained in the pretreated wool.

In the present invention, however, the preliminary acid treatment of the wool is carried out by passing continuously the wool fibers through an acidic bath of constant strength for a short time such as 10–50 seconds so that the wool fibers and particularly only the surface regions of said fibers may be made acidic in such a degree as to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; and then the thus treated wool is immediately subjected to chlorination by pouring a chlorination liquor on said wool at its position being introduced into a chlorinating bath while trans-

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ferring said wool through said bath so that the chlorinating bath having a pH of 1–4 may be continuously established.

Accordingly, this invention differs substantially from the above-mentioned conventional processes in its acid treatment and acidity of the chlorinating bath.

In the conventional processes, batch systems have been used substantially for the chlorination of wool, but the process of this invention is carried out continuously, whereby an effective improvement of wool chlorination is made possible.

Furthermore, in the conventional processes, yellowing of the treated wool is unavoidable; the chlorination is too intense to maintain the elasticity of the wool fibers in favourable condition; softness and natural touch of the wool are reduced by the degradation caused by the treatment; increase in alkali and acid solubilities of the wool due to chlorination is relatively large; decrease in dyeing affinity due to chlorination is relatively large; and the treating cost is relatively high.

According to the process of this invention, however, yellowing of the wool due to chlorination can be minimized or entirely avoided; strength, extensibility and elasticity of the wool are not unfavourably affected by the chlorination; softness and natural touch of the wool are not affected by the treatment; increase in alkali and acid solubilities of the wool due to chlorination can be minimized; fastness of the dyed colours of the chlorinated wool is hardly decreased by sun-light, washing, friction and sweat; and the treating cost is relatively low.

The process of this invention is preferably applied to the wool of sliver state, but may be applied also to the wool in the form of yarn or fabric.

In the embodiment of the process of this invention, dyeing can be carried out in any step of the manufacturing processes in wool industry, and it is of course permissible to carry out the dyeing prior to the chlorination, because variation of colour shade and decrease in the fastness of the dyed colour due to chlorination are negligible as long as the conventional dyes are used.

For the preparation of the acid bath of this invention, formic acid is preferably used, and acetic acid, oxalic acid, sulphuric acid, hydrochloric acid, phosphoric acid, boric acid, etc. may be also applied. Sometimes, any one of the anionic and non-ionic wetting agents may be preferably mixed in the acid for the uniform distribution of acid liquor on the wool fibers. Preferable pH value of the acidic bath is 1–3 and, more particularly, 1–2. It is preferable to carry out the acid treatment of the wool for such a short time that only the surface regions of the wool fibers can be made acidic and the interior regions thereof remain neutral.

As the chlorination agent in this invention, sodium hydrochlorite, calcium hypochlorite and other chlorine-liberating agents may be used, but sodium hypochlorite can be advantageously applied for conditioning pH of the chlorination liquor. The pH value of the chlorination liquor is controlled at a value between 11 and 6. This liquor is poured on the pretreated wool at its position being introduced into the chlorinating bath so that the chlorinating bath having a pH of 1–4 may be continuously established by instantaneous reaction of the poured liquor with the acid liberated from the surface regions of the wool fibers. The most preferable quantity of the chlorination liquor to be poured on the wool is about 10 to 25 times the dry weight of said wool. The quantity of the available chlorine contained in the sodium hypochlorite is controlled within the range of 1.5 to 3.0% of the dry weight of the wool under treatment in accordance with the degree of the chlorination. The above-mentioned pouring of the chlorination liquor is carried out

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continuously at one end of the chlorinating bath while charging the pretreated wool into said bath at the same end. The charged wool is continuously transferred toward the other end of said bath while completing the chlorination thereof and then led out from said bath, thus effectuating the continuous chlorination of the wool. In the process of this invention, for maintaining the pH value of the chlorinating bath at a constant value, it is extremely important to control the quantity and the pH value of the chlorination liquor to be poured, and the quantity of the available chlorine contained in the chlorinating bath and in the wool fibers. The pH value of the chlorinating bath should be maintained between 1 and 4 and the preferable time interval of the chlorinating treatment should be about 30 seconds. The wool thus chlorinated should be transferred as fast as possible into the following dechlorinating bath.

In this invention, sodium thiosulfate or acidic sodium sulfite, preferably the former, may be used as the dechlorinating agent; 4-6%, particularly 5% solution of the former; 1-3%, particularly 2% solution of the latter may be recommended as said bath.

