ABSTRACT OF THE DISCLOSURE

Wool is heated at 120–150 °F. for less than 15 minutes in an aqueous dispersion of 0.1–2 percent calcium hydroxide, washed and acidified to render it more receptive to dyestuffs without adversely affecting the physical properties of the wool.

This invention relates to the treatment of wool, more particularly to the treatment of wool to increase its affinity to hydrophobic dyestuffs and to dyeing processes comprising such treatment. This application is a continuation-in-part of application Ser. No. 219,730, filed Aug. 27, 1962.

The wool fiber is relatively resistant to dyeing with the complex, e.g., premetallized, and the hydrophobic dyestuffs, i.e., those containing one or more highly polar groups, e.g., sulfonic acid groups. The epicuticle appears to act as a barrier to such dyestuffs. Also, retarding agents used to obtain more level dyings or novel multicolor dyings, such as the formaldehyde-naphthalene sulfonic acid condensation products, increase the natural resistance of the wool fiber to dyeing with such dyestuffs. The result is poor dyestuff exhaustions, even with prolonged high temperature dyings which are damaging to the fibers.

It is known that treatments which damage or remove the epicuticle of the wool, e.g., chlorination and treatment with strong alkali, renders the wool fiber more receptive to hydrophobic and/or complex dyestuffs. However, for the most part, the dyeing trade prefers to use hydrophobic dyestuffs or dyestuffs of relatively low hydrophilicity or accept the long dyeing times and poor dyestuff exhausts associated with the use of highly hydrophobic dyestuffs rather than the wool fiber of strength, elongation, and hand and increased expense associated with these damaging pre-treatments. Also, some such pre-treatments, such as dry chlorination, require equipment not possessed by many dyers which necessitates obtaining the treated wool from special sources at considerably added trouble and expense. Also, other treatments require special knowledge and experience to achieve commercially acceptable results.

The present invention is a non-damaging inexpensive, low temperature aqueous treatment of wool which increases the affinity of the wool fiber to hydrophobic and complex dyestuffs and which can readily be performed by any dyer using conventional dyeing equipment.

According to this invention, wool is heated in the presence of a uniform aqueous dispersion of an alkaline earth hydroxide under conditions which are substantially non-damaging to the wool at the selected alkaline pH in the absence of the alkaline earth hydroxide.

It is known the treatment of wool under alkaline conditions can increase its affinity for hydrophobic dyestuffs due to damage to the wool fiber, e.g., by scale removal. See Kienle, et al., American Dyestuff Reporter, Jan. 29, 1938, p. 145; Ibid, Sept. 10, 1945, p. 359; Speaman et al., J.S.D.C., November 1938. Because of the highly adverse effect upon hand, tensile and elongation associated with an alkaline treatment of wool which significantly improves its dyeability with hydrophilic dyestuffs, such alkaline treatments are not generally practiced.

If the alkaline treatment is performed under milder conditions, which do not substantially adversely affect the properties of the wool fiber, e.g., those employed in conventional degreasing treatments of raw wool stock, the increased dyestuff reactivity is marginal at most. Therefore, a non-damaging alkaline wool treatment which significantly improves dyestuff reactivity is not known.

It is now possible to achieve the spectacularly increased dyestuff reactivity heretofore associated with a damaging alkaline treatment of wool under conditions which do not materially adversely affect the properties of the wool fiber.

A non-damaging alkali treatment of wool which materially increases the dyestuff affinity of the wool fiber can be achieved by treating the wool with a uniform aqueous dispersion of an alkaline earth hydroxide at a pH above 9.5, preferably above 10.5, e.g., from 11 to 12.5, but ordinarily below about 13, under relatively mild conditions of time and temperature.

The fact that no substantial damage has taken place as a result of treatment can be determined by a microscopic examination of the fibers, which will show the scale structure is retained in a substantially undamaged condition, and by tests for dry tensile and elongation, which properties should not be significantly lowered, i.e., at least 90 percent of the properties of corresponding untreated wool. Further indirect proof that no significant damage has taken place can be found in the fact that the wool, if undamaged, behaves substantially the same as normal wool, e.g., in felting shrinkage tests.

