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Conner

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[54] **PROCESS FOR BROWN MINERAL DYEINGS OF CELLULOSICS WITHOUT OXIDATIVE DEGRADATION (TENDERING), FROM A SINGLE BATH**

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[52] **U.S. Cl.** **8/52,** 8/74, 8/134

[51] **Int. Cl.** **D06p 3/60**

[58] **Field of Search** 8/52, 95, 17

[56] **References Cited**

UNITED STATES PATENTS

3,622,259 12/1971 Hamalainen et al. ..... 8/52 X

OTHER PUBLICATIONS

J. M. Matthews, "Application of Dyestuffs," New York, John Wiley and Sons, Inc., pp. 520–521, 1920.

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[57] **ABSTRACT**

Cellulosic textiles have been imparted controllable shades of "bistre-brown" or of "reddish-brown" coloration which have proved to be durable to laundering. These coloration have been imparted mainly to cotton fabrics through single bath mineral dyeings with inorganic compounds or mixtures thereof by impregnating the cellulosic textile with an aqueous solution containing potassium permanganate and a methylolated ethylene urea, removing the excess solution, then curing the wet impregnated textile. The reddish-brown varieties are prepared by incorporating small quantities of zirconia in the solutions. Whereas the treatment with permanganate alone severely degrades the cellulosic by oxidation, the incorporation of a methylol urea inhibits the cellulosic oxidation and subsequent degradation.

2 Claims, No Drawings

PROCESS FOR BROWN MINERAL DYEINGS OF CELLULOSICS WITHOUT OXIDATIVE DEGRADATION (TENDERING), FROM A SINGLE BATH

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to a process for imparting to cellulosic materials a brown (bistre) mineral dyeing, without degrading the material by permanganate oxidation. Specifically, this invention relates to a process for imparting to cellulosic materials, through a single bath application, a brown mineral dyeing of attractive color with good fabric hand, for resistance to water washing and actinic degradation, without adversely affecting the strength of the treated material from oxidation by permanganate in the treatment. More specifically, the invention relates to the in situ deposition of manganese dioxide brown mineral deposits from an oxidative inhibited permanganate bath, through conventional pad and cure procedures, where the oxidation inhibitor is oxidized during drying or curing, with subsequent in situ deposition of manganese dioxide into the cellulosic material without oxidative degradation of the treated cellulosic material. Among the number of useful items which can be fabricated from the materials treated by the process of this present invention, the following items are referenced: awnings, tents, tarpaulins, sails, life raft covers, cording materials, curtains, camouflage fabrics, wearing apparel, umbrellas, and shoe liners, as well as paper pulp products such as bags, wrapping paper, etc.

The prior art teaches the application of permanganate solutions to cellulosics to produce bistre brown mineral dyeings (reference: J. M. Matthews "Application of Dyestuffs," New York, John Wiley & Sons, Inc. pp 520–21, 1920). In all instances, the permanganate causes a severe oxidative degradation (tendering) of the treated cellulosic, with significant fabric strength losses as high as 50%, whether the wet treated material is air dried at 25° C or oven dried at 60° C to 100° C to produce the bistre brown (manganese dioxide) mineral dyeing. Consequently the application of manganese dioxide brown mineral dyeings from a single permanganate bath has not been feasible from the viewpoint of fabric strength loss (degradation).

Particularly attractive brown colorations are obtained in the cellulosic final products of the present invention, with good fabric hand, resistance to water washing, and without fabric oxidative strength loss (degradation). A significant feature of the present invention is that the brown dye shade can be varied from bistre brown to a reddish-brown by incorporation of zirconyl ammonium carbonate solutions with the methylolated substituted urea-permanganate system, to produce these shades from a single pad bath by simply wet padding and dry-curing.

The main object of this invention is to provide a single bath process to impart color shades of mineral brown, without fabric degradation from permanganate oxidation, by means of simple pad and cure procedures with inhibited permanganate systems.

A second object of this invention is to produce desired brown mineral dye shades (i.e. bistre brown and reddish brown), with reduced need for excessive investment in equipment by reducing oxidative degradation to a negligible factor, and making it feasible for a single bath permanganate system for brown mineral dyeing.

A third object of this invention is to provide a process which requires less chemical and heat curing controls than those now commonly employed in the art.

