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METHOD OF DYEING PEROXIDE-BLEACHED WOOL

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This invention pertains to the dyeing of wool and, more particularly, to the dyeing of wool which has been bleached with peroxide.

The natural coloring matter present in wool may be decolorized or bleached either by treating the wool with reducing agents or treating it with oxidizing agents after the wool has been cleaned or scoured. Water soluble agents are preferred to permit convenient treatment of the wool in conventional manner with aqueous solutions.

Bleaching with reducing agents suffers from the serious disadvantage that the bleach obtained is not permanent. The bleaching effect produced by reducing agents is due to the reduction of natural coloring matter to colorless compounds and these, under the influence of light and air, easily revert again to their oxidized, colored state, thus nullifying wholly or in part the effort expended in bleaching the wool.

Water soluble oxidizing agents, and particularly the water soluble peroxides, are very much more suitable for bleaching wool. They produce the desired bleaching effect by oxidative destruction of the natural coloring matter present in the wool and the bleach obtained is permanent under ordinary conditions. It is for this reason that wool is almost exclusively bleached with peroxides. The preferred peroxides are those yielding hydrogen peroxide upon dissolution in water, and particularly hydrogen peroxide itself.

Wool may be bleached with hydrogen peroxide under a variety of conditions of pH, temperature and time, by immersion in the bleach bath or by impregnation with the bleach bath, followed by steeping or direct drying. An outline of various commercially used procedures of bleaching wool has been given by I. E. Weber (J. Text. Inst. 24, p. 178–93) and a more recent process is described in Canadian Patent No. 332,484 of May 16, 1933, by Thomas E. Bell.

Of the various dyes applicable to wool, the acid dyes are the most important commercially. They are applied from a bath containing the dye, acids, and usually a salt. This dye bath is commonly applied at temperatures close to the boiling point for periods of time ranging from perhaps one-half to one hour.

If acid dyes are properly applied to peroxide bleached wool, commercially acceptable dyeings will result, but these dyeings are admittedly lacking in brightness and fullness of shade. In dyeing peroxide bleached wool to pastel shades in particular, shade variations are encountered even with the same blend of wool and the same bleaching and dyeing procedure. This often makes it difficult to match shades of the same color in the dye house procedure.

It has been recommended for the specific purpose of improving the degree of whiteness of peroxide bleached wool, to treat said wool with reducing agents. For example, Weyrich ("Das Bleichen und Farben der Textilfasern in Apparaten," Julius Springer, Berlin, 1937, p. 25) recommends treatment of peroxide bleached wool

with solutions containing 2 to 4 g. of sodium hydrosulfite per liter which, at conventional liquor ratios, corresponds to 10% to 20% of sodium hydrosulfite, based on the weight of the dry wool. Such treatment is carried out for times ranging from one hour to as much as 10 to 12 hours.

Wool which has been bleached with peroxide is sometimes subjected to an aftertreatment with acids such as oxalic acid. The oxalic acid is employed primarily for the removal of traces of iron which sometimes impart a noticeable yellowish tint to the bleached wool. In such instances, the oxalic acid is employed simply for its dissolving action upon the iron. Other acids are sometimes used for similar purposes, that is for removal of undesirable calcium or iron compounds or both which may be present in the bleached wool. Such procedures are referred to in Matthews, "Bleaching and Related Processes," Chemical Catalog Co., Inc., New York, 1921, page 140, and in Trotman, "Bleaching, Dyeing and Chemical Technology of Textile Fibers," second edition, London 1946, page 215.

Difficulties are, however, encountered if peroxide bleached wool, which has been treated with reducing agents to increase its whiteness, is to be dyed. Matthews ("Application of Dyestuffs," John Wiley & Sons, New York, 1920, p. 112) points out that wool bleached with reducing agents will retain substances deleterious to dyed colors. This fact is also discussed by Trotman ("The Bleaching, Dyeing and Chemical Technology of Textile Fibers," second edition, Chas. Griffin & Co., London 1946, p. 276). Both authors, in fact, recommend that wool treated with reducing agents should be further treated with an oxidizing agent, such as a peroxide, to remove deleterious residues which would interfere with proper dyeing (see Matthews, ibid., p. 109, and Trotman, ibid., p. 276).

In present day procedure, a large proportion of wool is dyed in the scoured, unbleached blended condition, due to the manifest difficulties in dyeing wool, whether bleached by peroxide or reducing bleaching agents, or a combination of such treatments, bleaching procedures being generally reserved for the production of white wool.

It is an object of this invention to provide means to produce on peroxide bleached wool, acid dyeings having a minimum of shade variations between successive batches of such wool.

It is also an object of this invention to provide means to produce in the application of acid dyes to peroxide bleached wool dyeings of improved hue, value and chroma, as defined in the Munsell Color System.

We have found that treatment of peroxide bleached wool with amounts of reducing agents so small as to effect no substantial bleaching action will result in dyeings of improved hue, value and chroma and that such dyeings, carried out in successive batches of the same blend of wool, bleached and dyed in the same manner, will have a minimum of shade variation between batches.