The dechlorination can be almost completed within the period of time between 30 seconds and one minute. The preferable quantity of the dechlorination liquor is from 100 parts to 400 parts per one part of the wool under treatment, but it may be more reduced as long as it is sufficient for dipping the wool under treatment. The concentration of the dechlorinating bath should always be controlled suitably. For the washing, a large quantity of the running water is used to carry out sufficient washing and this washing should be carried out immediately after the dechlorination. Since the chlorinated wool thus washed is yet acidic, its neutralization is necessary, so that the wool washed as described above is treated with hot solution of synthetic washing agent, soap or sodium ash and then washed with hot water.

The wool thus treated by this invention receives no substantial change in physical and chemical properties of natural wool, and has no appreciable degradation such as yellowing and decrease in fastness of dyed colour, and has an excellent unshrinkable property.

#### Example I

*The first step (acidification).*—A continuous bundle of a number of top slivers is passed for a short time through an acidic bath consisting of a mixture of 2% solution of formic acid and a conventional wetting agent of  $\frac{1}{200}$  part of the weight of the formic acid, while controlling the pH value of said mixture at a value between 1.8 and 2.0. By passing said bundle of slivers through said bath for a short time between 15 and 30 seconds, the acid is uniformly combined with only the surfaces of the wool fibers, whereby it is made possible to make the combined acid liberate easily and react with the pouring liquor in the next step to prepare a favourable chlorinating bath. The quantity of the acidic bath liquor may be minimized within the range suitable for the sufficient wetting of the wool fibers.

For maintaining the quantity of the acidic bath liquor, additional portion corresponding to the loss of the liquor carried away by the wool fibers must be successively added to the bath.

*The second step (chlorinated).*—The wool which has been treated in the first step is introduced into a chlorinating bath at one end thereof and continuously transferred toward the other end of said bath and then led out from the latter end. A solution of sodium hypochlorite is continuously poured on said wool at its position being introduced into the chlorinating bath. By the action of the chlorine liberated from the chlorinating agent due to the reaction of said agent with the acid liberated from the surfaces of the wool fibers, chlorination of the wool is completed within a period of time between 20 and 40 seconds. The thus chlorinated wool led out from the

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chlorinating bath is then introduced into a dechlorinating bath in the third step. The pH value of the chlorinating bath must be maintained within the range of 1-4 and the quantity of the chlorinating agent is controlled so that the quantity of the available chlorine contained in said agent may be 1-3% of the dry weight of the wool under charging.

*The third step (dechlorination).*—The completely chlorinated wool is passed through 5% solution of sodium thiosulfate or 2% solution of anhydrous sodium sulfite to subject said wool to dechlorination to remove the nonreacted chlorine from the surfaces of the wool fibers. This treatment is carried out for a time within the range between 30 and 60 seconds. The consumed quantity of the dechlorinating agent is measured by the iodometry and supplemented now and then.

*The fourth step (neutralization and washing).*—After the dechlorination, the treated wool is subjected to neutralization and washing with water in the conventional methods.

The final wool obtained by the process of this example shows a predominant resistance to laundry shrinkage, that is to say, its washability is very high. For example, when soaking characters of two patterns of the same fabric were tested five times with 0.5% solution of soap, at a temperature of 65° C., for 30 minutes and the tested fabrics were measured by a Lavado Meter, the shrinkage of the fabric treated according to this invention was below 5%, but that of the fabric not treated was about 27%.

#### Example II

In this example, an inorganic mineral acid is used in the first step and a conventional non-ionic wetting agent is mixed in the chlorination liquor in the second step, whereby the chlorination of the wool in the chlorinating bath is made more uniform.

*The first step (acidification).*—A continuous bundle of a number of top slivers is passed through an acidic bath for a time between 20 and 30 seconds, as in the case of the Example I. In this example, an acidic bath consisting of a mixture of 1-1.5% solution of sulfuric acid and a conventional anionic wetting agent of  $\frac{1}{200}$  part of the weight of said solution is used. By passing said bundle of slivers through said bath, the surfaces of the wool fibers are made acidic uniformly within a short time between 65 and 30 seconds.

The pH value of the acidic bath may be varied somewhat depending upon the kind of the wetting agent to be mixed, but it is maintained at a value between 1 and 1.2 in this example.

Since said acidification completes within a short time between 20 and 30 seconds, chemical combination of the acid with the wool fibers hardly occurs and only the surfaces of the wool fibers are made acidic uniformly, whereby control of the pH value of the chlorinating bath in the second step is made very easy.

*The second step (chlorination).*—The sliver having been treated in the first step is introduced into a chlorinating bath at one end thereof and continuously transferred therethrough toward the other end of said bath and then led out. A chlorinating solution as illustrated already is continuously poured on the wool at its position being introduced into the chlorinating bath. By the action of the chlorine liberated from the chlorinating agent due to the reaction of said agent with the acid liberated from the surfaces of the slivers, chlorination of the wool slivers is completed during its transference through the chlorinating bath and within a period between 20 and 40 seconds. The pH value of the chlorinating bath is maintained at a value between 2 and 3. In this example, a non-ionic wetting agent of 0.01% of the weight of said bath liquor is mixed in the chlorinating agent, whereby particularly uniform chlorination of the slivers is made to occur.

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When an inorganic mineral acid is used in the first step, the liberation of chlorine gas is made very rapid as compared with the case of the Example I. Accordingly, it is preferable to add a non-ionic wetting agent in the second step to obtain an effective and uniform chlorination.

*The third step (dechlorination).*—The chlorinated wool is passed through 2% solution of sodium sulfate to subject said wool to dechlorination to remove the non-reacted chlorine from the surfaces of the wool fibers. The time for the dechlorination is preferably 30 seconds.

*The fourth step (neutralization and washing).*—This step is entirely same as the Example I.

While I have described particular embodiments of my invention, it will, of course, be understood that I do not wish my invention to be limited thereto, since many modifications may be made and I, therefore, contemplate by the appended claims to cover all such modifications as fall within the true spirit and scope of my invention.

I claim:

1. A process for the chlorination of wool which comprises passing the wool to be treated through an acidic bath having a pH between 1 and 3 for a short time of the order of 10–50 seconds so that the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of hypochlorite having a pH between 11 and 6 on said pretreated wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool.

2. A process for the chlorination of wool which comprises passing the wool to be treated through an acidic bath having a pH between 1 and 3 for a short time of the order of 10–50 seconds so that the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of hypochlorite having a pH between 11 and 6 on said pretreated wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool, the quantity of the distributed hypochlorite solution being about 10 to 25 times the dry weight of the wool being charged and the quantity of the liquor in the chlorinating bath being about 10–25 times the weight of the wool immersed in the chlorinating bath.

3. A process for the chlorinating of wool which comprises passing the wool to be treated through an acidic bath having a pH of 2 for a short time of the order of 10–50 seconds so that the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of hypochlorite having a pH between

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11 and 6 on said pretreated wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool, the quantity of the distributed hypochlorite solution being about 10 to 25 times the dry weight of the wool being charged and the quantity of the liquor in the chlorinating bath being about 10 to 25 times the weight of the wool immersed in the chlorinating bath.

4. A process for the chlorination of wool which comprises passing the wool to be treated through an acidic bath having a pH between 1 and 3 for a short time of the order of 10–50 seconds so that only the surface regions of the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of hypochlorite having a pH between 11 and 6 on said pretreated wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the surface regions of the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool, the quantity of the distributed hypochlorite being about 10 to 25 times the dry weight of the wool being charged and the quantity of the liquor in the chlorinating bath being about 10–25 times the weight of the wool immersed in the chlorinating bath.

5. A process for the chlorination of wool which comprises passing the wool to be treated through formic acid bath having a pH between 1 and 3 for a short time of the order of 10–50 seconds so that only the surface regions of the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of sodium hypochlorite containing the combined available chlorine of an amount sufficient to the chlorinating reaction and having a pH between 11 and 6 on said pretreated wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the surface regions of the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool, the quantity of the distributed hypochlorite solution being about 10 to 25 times the dry weight of the wool being charged and the quantity of the liquor in the chlorinating bath being about 10–25 times the weight of the wool immersed in the chlorinating bath.

6. A process for the chlorination of wool which comprises passing the wool to be treated through a formic acid bath having a pH between 1 and 3 for a short time of the order of 10–50 seconds so that only the surface regions of the wool fibers will be made acidic to a degree sufficient to maintain the pH value of the chlorinating bath in the following step at a value between 1 and 4; continuously introducing said pretreated wool without intervening chemical treatment into a chlorinating bath at one end thereof and transferring it therethrough toward the other end; and distributing a dilute aqueous solution of sodium hypochlorite containing the combined available chlorine of 1.5 to 3%, by weight, of said solution and having a pH between 11 and 6 on said pretreated

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wool as it is being introduced into the chlorinating bath so that a pH of 1 to 4 will be established in the chlorinating bath by instantaneous reaction of the distributed hypochlorite solution with the acid liberated from the surface regions of the wool fibers, whereby said chlorinating bath in which said wool is immersed has a pH of 1 to 4 throughout the chlorination of said wool, the quantity of the distributed hypochlorite solution being about 10 to 25 times the dry weight of the wool being charged and the quantity of the liquor in the chlorinating bath being about 10-25 times the weight of the wool immersed in the chlorinating bath.

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