In general, this present invention can best be described as a process for imparting to cellulosic fabrics a mineral dyeing of manganese dioxide base from a single bath of aqueous potassium permanganate and a substituted methylolated urea, with or without zirconyl ammonium carbonate, comprising:

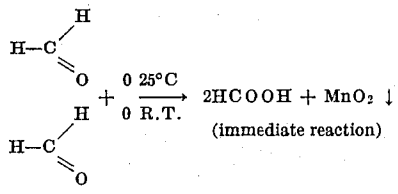
a. impregnating a cellulosic material with a solution containing 0.5% to 4.0% potassium permanganate ($KMnO_4$) and 1.40% to 7.0% of a methylolated ethyleneurea (such as "Permafresh 183" of Sun Chemical Company) where a bistre brown dyeing is desired, or

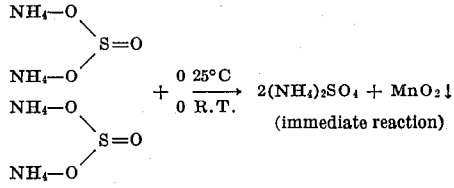
b. impregnating a cellulosic material with a solution containing 0.5% to 4.0% potassium permanganate $(KMnO)_4$ and 1.40% to 7.0% of a methylolated ethylene urea (such as "Permafresh 183" of Sun Chemical Company) with enough zirconyl ammonium carbonate solution (10% ZrO_2) to add 1.5% to 3.5% Zirconia (ZrO_2) to the bath, where reddish-brown mineral dyeings are desired, and

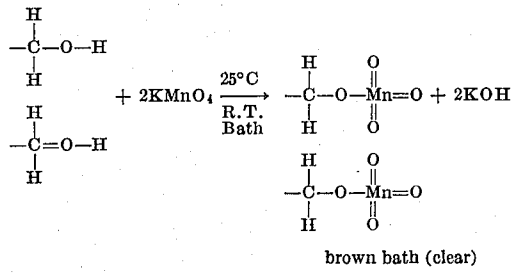
c. removing the excess solution from the impregnated cellulosic material to obtain about from 50% to 80% wet pickup, and

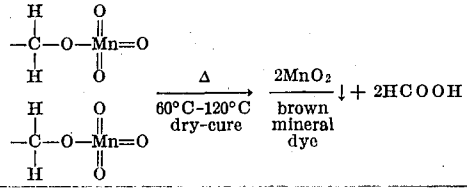
d. air drying the material at 25° C for 45 minutes to 2 hours or oven drying the wet, impregnated cellulosic material for about from 6 minutes to 10 minutes of time, at temperatures about from 60° C to 120° C, using the longer drying times with the lower temperatures and the shorter drying times with the higher temperatures, to effect complete reduction of the permanganate to manganese dioxide.

Potassium permanganate is reported in the literature as a powerful oxidizing agent, causing some organic materials to ignite from the heat of oxidation [i.e., glycerol, alcohols, cellulose, etc.]. Consequently, when an aqueous solution of permanganate evaporates to dryness in contact with a cellulosic material, the concentration of the permanganate increases to produce oxidation of the cellulose with subsequent reduction in material strength along with deposition of manganese dioxide (brown) by complete reduction of the permanganate. However, certain inorganic and organic materials have a greater affinity for the permanganate oxygen than cellulose. Some of these materials were found to be inorganic sulfites, organic aldehydes, and organic methylolated substituted ureas. The oxidation affinity of the sulfites and alkehydes is so great that complete reduction of the permanganate takes place in the bath, resulting in immediate percipitation of manganese dioxide, which makes these oxygen acceptors impractical for use in the bath for single bath mineral dyeing. The methylolated ethylene urea compounds (i.e. Permafresh 183) do not completely reduce the permanganate and produce a clear brown bath solution without precipitation of manganese dioxide. This may be explained by the fact that the formaldehyde is inhibited by the methylol structure ($-CH_2OH$) at room temperature. The following mechanisms serve to demonstrate the above explanations:

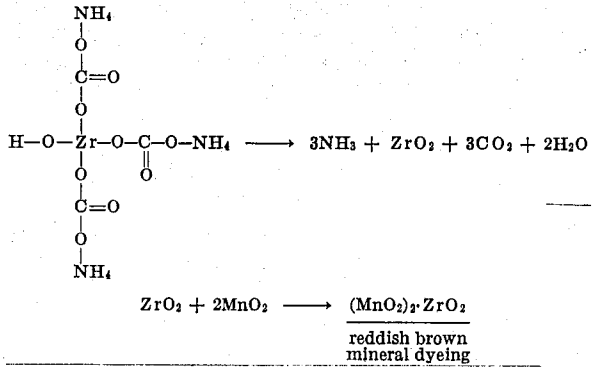
1.


