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PROCESS OF LOW TEMPERATURE DYEING OF WOOL

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This invention relates to improvements in wool dyeing and more particularly to dyeing wool with chrome dyestuffs, neutral premetallized dyestuffs, and acid, milling, or polar dyestuffs, using selected dye assistants, carriers, or solvents in the dye bath.

Conventional dyeing methods use dye baths having boiling temperatures (205°–212° F.). Immersion therein of the wool stock to be dyed is required to last thirty to sixty minutes. Where chrome dyestuffs are used an additional forty-five to sixty minutes of immersion is required after adding the chrome, during which the boiling temperature is maintained.

This long immersion at the boil, as well as the chemical action of the chrome on the wool where chrome dyestuffs are used, causes physical and chemical deterioration of the wool fiber, loss in textile strength, and increase in brittleness. This not only results in a lessening of the quality of the woven cloth, but a necessary loss in the efficiency of the carding, spinning, and weaving operations themselves. In addition, this conventional group of methods may have such other shortcomings as a difficulty in obtaining uniform dyeing at all levels in the dyeing kettle, and further difficulty in yielding dyeing which will be retained in the wool, for example when the latter is washed.

In recent years, carrier, or solvent-assisted, dyeing, originally developed in connection with the special needs of synthetic or hydrophobic textiles, has been applied experimentally with considerable success to the dyeing of hydrophilic or natural fibers, just as well. Chemists have not agreed on the exact means through which these carriers or solvent assistants achieve their effects, but it has become apparent that their use has reduced materially the time required for dyestuff exhaustion (the term used in the trade for transfer of the dye from the dye solution to the fiber being dyed), improved the wet-fastness of the dyed material, made possible the use of dyes not previously employable, and, as corollaries for the foregoing, effected minimal damage to the fibers and made possible the automated, continuous processing of textile stock through the dyeing stage.

Carrier-, or solvent-assisted dyeing involves the addition of a selected reagent to the dye bath at or before the introduction of the dyestuff. This reagent is believed not to be simply a catalyst, since it is consumed during the process. Several theories, as suggested above, have been advanced to explain its behavior.

The reagent, which is immiscible or at most sparingly soluble in water, tends to form a separate phase within the dyebath, and to attract the dyestuff grains into this separate phase. This preliminary transfer takes place, and the dyestuff goes into extremely fine solution within the reagent phase of the aqueous dyebath. Simultaneously the reagent acts physically upon the fiber stock, making accessible more of its surface area, and also chemically, unloosing the interior hydrogen bonds and interchain forces in the fiber, thus facilitating molecular dispersion of the dye therethrough, and not merely mechanical precipitation of the dye therein.

It has also been suggested that the reagent is adsorbed on the fiber surface, therefore forming a layer having a concentration of dye greater than that elsewhere in the dyebath, resulting in a correspondingly higher concentration gradient with respect to the fiber and diffusion rate thereinto. Especially where, as noted, the dye or solvent

has limited water solubility, the natural tendency to precipitate in a layer has the effect of concentrating the dye at the fiber surface, which is commercially the most efficient result.

The reagent referred to above is called in the trade a "carrier" or "dye assistant," and in practice will be one of a number of such substances chosen for their individually good consequences when used with correspondingly selected categories of dyestuffs. Sparingly soluble amines, alcohols, and phenols have been found best.

Carrier-, or solvent-assisted dyeing has, however, had its limitations. A number of the carriers or assistants are prohibitively expensive for commercial use. In other instances, the cost has not been prohibitive in the absolute, but it has been necessary to include a retrieval step in the dyeing process, to enable the assistant or carrier to be re-used. Furthermore, carrier or assistant dyeing has been of negligible success in chrome dyeing, among other categories. Steaming has continued to be an important requirement. Even dyeing has not been reliably obtained. And the incorporation of some low-temperature steps into a continuous dyeing process has resulted in change of shade and loss of control of shade when dyed fiber stock has been subjected to higher temperatures at other points in the process.

A principal object of the present invention, is, therefore, the provision of a low-cost, lower-temperature method of dyeing, capable of incorporation into continuous processes, yielding colorfast and evenly dyed shades. Another principal object is the provision of a more rapid method of dyeing, applicable to all major categories of fabrics and dyestuffs. Still another principal object is the elimination of the retrieval step for, and limitation in, choosing dye assistants, carriers, or solvents.

Moreover, I provide a dyeing method which involves minimal damage to fibers, achieving some of its economy by thus making possible the processing of lower-grade and more easily damaged stock than was heretofore usable. In particular, I provide for the use of tridecyl alcohol, ethylene glycol, other specified glycols, and certain other selected substances to accomplish the exhaustion of the dyestuff and the chroming, where chrome dyestuffs are used, rapidly at the said lower temperature, to level the dyeing results, and to bind the selected carrier or assistant compounds and mixtures.