Any chemical or other agent easily oxidizable by the peroxide bleached wool as it exists after bleaching, will be able to act as a reducing agent in the sense of this invention. As is known those materials which act as reducing agents relative to hydrogen peroxide are those with an electric potential E_0 as negative or more so than the electric potential of bisulfite. E_0 is the symbol commonly used for the normal oxidation potential of an electrode and is described in "Principles and Applications for Electrochemistry," J. H. Creighton, volume 1, page 230 (1943). The practical choice of reducing agent will, however, be influenced by availability, simplicity of use, low cost, lack of interference with the intended dyeing

process and lack of deleterious effects on the wool fiber. Reducing agents meeting these requirements are the bisulfites, hydrosulfites, sulfoxylates, thioglycolates, hypophosphites and yeast, among others.

Of such reducing agents, amounts of 0.1% to 1% based on the weight of the dry wool will produce the desired effects. The reducing agent chosen is applied to the wool in form of an aqueous solution or, in the case of yeast, an aqueous suspension and treatment is carried out by immersing the peroxide bleached wool at room temperature for periods of 2 to 5 minutes in that solution. Excess of treating solution may then be removed, whereupon the wool is ready to be dyed. Alternately, the reducing agent chosen may be added to the dye bath and the peroxide bleached wool dyed in the otherwise customary manner.

In contrast to the recommendations made in the prior art for the employment of reducing agents, either alone or in combination with an oxidizing agent, the process of the present invention uses reducing agents, following a peroxide bleach, in amounts too small to have a bleaching effect of their own. Moreover, the treating time is a matter of minutes. Whereas the prior art, to improve the bleaching effect obtained with an oxidizing bleaching agent, applied as much as 10% to 20% of reducing agents, based on the weight of the dry wool, and applied these quantities for times ranging from one to many hours, we apply reducing agents in amounts and in a manner which would be inacceptable to anyone wishing to improve by such a treatment the white obtained by a peroxide bleach. The quantities of reducing agents employed in the process of this invention are of the order of about $\frac{1}{10}$ and the duration of treatment is of the order of about $\frac{1}{100}$ of those recommended in the prior art for improving the bleach.

Actual measurements of the bleaching effect obtainable, when treating peroxide bleached wool with minor amounts of reducing agents, were carried out by determining the brightness difference, ΔB, with a Hunter Multipurpose Reflectometer. For this purpose, a representative wool sample was bleached with hydrogen peroxide and then treated with a solution of sodium bisulfite containing a very small quantity of the latter based on the weight of the wool. The brightness difference, ΔB, was determined after every step and the results, summarized in the following Table I, indicate clearly that such treatment did not change the brightness of the wool as obtained in the peroxide bleach.

TABLE I

Wool Sample	Change in Brightness Based on Original Sample ΔB
Scoured	0
Scoured, bleached with H_2O_2	3.15
Scoured, bleached with H_2O_2, treated with 0.1% sodium bisulfite on basis of dry wool	3.10

Thus, our treatment of peroxide bleached wool with sodium bisulfite is carried out in a manner not suitable to produce an improved bleach. Comparable results are obtained with the other reducing agents mentioned above, namely, hydrosulfites, sulfoxylates, thioglycolates, hypophosphites and yeast.

The principle of the process of this invention will now be illustrated by examples. In these examples, the Munsell Color System is used to characterize the dyeings obtained. Alizarin Sapphire BN is used as a representative acid dye, although comparable results are obtained with other acid dyes.

Example I

A sample of a medium colored blend of scoured wool, here identified as "Blend A," was bleached with hydrogen peroxide.

This wool was then dyed with 0.1% Alizarin Sapphire BN in a bath containing 5% sodium sulfate, 4% acetic acid and 0.5% sulfuric acid, these percentages being based on the weight of the dry wool. Dyeing was carried out for 60 minutes at the boil, the liquor ratio being 1:50. The bleached and dyed wool was rinsed with water and dried, and then matched Munsell Color 5.0 B 8/3.

Example II

Another sample of "Blend A" was bleached with hydrogen peroxide as in Example I and the bleached wool was then immersed for 3 minutes at room temperature in a solution containing 0.1% sodium bisulfite based on the weight of the dry wool at a liquor ratio of 1:50. There was no perceptible brightness increase by reason of the latter treatment.

The peroxide bleached and treated wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 9.0 B 7.5/4.

Example III

Another sample of "Blend A" was bleached with hydrogen peroxide. Upon immersion of the bleached wool for 3 minutes, at room temperature, in a solution containing 0.3% sodium hydrosulfite ($Na_2S_2O_4$) based on the weight of the dry wool at a liquor ratio of 1:50, no brightness increase was discernible.

The peroxide bleached and treated wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 7.5 B 7.5/4.

Example IV

A sample of a medium colored blend of scoured wool, different in origin from "Blend A," and designated here as "Blend B," was bleached with hydrogen peroxide.

This wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 10 BG 6.5/2.

Example V

Another sample of "Blend B" was bleached with hydrogen peroxides. The bleached wool was then immersed for 5 minutes at room temperature in a solution containing in suspension 0.25% baker's yeast, based on the weight of the dry wool, at a liquor ratio of 1:50. There was no measurable increase in the brightness of the wool.

The peroxide bleached and treated wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 5.0 B 7/4.

Example VI

A sample of a medium colored blend of scoured wool, different in origin from "Blend A," and designated here as "Blend C," was bleached with hydrogen peroxide.

This wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 7.5 B 6/4.

Example VII

Another sample of "Blend C" was bleached with hydrogen peroxide. The bleached wool was then immersed for 3 minutes at room temperature in a solution containing 1% sodium thioglycolate, based on the weight of the dry wool. The liquor ratio used was 1:50. The brightness was substantially the same as before the thioglycolate treatment.

The bleached and treated wool was then dyed as described in Example I, and matched Munsell Color 7.5 B 6/6.

Example VIII

Another sample of "Blend C" was bleached with hydrogen peroxide. The bleached wool was then immersed for 5 minutes at room temperature in a solution containing 0.5% sodium hypophosphite, based on the weight of the dry wool. The liquor ratio used was 1:50. The

brightness of the sample after the hypophosphite treatment was substantially the same as before such treatment.

The bleached and treated wool was then dyed as described in Example I and, after rinsing and drying, matched Munsell Color 7.5 B 6/6.

The following Table II summarizes these results:

TABLE II

Wool Sample	Munsell Color
1. Blend A, bleached and dyed	5.0 B 8/3
2. Blend A, bleached, bisulfite treated, dyed	9.0 B 7.5/4
3. Blend A, bleached, hydrosulfite treated, dyed	7.5 B 7.5/4
4. Blend B, bleached and dyed	10.0 B G 6.5/2
5. Blend B, bleached, yeast treated, dyed	5.0 B 7/4
6. Blend C, bleached and dyed	7.5 B 6/4
7. Blend C, bleached, thioglycolate treated, dyed	7.5 B 6/6
8. Blend C, bleached, hypophosphite treated, dyed	7.5 B 6/6

That it is possible to modify the procedure used in Examples I to VIII, and to incorporate a reducing agent directly into the dye bath, is shown in the following.

Example IX

A further sample of "Blend A" was bleached with hydrogen peroxide. To a prepared dye bath was then added 1% sodium hydrosulfite based on the weight of the dry wool, and dyeing carried out as described in Example I. After rinsing and drying, this bleached and dyed wool matched Munsell Color 7.5 B 8/4.

The Munsell Color data clearly indicate and visual observation strikingly shows the improvement in color value obtained by the process of this invention.

The wool treated may be raw stock, yarn or piece goods, and the peroxide treatment employed is one appropriate for the product being treated. In broad outline, as is known in the art, the peroxide solution should not be so strongly alkaline as the baths used for cotton bleaching, due to the susceptibility of wool to be attacked by alkali. Generally, the alkalies if used in the bath are mild alkalies such as ammonia or phosphate, and the pH is low, from slightly acid to pH 8–9 in some instances.

Where raw stock is being bleached, economic consideration will probably dictate that the wool be impregnated with the peroxide solution and the latter dried into the wool. In the case of yarn and piece goods, the wool is bleached by immersion in the peroxide bleaching solution or the wool padded therewith and permitted to steep.

While it is not now definitely known what the mechanism is of the action of the reducing agent upon the peroxide bleached wool, it is believed from available data that wool, probably due to its unusual physical and chemical condition, retains either upon its surface or within the wool itself, a small amount of active oxygen material picked up during the peroxide bleaching treatment, even though the wool be washed after the peroxide bleach to a negative titanium test for peroxides.

If the wool be immediately dyed after peroxide treatment, the depth and hue of the dye are quite unpredictable. However, if the wool be treated with an agent capable of reducing peroxide, even though the wool by known sensitive tests, does not show its presence, then good dyeing is obtained which gives an excellent degree of matching.

What is claimed is:

1. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% based on wool of a reducing agent with an electric potential at least as negative as that of bisulfite and thereafter dyeing the wool.

2. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% based on wool of a reducing agent capable of decomposing hydrogen peroxide and thereafter dyeing the wool.

3. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% of a hydrosulfite, based on the wool, and thereafter dyeing the wool.

4. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% of a bisulfite, based on the wool, and thereafter dyeing the wool.

5. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% of a thioglycolate, based on the wool, and thereafter dyeing the wool.

6. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% of a hypophosphite, based on the wool, and thereafter dyeing the wool.

7. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises first applying to the wool 0.1% to 1% of a yeast, based on the wool, and thereafter dyeing the wool.

8. The method of controlling the hue and variations in shades in the dyeing of peroxide-bleached wool which comprises decomposing residual peroxide by incorporating into the dye bath about 0.1 to 1% based on the wool of a reducing agent having an electric potential at least as negative as that of a bisulfite, the said percentage being an amount insufficient appreciably to bleach said wool, and dyeing the wool with said bath.

9. The method of controlling the hue and variations in shades in the dyeing of peroxide bleached wool which comprises decomposing residual peroxide by incorporating in the dye bath about 0.1 to 1% based on the wool of a hydrosulfite and dyeing the wool with said bath.

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