The treating compounds of the process of this invention are alkaline earth hydroxides, e.g., the hydroxides of the Group II–A elements of an atomic number from 12 to 18, preferably calcium hydroxide, barium hydroxide and magnesium hydroxide, in that order of preference. The hydroxide can be used as such or formed in situ by the use of a salt of a Group II–A element which at least partially decomposes at a pH above 9.5 to form the alkaline earth hydroxide in situ. For example, the wool can be wet out with the solution of the selected salt and the pH gradually raised at the selected treatment temperature.

Because of the limited water solubility of the alkaline earth hydroxides, it is important the aqueous dispersion of the hydroxide is uniform. Uneven distribution of the alkaline earth hydroxide throughout the wool, as determined results in non-uniform increased reactivity to hydrophobic dyestuffs, which will tend to result in uneven dyes. Therefore, when using the hydroxide dispersed in an aqueous liquor, vigorous agitation of the wool and/or rapid bath circulation are important. Also, hydroxides of fine particle size should be employed.

The amount of hydroxide used is not critical over a wide range. Generally a 0.1 to 2 percent aqueous dispersion is used, i.e., about 5 to 500 percent, calculated on the weight of the wool. Because of the high alkaline content, addition of a reducing agent is necessary. The temperature at which dyeing is to be done is not critical under these conditions, however, a temperature of about 110°F is preferred. When short reaction times are employed, e.g., a few seconds to 5 minutes, somewhat higher temperatures are sometimes required.
With finer grades of wool, e.g., 64's quality or better, about 120° F. to 140° F. is the preferred temperature range. With the coarser grade wools, e.g., 36's or less, a somewhat higher range, e.g., about 130 to 150° F., is preferred. Ordinarily, a temperature below about 180° F., and preferably below 160° F., should be used to avoid fiber damage.

A means for determining the maximum time which can be employed at the selected reaction temperature is to treat samples of wool for various periods of time, at the above alkaline earth hydroxide, at the pH at which the treatment is to be performed and then by appropriate tests to determine the time at that pH when significant loss of properties begins. The optimum reaction time will be somewhat less than the time at that temperature and pH when such damage begins. A water soluble base, e.g., sodium hydroxide, can be used to provide the requisite pH for the test.

The minimum time required to substantially increase the affinity of the wool fiber to hydrophobic dyestuffs is, within the pH range of 9.5 and 13, determined primarily by reaction temperature. If the pH of the treatment bath is that provided by the alkaline earth hydroxide, at 120° F., usually a treatment time of at least 7 minutes is required; at 140° F., at least 4 minutes; and at 160° F., at least one minute. If the pH is to be higher than that provided by the alkaline earth hydroxide, e.g., by adjusting it upward with sodium carbonate or sodium bicarbonate, correspondingly shorter reaction times will be necessary. At a pH from 9.5 to 13, preferably at the pH provided by the alkaline earth hydroxide, and at a temperature within the preferred range of 120 to 150° F., preferably 130 to 140° F., a treatment time between 2 and 5 minutes ordinarily is employed, preferably less than 10 minutes, e.g., 5 to 10 minutes, to ensure no substantial damage to the fiber.

Unless shorter reaction times or lower reaction temperatures are desired, the preferred pH is that provided by the alkaline earth hydroxide. However, any pH above 9.5, but preferably below 13, is operable and can be obtained with added alkali-metal hydroxide or basic salt thereof, e.g., Na₂SO₄, Na₃PO₄, Na₂CO₃, NaBO₃. Preferably, a pH from 10.5 to 12 is employed.

The wool can be treated in raw stock, top, roving yarn, fabric, cloth and carpet form. Advantageously, the treatment can be incorporated into the alkaline scour of raw wool stock conventionally used to remove the wool fats. Highly desirable results are obtained with top as the alkaline earth hydroxide can readily be uniformly distributed throughout and then washed out of the top.

A convenient means of treating the wool involves adding the wool fibers in stock or top form to an aqueous solution or dispersion of the selected alkaline earth compound at the desired temperature, maintaining the wool in the solution for the selected time with sufficient agitation and/or liquor flow to ensure uniform distribution of the liquor amongst the fibers and uniform dispersion of the alkaline earth compound, removing the treating liquor, and then promptly thereafter cooling, washing, and acid scouring the fibers to insure the reaction is terminated and substantially all the alkaline earth compound is removed. The fibers can then be dried by conventional means and, if desired, tinted with a fugitive tint for identification purposes, and treated with lubricating oils and anti-static agents so as to be in proper condition for future processing.