I thus provide, by inclusion of new steps and substances and by omission of old steps and substances, novel and improved means of dyeing, especially applying the said means to wool. Other objects and features of the present invention will appear from a careful consideration of one preferred embodiment thereof, illustrating the dyeing of wool stock with Mordant Black 11, Index Number 14645 in the International Color Index recognized by the British and the American textile industries. It is, of course, understood that similar steps occur in the use of other dye assistants with other dyestuffs and other kinds of stock.

In the accomplishment of the foregoing and other objects of my invention, I provide a quantity of wool stock in an amount usual for processing, for example, five hundred pounds of AA Pulled Wool, and a correspondingly-sized container of any of severally commercially-available types: for example, a Riggs & Lombard five hundred pound capacity stock dye kettle, properly installed with associated means for supplying thereto heat, water and other utilities as needed.

The wool is placed in the kettle and is wet thoroughly with warm water, the useful temperature range of which may vary as desired from about room temperature (70° F.) to over 140° F. Enough dye assistant in the particular composition best suited to the dyeing of the said wool with the said Mordant Black 11 is now added to the kettle to form with the said warm water, a solution by weight of

between 0.1% and 0.25%. In this example, any of several dye assistants I have developed may be used, and in particular one of those hereafter defined in detail which I denominate K–12, K–12 Modified, K–20 and P.

A standard 56% acetic acid solution is now added to the kettle in an amount depending upon the pH of the wool stock. In general, the acetic acid added amounts to between 3.0% and 6.0% by weight of the stock to be dyed which approximates the amount used conventionally, the addition of acetic acid being, in itself, a step well known in the art. However, in the conventional process, only about half the acetic acid used is added at this point, the remainder being added much later, as will be pointed out.

The dyestuff to be used, here Mordant Black 11, is now added to the kettle, preferably in an already-dissolved condition, and the temperature of the kettle solution, or dyebath, is now raised by appropriate conventional means, during a fifteen to thirty minute period, from the said initial temperature (70° to 140° F.) as perhaps slightly cooled by the addition of the previously mentioned substances and the interval so far elapsed, to between 170° to 175° F., or somewhat less than 80° C., and is held at this latter temperature for about fifteen minutes more. During this period of between thirty and forty-five minutes, the dyestuff transfers in solution from the water phase to the carrier or assistant phase, and from this solution-within-a-solution to the wool stock itself which is thus dyed black in the shade desired. The normal time required for conventional exhaustion of the dyestuff is from eighty-five minutes to two hours twenty minutes, which includes heating the solution of warm water, acetic acid, and Mordant Black 11 to boiling, taking between forty-five and sixty minutes to do this, holding at boiling for another twenty to forty minutes, and completing the exhaustion with the remaining 2.0% or so of acetic acid and a further waiting period of twenty to forty minutes, still at the boil. It will, therefore, be observed that my method does away with the delays and unwieldinesses of twice adding acetic acid instead of once.

A chroming fixative, sodium bichromate, is now added, at the 170°–175° F. temperature in my process, and satisfactorily reacts with Mordant Black 11 at this temperature to give the correct shade and fastness. This is not possible without the use of dye assistants. I then maintain this solution and stock and their temperature for fifteen minutes.

My process is now concluded by rinsing the wool stock free of its kettle solution or dyebath. And, as noted, the low cost of the dye assistant (K–12, K–12 Modified, K–20 or P) makes it feasible to dispose of the exhausted bath and of such matter as can be washed free of the stock as waste without attempting retrieval for reuse.

It is sometimes necessary to include an after-treatment to eliminate the yellow impurity which tends to bleed from wool dyed with Mordant Black 11. Since this is true of wool dyed by conventional dyeing methods, as well as by my method, and this after-treatment is well known in the art, it is unnecessary to describe this step in detail.

The dye assistant, carrier, or solvent K–12, mentioned above, is composed, in the principal form I have devised, of the following weight percentages of components: 27.5% tridecyl alcohol, 35.0% ethylene glycol, 12.5% diethylene glycol, 10.0% hexylene glycol, 7.5% Igepal CO–730 (a nonylphenol polyoxyethylene ethanol), and 7.5% Tergitol Nonionic TMN (trimethyl nonanol polyoxyethylene ethanol).

The assistant K–12 Modified, which as I have stated may be used in the above embodiment in place of K–12, is composed as follows: 12.5% tridecyl alcohol, 41.0% ethylene glycol, 17.5% diethylene glycol, 14.0% hexylene glycol, 7.5% Igepal CO–730, and 7.5% Tergitol Nonionic TMN.