2.


3.




When zirconyl ammonium carbonate solutions are mixed with the bath formulation represented by (3) above, the compound is compatible with the other components, and on heat decomposition, in drying, produces mineral dyeings consisting of MnO_2 and ZrO_2, which are reddish-brown in color:



It is also expected that the zirconia would attribute good resistance to active degradation and resistance to algae growths (U.S. Pat. No. 3,446,656).

EXAMPLE 1

Demonstration of oxidative degradation of cellulosics by potassium permanganate concentration on the material regardless of drying temperatures.

1.00 gram potassium permanganate ($KMnO_4$)
26.00 grams distilled water
27.00 grams Plain Permanganate Bath

Three pieces of scoured duck, 8" × 9", were wetted with this bath, squeezed free of excess liquid, and subjected separately to the following dry-cure cycles:

a. air dry at 25° C for 45 minutes
b. oven dry at 60° C for 10 minutes
c. oven dry at 100° C for 6 minutes

In all three instances, a bistre brown (MnO_2) mineral dyeing was produced. All three samples were then tested for tensile breaking strength in the warp direction. The following results were obtained with (a), (b), and (c):

a. average percent strength loss = 38%
b. average percent strength loss = 40%
c. average percent strength loss = 42%

These values show practically the same strength loss, demonstrating that the oxidative degradation of the fabric is related to the concentration of permanganate rather than to the temperature of cure, making any plain permanganate cellulosic treatment impractical because of severe strength losses.

EXAMPLE 2

Demonstration of oxidative degradation of cellulosics by potassium permanganate with zirconyl ammonium carbonate.

1.00 gram potassium permanganate ($KMnO_4$)
21.00 grams distilled water
5.00 grams zirconyl ammonium carbonate solution (10% ZrO_2)
27.00 grams permanganate-zirconyl ammonium carbonate bath

Three pieces of scoured duck, 8" × 9", were wetted with this bath, squeezed free of excess liquid, and subjected separately to the same dry-cure cycles as in Example 1. In all three instances a reddish-brown mineral dyeing was produced. All three samples were then tested for tensile breaking strength in the warp direction. The following results were obtained with *a*, *b*, and *c*:

a. air dry average percent strength loss = 41.6%
b. 60° C dry average percent strength loss = 36.5%
c. 100° C dry average percent strength loss = 47.5%

Although sample (c) showed a slightly higher loss as a result of higher cure temperature, the samples in general, reflect oxidative degradation relative to the concentration of permanganate, regardless of the presence of zirconia.

EXAMPLE 3

Demonstration of the immediate reduction of potassium permanganate by ammonium sulfite in the bath.

1.00 gram potassium permanganate ($KMnO_4$)
24.00 grams distilled water
2.00 grams ammonium sulfite
27.00 grams bath (incompatible)

As soon as the ammonium sulfite was added, the bath turned opaque and brown, and a heavy precipitate of manganese dioxide was produced. This instantaneous reduction to MnO_2 makes the system not feasible.

EXAMPLE 4

Demonstration of the immediate reduction of potassium permanganate by 40% formalin (formaldehyde) in the bath.

1.00 gram potassium permanganate ($KMnO_4$)
24.00 grams distilled water
3.00 grams of 40% Formalin (HCHO)
28.00 grams of bath (incompatible)

After the addition of the formalin, a reaction was shortly evidenced by a color change from purple to brown. Within a few minutes, all of the permanganate was reduced to insoluble brown manganese dioxide in the bath, showing the formalin approach to be incompatible and not feasible.

EXAMPLE 5

Demonstration of the compatible inhibited oxidation acceptor as a methylolated ethylene urea (Permafresh 183" Sun Chemical Company), with plain permanganate.