Another convenient method involves applying the alkaline earth hydroxide to the top, yarn, fabric or cloth as a viscous uniform emulsion or suspension, e.g., calcium hydroxide and British gum paste, using conventional techniques, e.g., with a Vireuxmex machine, followed by drying so that the fibers are heated to 140-160° F. for several minutes. This is a useful technique for treating carpet to obtain multicolored dyings as described below. The dispersion can be applied uniformly or as a random or predetermined pattern, if novel dyeing effects are desired.

Using wool pretreated with alkaline earth hydroxide in the manner described herein, it is possible at the same dyeing temperature to obtain higher and usually complete dyestuff exhaustion of hydrophobic and complex dyestuffs which normally do not exhaust or do so with great difficulty. This means darker shades can be obtained and/or less fiber damage because of shorter dyeing times. Solid shades can be obtained with polysulfonic acid dyestuffs which heretofore could not be used on wool because they produced a skittery, non-solid shade. With hydrophobic dyestuffs which normally exhausted well at the boil, it is now possible to achieve complete exhaustion at temperatures well below the boil, e.g., 160-180° F. or lower, which means less fiber damage. Whole new classes of dyestuffs which heretofore could not generally be used with wool, especially the polysulfonic acid dyestuffs, now can be used to produce excellent dyings on wool.

The alkaline earth hydroxide treatment can be incorporated into the dyeing process and made an integral part thereof by adding the wool to an aqueous dispersion of the alkaline earth hydroxide, bringing the bath to treatment temperature for the selected time, rinsing thoroughly with water below the treatment temperature, and bringing to a mildly aci d pH with the acid used for the dyeing and then dyeing in the conventional manner, usually with appropriate shortening of dyeing time and/or lowering of dyeing temperature.

With the wool treatment process of this invention, it is also possible to achieve sharply contrasting novel multicolor and color and white dyed effects on wool in yarn, either before or after forming into fabric and piece form, in a single dye bath by dyeing wool yarns consisting essentially of a mixture of normal wool, i.e., wool not chemically modified to alter its dye receptivity, and wool pretreated with an alkaline earth hydroxide as described herein, in a single dye bath containing a water-soluble condensation product, a suitable acid and a polysulfonic acid dyestuff and preferably also a dyestuff containing less than a total of 2 sulfonic acid and reactive groups, all as defined hereinafter.

To obtain the novel dyeing effects, the treated wool is blended or otherwise combined with normal wool, i.e., wool which has not been chemically modified to alter its dyestuff affinity, prior to dyeing, using conventional techniques. For example, the two types of wools can be in the form of separate ends of a plied yarn, or blended and spun out of the top to achieve best effects, the normal and treated wool each constitute at least 25 percent and preferably at least 35 percent of the mixture. The mixture is then dyed in an aqueous dye bath containing a dyestuff containing at least 2 sulfonic acid groups; and an amount greater than 0.05 percent, calculated on the weight of the wool, insufficient to reserve the dyestuff, of a water-soluble condensation product of an aryl sulfonic acid and an aldehyde, at an initial dye bath pH in the presence of the wool of less than 5.9. Preferably, the dye bath additionally contains a dyestuff containing a total of less than 2 sulfonic acid and reactive groups. The polysulfonic acid dyestuffs contain at least 2 sulfonic acid groups, but preferably 3 or more, e.g., 4, 5 or 6 such groups. The term "sulfonic acid group" excludes those groups in which the sulfonic group is in the form of an inner salt with a basic group. These dyestuffs can additionally contain reactive groups, e.g., vinyl sulfone or cyanuric chloride groups, are referred to in the dyeing art as "reactive" dyestuffs. Desirably, the sum of the sulfonic acid groups and reactive groups is at least 3 or 4. Included in the dyestuffs containing 2 or more sulfonic acid groups are those referred to in the dyeing art as acid dyestuffs, milling dyestuffs, direct dyestuffs, cotton dyestuffs and cotton reactive dyestuffs.
stuffs. These dyestuffs are ordinarily supplied commercially in the form of their sodium salts.

The condensation products employed to achieve multicolor dyeings are generally known as "rearing" or "levelling" agents. They are characterized chemically as condensation products of aryl, usually carboxyclic, sulfonic acids and an aldonate. The term "aldonate" as used herein means an aldehydic or ketonic carbonyl compound, e.g., formaldehyde, acetaldehyde, benzaldehyde, benzoin, acetone, etc. These are a well-known and commonly employed class of compounds in the dyeing art. They each possess a sulfonic acid substituted aryl group in the molecule and at least 1 additional acidic group, e.g., phenolic, carboxylic or sulfonic. Compounds within this definition are mono, di, or trisulfonic acid substituted benzene or naphthalene which can further be substituted with lower-alkyl, hydroxy, nitro, amino, etc., groups, and which have been condensed with an aldonate as described above to produce a dimer, trimer or polymer linked by the aldonate by a reaction well known in the art. Compounds such as dihydroxy-diphenyl sulfone can also be incorporated in the condensation reaction to produce a mixed condensation product. See U.S. 2,625,806. These compounds include the condensation products of naphthalene-2,7-disulfonic acid and formaldehyde and the alkali-metal-salts thereof. Others include the condensation products of phenol or cresol sulfonic acid and formaldehyde and the corresponding alkali-metal salts thereof. Still others include the condensation products of phenol, cresol, or naphthalene sulfonic acid and benzoin or acetone and their alkali-metal salts. These condensation products preferably are also included in the solid shade dyeing described herein.

Specific examples of such condensation products are

dinaphthylmethanesulfonic acid,
diphenylmethanesulfonic acid,
dihydroxynaphthylmethanesulfonic acid,
dioxynaphthylmethanesulfonic acid,
dinaphthylmethanesulfonic acid,
dichloronaphthylmethanesulfonic acid,
diaminonaphthylmethanesulfonic acid,
diphenylmethane-2,7,2',7'-tetralsulfonic acid and the sodium salts of each.

The amount of aryl sulfonic acid-aldonate condensation product employed in the dyebath is at least 0.5 percent, calculated on the weight of the wool, but less than the amount which will reserve the dyestuff employed. An amount between about 1 percent and 5 percent is the usual range.

As in conventional acid dyeings, the dyebath will contain an organic or inorganic acid conventionally used in the dyeing art, e.g., acetic acid, formic acid, hydrochloric acid, sulfuric acid, phosphoric acid, lactic acid, citric acid or other strong acid which will provide an initial pH to the dyebath in the presence of the wool of less than 5, e.g., between about 2.8 and 4.9, preferably below about 4.5. If desired, the pH can be varied during the dyeing by employing ammonium sulfate or phosphate and then permit the pH to drift lower during dyeing. The amount of acid to be employed will depend upon the affinity of the dyestuff or dyestuffs employed in the dyeing to the wool in the presence of the condensation product as defined herein. Also, to enhance exhaustion of the dyestuff, additional amounts of acid can be added during the dyeing, according to techniques well known in the art.

The usual dyestuff additives, e.g., Glauber’s salt or other materials used as leveling agents or nonionic wetting agents, may be added to the dyebath to facilitate the dyeing process. However, as with other dyeings, such additives may alter somewhat the results obtained. For example, cationics should be avoided and it is preferred to keep these other additives to a minimum.

A striking effect can be obtained when the dyebath contains both a polysulfonic acid dyestuff and one containing less than 2 sulfonic acid and reactive groups, particularly if an amount of the polysulfonic acid dyestuff is used which will be readily absorbed by the alkaline earth hydroxide treated portion of the wool yarn, and if an amount of another dyestuff of a distinctly different color and containing less than 2 sulfonic acid and reactive groups is employed which will be readily absorbed by the normal wool.

If desired, the combined wool can, prior to dyeing, be given a pretreatment with acid and formaldelyde or paraformaldehyde or with a sulfonic acid condensation product as described herein in the presence or absence of acetic, formic, hydrochloric or like acid and/or formaldehyde or parafomaldehyde, to enhance the subsequent dyeing effect obtained.

For a further description of the techniques which ought to be employed, see U.S. 2,999,731 and British 680,862. The following is illustrative of the process of this invention and is not to be construed as limiting.

EXAMPLE I

(a) To a 0.3 percent aqueous dispersion of calcium hydroxide heated at 140° F. add an amount of New Zealand 44%-50’s carpet quality wool fibers which will provide a liquor to wool ratio of at least 10:1 and preferably at least 20:1, e.g., 100:1 or greater. The solution desirably contains a wetting agent, e.g., Mercurial 3.3, Tergitol NPX, nonionic wetting agents. Maintain the wool in the solution for about 2 to 10 minutes at the selected temperature while providing sufficient agitation of the wool and/or aqueous solution to ensure a uniform treatment. Remove the wool after the selected time of reaction and immediately wash the wool thoroughly, including an acid scour. Dry the wool in the conventional manner. Microscopic examination of the fibers can be used to determine the maximum reaction time which may be used, along with tensile and elongation tests.

(b) The increased affinity of the treated wool for hydrophilic dyestuffs can be demonstrated by dyeing the thus treated wool in fiber form in the presence of comparable normal wool.

(c) Dye the above treated wool in the presence of an equal weight of normal wool fibers at 200° F. for thirty minutes using 2 percent formic acid, 2 percent Synwool S.N., a formaldelyde-naphthalene sulfonic acid condensation product, and 0.5 percent Procion Black HG, a cotton reactive dyestuff containing at least 2 sulfonic acid groups, followed by boiling for 15 minutes in the presence of an additional 1 percent each of Synwool S.N. and formic acid, all amounts calculated on the weight of the wool. In each instance, the pretreated wool fibers are dyed substantially darker than the untreated wool fibers.

EXAMPLE II

(a) Follow the procedure of Example I, treating 20 lb. top pre-scoured with a non-ionic detergent and rinsed, in a top dyeing machine with a 0.3 percent dispersion of aqueous calcium hydroxide (standard U.S. Grade Gypsum) at a 30:1 liquor ratio at 137° F. with circulating liquor for 7 minutes. Rinse several times with 140° F. water followed by an acid-acid rinse to bring the pH of the top to 5.5.

The thus treated wool can readily be dyed to exhaustion below the boil with dyestuffs which with normal wool do not exhaust or require long dyeing at the boil or above excessively damaging to the fiber. The following dyeing illustrates this ability.

(b) To the above described acetic acid liquor and top at pH 5.5 was added, calculated on the top, 0.5 percent each Tannosol D dimethylamino sulfonic acid and Cibalan Black B.G.L., a premetallized dye containing less than 2 sulfonic acid groups. The temperature of the circulating liquor was raised to 150° F. for 20 minutes and
then to 160°F. for an additional 30 minutes. The dyeing was complete and comparable in light fastness, etc., to conventional ones at the boil.

The following illustrate methods for obtaining color and white and multicolor effects.

(c) In a dyebath with about a 20:1 liquor ratio containing 1.3 percent Cibacon Brown BR (a polysulfonic acid dyestuff), 0.5 percent Anthraquinone Blue SWF (a sulfonic acid dyestuff), 2 percent Tamol SN (a naphthalene sulfonic acid-formaldehyde condensation product), and 2 percent of acetic acid, calculated on the weight of the wool, the dyebath having an initial pH of about 4 in the pretreated wool, dye wool singles yarn of about 62-64's quality consisting of a blend of about 50 percent normal wool fibers and 50 percent of wool fibers treated according to the procedure of Example II(a) before blending with the normal wool. Bring the solution to the boil in 45 minutes and dye at the boil for one hour or until exhaustion. A sharply contrasting bright blue and orange-brown stock dyed effect is obtained with the alkaline pretreated wool fibers being dyed blue with flecks of brown and the normal wool fibers being dyed orange-brown with an undertone of light blue.

If the yarn is in the form of a 2-ply yarn with one end consisting entirely of the wool fibers treated according to the procedure of Example II and the other end consisting entirely of normal wool fibers, a novelty effect is obtained with a predominantly blue end spiraling around a predominantly orange-brown end.

The same stock dyed and novelty spiral effects are obtained when such yarns are knitted or woven into fabric before dyeing.

If the arylsulfonic acid-formaldehyde condensation product is omitted from the above dyeings, a faint two-tone effect is obtained which is distinctly different from the highly contrasting effect obtained in the presence of the condensation product.

(d) Substantially the same dyeing effect is obtained as in Example II(c) using as the pretreated wool portion, fibers treated in the manner described in Example II(a) with an aqueous solution containing 5 percent CaCl₂, 5 percent Na₂CO₃ and 2 percent Na₂S at 140°F. for 5 minutes.

(e) Follow the procedure of Example II(d) using carpet woven from 2-ply yarn, one end of which consists of 66% New Zealand carpet quality wool and one of which consists of 44-48's New Zealand wool which has been treated for 5 minutes at 140°F. at pH 12 according to the procedure of Example II(a). Dye in a carpet piece dyeing machine with constant rotation of the carpet in open width form through the liquor. Bring to the boil in 45 minutes and dye at the boil until substantial exhaustion of the dyestuff is achieved.

The carpet is dyed a brilliant two-color effect caused by the spiraling of the plies of the yarn, one color being a bright blue on the normal wool and the other an orange-brown with a bluish tone on the alkaline-pretreated wool.

(f) Dye fabric knit from singles yarn, formed of a 50:50 mixture of 64's quality normal wool and 64's quality wool treated with calcium hydroxide according to the procedure of Example II(a), in a dyebath containing the following ingredients, the percentages being calculated on the weight of the wool:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrazol Red 7 BSW (a 6 sulfonic acid dyestuff)</td>
<td>1.35</td>
</tr>
<tr>
<td>Anthraquinone Blue SWF (a sulfonic acid dyestuff)</td>
<td>0.25</td>
</tr>
<tr>
<td>Tamol SN (a naphthalene sulfonic acid-formaldehyde condensation product)</td>
<td>2</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>3</td>
</tr>
<tr>
<td>Paraformaldehyde</td>
<td>1</td>
</tr>
</tbody>
</table>

The initial dyebath pH is below 4. Dye in the manner described above. A striking burgundy mixed with reddish blue stock dyed effect is obtained. If the yarn is 2 ply with one end normal and the other end alkaline-pretreated wool, the normal wool end is dyed a bright blue tinged with red and the pretreated wool end is dyed a burgundy. If the Tamol SN is omitted a substantially solid reddish purple shade is obtained.

Example III

Follow the procedure of Example I using a 1 percent dispersion of calcium hydroxide in water, with the solution brought to a pH above 11, if desired, with some sodium hydroxide. At pH 11, heat to about 120°F. for about 5 minutes or less for the fine grade woods and at about 140°F. for 5 minutes or less for lower grade qualities of wool. In the absence of strong base, heat between 4 and 10 minutes.

Following the above procedure, using barium hydroxide at a concentration between 0.1 and 1 percent. Similarly, magnesium hydroxide can be used but the optimum treating temperature is about 10°F. or more, higher than for calcium and barium hydroxide.

Example IV

(a) Follow the procedure of Example III, solubilizing the calcium hydroxide with sufficient sucrose to provide a 10 percent solution, heating at 140°F. for 5 minutes at a pH of about 11. Substantially the same results are obtained when the wool is heated from about 2 to 15 minutes, but damage begins to occur at longer heating times.

(b) Form a 2 ply yarn of 64's quality normal wool blended in about a 30:70 mixture with 64's quality wool treated with calcium hydroxide in the above-described manner.

Dye the yarn in a dyebath at about a 20:1 liquor ratio containing the following ingredients, the percentages being calculated on the weight of the wool:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procian Orange G (a polysulfonic acid dyestuff)</td>
<td>0.14</td>
</tr>
<tr>
<td>Anthraquinone Blue SWF (a sulfonic acid dyestuff)</td>
<td>0.2</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>3</td>
</tr>
<tr>
<td>Tamol SN (a naphthalene sulfonic acid-formaldehyde condensation product)</td>
<td>1</td>
</tr>
<tr>
<td>Paraformaldehyde</td>
<td>1</td>
</tr>
</tbody>
</table>

The dyebath has an initial pH below 4 in the presence of the wool. Bring to the boil in about 45 minutes and dye at the boil to dye bath exhaustion. A stock dyed effect of a bright light blue mixed with a bluish orange is obtained. If the yarn consists of one end of normal wool and one end of alkaline-pretreated wool, a spiral effect is obtained with the normal wool end being dyed a light blue and the pretreated wool end being an orange with a bluish tint.

If the Tamol SN is omitted, an overall blue effect tinged with orange is obtained in the case of the blended yarn and a slight two-tone effect is obtained in the case of normal wool end plied with the alkaline pretreated wool end.