The assistant K–20, which as stated may be substituted for K–12 or K–12 Modified in the above example, is composed of 17.5% tridecyl alcohol, 50.0% ethylene glycol, 12.5% diethylene glycol, 5.0% hexylene glycol, 5.0% Igepal CO–730, and 10.0% Igepal CO–710, which last differs from the CO–730 only in the number of moles of ethylene oxide.

Additional examples of dyeing in colors by my method are:

Brown Shade—B Super Wool, 25 lbs. in 50 lb. Riggs & Lombard stock dye kettle:

Wet out stock @ 120° F.
Add:
2.5% dye assistant K–12
Hold 5 minutes @ 120° F.
Add: 3.0% acetic acid (56%)
Add:
2.5000% Mordant Brown 15
0.1625% Mordant Black 13
0.1375% Mordant Red 7
0.2375% Mordant Orange 6
Raise in 30 minutes to 180° F.
Hold 10 minutes
Add:
1.25% sodium bichromate
Hold 20 minutes @ 180° F.

In comparison, the conventional method of Brown Shade dyeing is:

Wet out at 90–100° F.
Add: 1.0 to 2.0% acetic acid (56%)
Add:
Dyestuff
Raise in 45 to 60 minutes to boiling point (212° F.)
Hold 30 minutes
Add:
1.0% to 2.0% acetic acid
Hold 30 minutes
Add:
1.25% sodium bichromate
Hold at boil 45 minutes

This comparison shows very clearly the advantages of my method.

My method is also applicable to dyeing chrome colors by the chromate method, as shown by the following example.

Grey shade:

Wet out stock @ 120° F.
Add:
2.5% dye assistant K–12
Run 5 minutes @120° F.
Add:
3.0% acetic acid (56%)
Run 10 minutes @120° F.
Add: 0.5% sodium bichromate
Add:
0.1125% Mordant Black 13
0.0437% Mordant Red 7
0.0375% Brilliant Alizarine Milling Blue BL
0.0063% Mordant Yellow 1
Raise temperature to 180° F. in 45 minutes
Hold 15 minutes

As seen, my process thus reduces the time required for chrome color dyeing from on the one hand, roughly two hours twenty-five minutes to three hours thirty-five minutes, to, on the other hand, forty-five to sixty minutes. It also eliminates one of the insertions of acetic acid, does not require, though permits, increase in the amount of said acid used, without increasing harm to the fiber stock, eliminates the cooling step involved in the chroming. Besides the improvements previously noted, therefore, it thus makes further contribution to economical and efficient dyeing.

Certain chrome dyestuffs require slight modifications of my above-described method. For example, in the embodiment of my process wherein 250 lbs. of laps are

chrome-dyed Navy Blue in the kettle, a five-minute wait follows the addition of the K–12 before the acetic acid is added; another five-minute wait follows; the sodium bichromate is added with the coloring (1.825% Acid Blue 113, 0.840% Acid Green 25, and 0.041% Mordant Yellow 1); and the temperature is raised during forty-five minutes from an initially-recommended 120° to 180° F. This results in best colorfastness for this dye and wool, and in this instance a truer shade, because a temperature near or at the boil is not necessary.

Other substances conventionally used for various subsidiary purposes in dyeing may be employed as usual in my invented process. Among these is Versene 100 (in dyeing yarn black). It may be of further interest to observe that, in a second example, a quantity of 686 lbs. of 62/64s grade wool is dyed by being wet out at room temperature (70° F.), having dyestuff added to the kettle in a cold-water solution, and having several dye assistants and certain of their components, including the assistants K–20 and P (80.0% ethylene glycol, 10.0% diethylene glycol, and 10.0% Igepal CO–730), added together, the dyebath temperature then being raised to 180° F. in fifteen minutes.

In addition to chrome dyeing, my process is successfully applied to neutral premetallized dyestuffs under the above general conditions. Divergences which are not considered to be substantially different from the above descriptions include the running of the initial water solution through the wool stock at 140° F. for five minutes; the addition of ammonia or diammonium phosphate, in alternate situations, together with the acetic acid and the K–12, during a further five minutes; the addition of mixed colors and the heating of the bath to 180° F. in twenty-five minutes; and the holding of the solution at this temperature for another twenty minutes before the concluding rinsing.