1.00 gram potassium permanganate ($KMnO_4$)
25.00 grams distilled water
1.00 gram Permafresh 183 (45% solids)
27.00 grams clear brown "Bistre Brown" bath

The formulation produces a deep brown clear liquid bath, with no precipitation of manganese dioxide at room temperature. An 8" × 9" piece of scoured duck was wetted with the bath, squeezed free of excess liquid, and was first oven dried at 60° C for 8 minutes, followed by oven cure at 100° C for 2 minutes. An attractive, bistre brown, uniformly dyed fabric resulted. Fabric hand was excellent and smooth, and the dye was completely resistant to water washing. Tensile breaking strength in the warp direction showed only a 10% strength loss, whereas permanganate alone showed 40% reduced strength (Example 1).

EXAMPLE 6

Demonstration of the compatible inhibited oxidation acceptor as a methylolated ethylene urea (Permafresh 183), with permanganate and zirconyl ammonium carbonate (reddish-brown mineral dyeing).

The following formulation was prepared to show the effect of methylolated ethylene urea with permanganate and zirconyl ammonium carbonate:

1.00 gram potassium permanganate ($KMnO_4$)
25.00 grams distilled water
1.00 gram Permafresh 183 (Sun Chemical Co.)
5.00 grams zirconyl ammonium carbonate solution (10% ZrO_2)
32.00 grams reddish-brown mineral dye bath (clear)

A sample of scoured duck was treated with this bath and the same procedure followed as in Example 5. The cured, treated fabric showed an attractive reddish-brown mineral dyeing of excellent hand, and complete resistance to water washing. Tensile breaking strength in the warp direction, showed a negligible 9% strength loss.

EXAMPLE 7

Demonstrating the effect of increasing the methylolated compound in the baths of Examples 5 and 6 for physical strength effects.

The Permafresh 183 contents of the baths in Examples 5 and 6 were increased to 2 grams in each formulation. The fabric treatments were repeated, and warp tensile strength losses were in the range of 0% to 6% (negligible).

EXAMPLE 8

Demonstrating the effect of formaldehyde and methylolated ethylene urea with permanganate solutions:

1.00 gram potassium permanganate ($KMnO_4$)
25.00 grams distilled water
26.00 grams permanganate solution

The prepared bath was divided into two equal portions (13.0 grams) and poured into two test tubes. To one was added 1 gram of 40% formalin solution. To the other was added 1 gram of Permafresh 183 (methylolated ethylene urea). In 3 minutes, the Formalin mix showed an opaque brown color and precipitate of manganese dioxide in the liquid and on the walls of the tube. The methylolated mix turned brown in color, remained clear, and did not precipitate manganese dioxide. This demonstrates the inhibited formaldehyde in the methylolated structure as compared with the active reducing characteristics of the formaldehyde in the formalin solution.

I claim:

1. A process for imparting to cellulosic textiles "bistre-brown" coloration which is relatively durable to laundering, said coloration being accomplished through mineral dyeing with inorganic compounds, and said coloration being controllably intensifiable through increase of concentration of the said inorganic substances, said process comprising:
   a. impregnating a cellulosic textile with an aqueous solution containing about from 0.5% to 4.0% of potassium permanganate and about from 1.4% to 7.0% of a methylolated ethylene urea,
   b. removing the excess solution from the wet impregnated cellulosic textile to obtain a wet pickup of about from 50% to 80%, and
   c. drying the wet impregnated cellulosic textile at temperatures about from 25° to 120° C for periods of time about from 10 to 120 minutes, using the longer periods of time with the lower temperatures, thereby effecting a complete reduction of the potassium permanganate deposited on the textile to manganese dioxide.

2. A process for imparting to cellulosic textiles a "reddish-brown" coloration which is relatively durable to launderings, said coloration being accomplished through mineral dyeing with inorganic compounds, and said coloration being controllably intensifiable through increase of concentration of the said inorganic substances, said process comprising:
   a. impregnating a cellulosic textile with an aqueous solution containing about from 0.5% to 4.0% of potassium permanganate, about from 1.4% to 7.0% of a methylolated ethylene urea, and a quantity of 10% aqueous zirconyl ammonium carbonate sufficient to add about from 1.5% to 3.5% zirconia (ZrO_2) to the aqueous solution,
   b. removing the excess solution from the wet impregnated cellulosic textile to obtain a wet pickup of about from 50% to 80%, and
   c. drying the wet impregnated cellulosic textile at temperatures about from 25° to 120° C for periods

of time about from 10 to 120 minutes, using the longer periods of time with the lower temperatures, thereby effecting a complete reduction of the potassium permanganate deposited on the textile to manganese dioxide.

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