(c) Follow the procedure of Example II(e), dyeing woven carpet formed of the 2-ply yarn prepared as described in Example IV(b) in a dyebath containing the following ingredients, the percentages being calculated on the weight of the wool:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cibacon Brilliant Blue BR (a polysulfonic acid reactive dyestuff)</td>
<td>1.35</td>
</tr>
<tr>
<td>Xylene Yellow 2GP (1-sulfonic acid dyestuff)</td>
<td>0.3</td>
</tr>
<tr>
<td>Tannsol D (the acid form of a naphthalene sulfonic acid formaldehyde condensation product)</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5</td>
</tr>
</tbody>
</table>

The initial dyebath pH is less than 5.4 in the presence of the wool. Dye in the manner described in Example II(e). The normal wool end of the yarn is dyed a greenish yellow and the alkaline-pretreated wool end is dyed a bright blue, producing a striking 2-color effect on the carpet.
(d) Follow the procedure of Example IV(b) using a dyebath containing

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>Procian Black HG (a polysulfonic acid dyestuff)</td>
</tr>
<tr>
<td>2</td>
<td>Tamol SN (a naphthalene sulfonic acid)</td>
</tr>
<tr>
<td>2</td>
<td>Formic acid</td>
</tr>
</tbody>
</table>

The dyed yarn has a stock dyed blue-gray and white effect. The white effect can be enhanced by adding wool brighteners, preferably those containing less than 2- sulfonic acid groups, or other dyestuffs or materials with little tintoral properties which have a greater affinity for the normal wool than the calcium hydroxide pretreated wool.

**EXAMPLE V**

To a carpet woven of 44-48's quality normal wool apply a solution of 1 percent Ca(OH)₂, 10 percent sucrose and 2 percent Keltext sodium alginate by a rotating circular nylon brush which picks up the solution and then presses against a bar so as to splatter the solution onto the face of the carpet, thereby covering about one-third—one-fifth of the surface of the carpet. Steam the carpet at 212° F. for ten minutes or less, wash thoroughly, including an acid scour.

When the thus-treated carpet is dyed in a dyebath described in Example II(f) or Example IV(b), (c) or (d), speckled color and white and 2-color effects are obtained.

**EXAMPLE VI**

(a) Agitate knitted fabric in a 0.3 percent aqueous dispersion of double hydrated calcium hydroxide at about a 30:1 liquor ratio for 6 minutes at 136° F. Rinse thoroughly at that temperature and then with cold water and finally with acetic acid until a liquor at pH 5.5 was obtained.

Alternatively, the dry fabric can be wet out with a 0.3 to 1 percent calcium chloride solution containing a nonionic wetting agent, the temperature brought to 155–140° F. and the pH gradually brought to 10.5–11.5 with NaOH while rapidly agitating the fabric and treatment bath, with a treatment time at that pH of 5 to 8 minutes.

(b) To the acetic acid liquor add 1 percent calculated on the wool, Cibalum Black BGL, a premetallized chromium containing dyestuff. Bring the temperature to 160° F. for 30 minutes while agitating the liquor and fabric, thereby exhausting the liquor.

**EXAMPLE VII**

(a) Treat worsted cloth of 56's quality with a 0.3 percent aqueous dispersion of double hydrated calcium hydroxide at a 30:1 liquor ratio for 6 minutes at 138° F. Rinse several times with 140° F. water and then 3 times with cold water. Add sufficient acetic acid to bring the pH to 5.5.

(b) To the cloth thus treated in water at a 20:1 liquor ratio, add 8 times the weight of the cloth of 0.5 percent acetic acid and, calculated on the weight of cloth, 0.5 percent Tannasol D and 1 percent Procian Black HNS (ICI), a reactive dyestuff. Bring the temperature to 160° F. and dye at that temperature for 60 minutes while circulating the liquor. Exhaustion is good and the resulting gray-white fleck effect dyeing has a 5–6 light fastness.

What is claimed is:

1. A process for enhancing the dyestuff receptivity of wool which comprises the steps of
   (a) heating the wool in an aqueous bath containing a uniform 0.1 to 2 percent dispersion of an alkaline earth hydroxide at a pH from 9.5 to 13 at a temperature from 120 to 150° F. for a period of time less than 15 minutes which is non-damaging to the wool at the selected pH and temperature in the absence of the alkaline earth hydroxide, whereby enhancing dyeability of the wool fiber while retaining the scale structure of the wool in a substantially undamaged condition and maintaining original tensile and elongation;
   (b) thoroughly washing the wool; and
   (c) bringing the wool to an acid pH.

2. A process according to claim 1 wherein the alkaline earth hydroxide is calcium hydroxide.

3. A method according to claim 1 wherein the alkaline earth hydroxide is calcium hydroxide.

4. A process according to claim 3 wherein the pH is about that provided by the calcium hydroxide, and the wool is treated for from 2 to 10 minutes.

5. A method according to claim 3 wherein the wood is in the form of top.

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