The presently-invented process is also successfully applied to acid dyeing of wool piece goods, using a kettle solution of 10.0% glauber salt introduced after an initial wetting at just above room temperature (suggested 80° F.) with the dye assistant AB–8 in 1.25% solution by weight. AB–8 consists in the following: 10% tridecyl alcohol; 40% ethylene glycol, 35% hexylene glycol, 10% Tergitol Nonionic TMN, and 5% Igepal CO–730. The dyebath is held for ten minutes, color and sulfuric acid are then added, as is conventional, the temperature is raised to 160°–165° F. during forty-five minutes, and this is maintained for a final waiting period of thirty minutes more before the rinsing. It is noted that the total time for this application is longer than for those previously set forth, being about one hour twenty-five minutes, but this is still substantially less than conventionally required and is not considered to impair the novelty or usefulness of the invention.

It should be understood that the foregoing description of preferred embodiments of my dyeing methods is to be construed in extension and not in limitation of the invention herein disclosed, and that the latter may be practiced broadly within the full scope of the appended claims, being limited only by the prior art. It is to be noted that alternative embodiments, including inconsequential variations of the component percentages given above, are now or may be expected to become apparent from this disclosure to those skilled in the art, which embodiments must nevertheless be considered as coming within the protection here secured. The component percentages referred to are to be construed as constituting presently-preferred forms of the dye assistants only, and not as a narrow and artificially inappropriate limitation or renunciation of any part of my invention.

I claim:

1. A process of low temperature dyeing of wool, comprising the steps of placing a predetermined quantity of wool stock in a container adapted to receive it; wetting the said wool stock with a predetermined quantity of water at a selected temperature below 150° F.; adding a predetermined quantity substantially less than 1% by weight on the weight of the water of a dye assistant composed at least in part of ethylene glycol and at least one nonylphenol polyoxyethylene ethanol surfactant; adding a predetermined quantity of acetic acid; adding a predetermined quantity of dyestuff at the said selected temperature less than ten minutes after the wetting of the said wool sock has been completed; raising the temperature of the dyebath composed of the said water, the said dye assistant, the said acetic acid, and the said dyestuff, to a predetermined point between 160° F. and 185° F. during a period of less than forty-five minutes; maintaining the said dyebath at the said predetermined temperature point for less than thirty minutes more; and rinsing the said wool stock so that the said wool stock retains a predetermined shade of dye with substantial fastness.

2. The process of dyeing wool defined in claim 1, further characterized by the said dyestuff being a chrome dyestuff; the said dye assistant containing a predetermined quantity of diethylene glycol; and a predetermined quantity of sodium bichromate being added to the said dyebath before the said rinsing.

3. The process of dyeing wool defined in claim 1, further characterized by the said dyestuff being a neutral premetallized dyestuff.

4. The process of dyeing wool defined in claim 1, further characterized by the said dye assistant containing a predetermined quantity of tridecyl alcohol.

5. A process of low temperature dyeing of wool by use of a dye assistant, comprising: placing a predetermined quantity of the said fibrous material in a container adapted to receive it; wetting the said fibrous material with a predetermined quantity of water at a predetermined temperature below 185° F.; adding thereto a predetermined quantity substantially less than 1% by weight on the weight of the water of a dye assistant composed at least in part of ethylene glycol, tridecyl alcohol and a nonylphenol polyoxyethylene ethanol surfactant; adding thereto a predetermined quantity of a selected dyestuff; and rinsing the said fibrous material so that it retains a predetermined shade of dye with substantial colorfastness, the temperature of the aforesaid components in the said dyeing process always remaining less than the said 185° F.

6. The process of dyeing wool by use of a dye assistant defined in claim 5, further characterized by the said dye assistant containing diethylene glycol.

7. In the process of dyeing wool, the use, as a dye assistant, of between 0.1 and 0.25 percent by weight based on the weight of the dye bath of a mixture comprising a water insoluble alcohol, a water soluble glycol and a nonionic surfactant.

8. The process as claimed in claim 7 in which the dye assistant comprises per hundred parts by weight 10 to 27.5 parts of a water insoluble alcohol, 10 to 15 parts of a nonionic surfactant and the remaining parts of a water soluble glycol.

References Cited in the file of this patent

UNITED STATES PATENTS

1,775,543	Abbott	Sept. 9, 1930
1,926,556	Nuesslein	Sept. 12, 1933
2,878,294	Kress	Mar. 17, 1959
2,983,651	Seemuller	May 9, 1961
3,056,644	Radley et al.	Oct. 2, 1962

OTHER REFERENCES

Stevens et al.: J.S.D.C., March 1956, page 100.

Colour Index, 2nd Ed., 1956, The Society of Dyers and Colourists, vol. 1, page 1590, Entry CI 1464–5.

Appel: Technical Manual of the Amer. Assoc. of Textile Chemists and Colorists, Col. 35, 1959, page 495.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,112,983 December 3, 1963

Daniel P. Collins

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, line 4, for "49 Blanchard St." read -- 12 Byron St. --.

Signed and sealed this 8th day of September 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents