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PROCESS OF DYEING WOOL

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This invention relates to an improved process for dyeing wool. It is an object of this invention to provide a process for dyeing wool fabric in level, well-penetrated shades, of good fastness qualities to light and to washing. Other objects and achievements of this invention will appear as the description proceeds.

The classical method of dyeing wool is by means of acid dyestuffs, that is dyestuffs having sulfo or carboxy groups, and being applied from an acid bath. Most commonly, dyestuffs of the various azo types (monoazo, disazo, etc.) are employed for this purpose. Such dyes, however, are generally insufficiently fast to light, or washing or both.

It has been known for some time that the fastness of azo dyes to light and to washing is very much improved if the dyeing or the dyestuff itself before application is treated with a reagent yielding chromium or cobalt to form a metal complex with the dye molecule. The dyestuff in such a case has to have a hydroxyl group in ortho position to the azo bridge, and the resulting compounds are generally referred to as metallized ortho-hydroxyazo dyes. One subgroup of this general class is characterized by possessing further a sulfo group in the molecule, and their application to wool has generally been from a strongly acid bath, for instance one containing sulfuric acid to a concentration of 8% by weight. Although wool is generally resistant to acid, the application of such strong acid, at boiling temperatures, may nevertheless exert a harmful effect on the fiber. In any event, the process becomes inapplicable where the material treated is a fabric having cotton effect threads or other admixture of fibres which are sensitive to acid.

In recent years, another group of water-soluble, metallized azo dyes has been developed, which is characterized by freedom from salt-forming acidic substituents such as sulfonic acid and carboxylic acid groups.. They are prepared by reacting with metal salts, whereof the metal is chromium or cobalt, upon ortho-hydroxy monoazo dyes, whereby to obtain a 2:1 metal complex, that is, a complex compound which embraces in its structure two molecules of said monoazo dye and 1 atom of said metal. Their direct application to wool, however, does not produce level, well-penetrated dyeings. The lack of the levelness is particularly objectionable when the wool is in the form of a fabric (so-called piece goods) or in the form of yarn.

Now, according to our invention, the dyeing qualities of neutral dyeing, metallized azo dyes are improved, and level, well-penetrated dyeings upon wool piece goods are obtained, if the wool is treated either before the dyeing or simultaneously therewith with an auxiliary polyoxyalkylene glycol agent as more fully defined below, the dyeing itself being effected in the absence of strong concentrations of mineral acid, but in the presence of agents which liberate acid in the dye bath during the process of dyeing.

The polyoxyalkylene glycol used as auxiliary agent

in our invention is a reaction product of ethylene oxide upon a polyoxypropylene glycol, of the class described more fully in L. G. Lundsted's U. S. P. 2,674,619. We prefer for our invention the product obtained by starting with a polyoxypropylene glycol having a molecular weight in the range of 900 to 2000, and reacting upon it with ethylene oxide until its molecular weight has increased to about 7000 to 9000. Under these conditions, the condensation product may be said to consist of some 10 to 22 wt. percent of polyoxypropylene glycol and 90 to 78 wt. percent of polyethylene oxide. This product is water soluble, and may be readily applied to the fabric from an aqueous bath at a temperature of 190° to 225° F.

That this agent should at all be helpful in the dyeing of wool is very surprising, inasmuch as the agent itself is basically a discharge agent. When applied to dyed wool in quantity of 10% by weight (based on the weight of the fiber), it will strip the fiber of about 80% of its color. In smaller concentrations, but exceeding 2% on the weight of the fiber, it acts in the dye bath as a resist or reserve, diminishing the tendency of the dye to go on the fiber. But we find that the agent assists in achieving the purposes of this invention, if applied to the wool in a quantity of 0.5 to 2% by weight of the fiber.

The application of the mentioned auxiliary agent to the wool fiber may be made in a separate treatment from an aqueous bath, prior to treatment with the dye bath, or the agent may be added directly to the dye bath. Where the pre-treatment course is followed, the fabric may be heated in the aqueous solution of the auxiliary agent, at 190° to 225° F. for a few minutes, whereupon the dye may be entered into the same bath, and heating continued for an hour or more. In such a case, the acid generating agent may be either added to the pretreatment bath or entered with the dyestuff.

The acid generating agent is preferably an ammonium salt of an inorganic or organic acid, for instance ammonium sulfate, diammonium acid phosphate, ammonium chloride, ammonium tartrate, ammonium acetate or mixtures thereof. But it may also be an ester which readily undergoes hydrolysis at the dyeing temperature, for instance ethyl formate, methyl lactate, or other lower alkyl ester of a water-soluble aliphatic acid. The esters are preferred to the ammonium salts when dyeing is done at a temperature above the boiling point, inasmuch as here a closed vessel is required, and unless vented occasionally the accumulated ammonia may exert a neutralizing effect on the acid liberated in the dye bath.

Concentrations of the acid generating agent corresponding to about 2 to 7% based on the weight of the fiber are generally satisfactory. As for the concentration of the dyestuff, this will naturally vary with the strength of dyeing desired, and may follow the customary practice. Variations of 0.2 to 5% of dyestuff, on the weight of the fabric come into consideration from this view point.

The dyeing generally begins at an initial pH of about 7.0 to 7.5 and ends at a final pH of about 6.0, as ammonia is driven off or the acid generating agent hydrolyzes during the dyeing cycle. The addition, near the end of the dyeing, of 0.5% acetic acid (based on the weight of the fiber), when dyeing heavy shades, is sometimes desirable to effect an efficient exhaustion of color from the bath. This lowers the final pH to about 5.5.

Following dyeing, the fabric may be rinsed and dried in ordinary manner.

Although this invention is directed primarily to the use of neutral, metallized azo dyes, selected neutral-dyeing unmetallized wool dyes also apply more levelly in this process, but they show inferior wet fastness to the

metallized dyes. They are useful for shading, especially where brightness is desired.

In lieu of a single dyestuff, mixtures of dyestuffs of the class above indicated may be employed. It is a special, unforeseen advantage of our invention that slow-dyeing and rapid-dyeing dyes of the class mentioned may be used together, inasmuch as our special process seems to level off their rates of dyeing so that they apply uniformly, producing pleasing, level blends.

Without limiting our invention, the following examples are given to illustrate our preferred mode of operation. Parts mentioned are by weight. "(O. w. f.)" means based on the weight of the fiber.

Throughout these examples, the auxiliary agent employed was an ethylene oxide-polyoxypropylene glycol condensation product of about 8000 to 9000 molecular weight and in which the polyoxypropylene component constituted about 10 to 22% by weight. The procedure of treatment was as follows:

Example 1

5 parts of wool gabardine were placed in 165 parts of water, at room temperature, containing 0.2 part (4.0% o. w. f.) of ammonium sulfate and 0.05 part (1.0% o. w. f.) of the auxiliary agent above indicated. The mass was heated to the boil and held there for 10 minutes. The dye (of identity and quantity indicated in the table below) was then added, and dyeing at 212° F. was continued for 1.25 hours, whereupon the dyed fabric was removed, rinsed and dried in the usual manner.

By the above procedure, the following dyes were tested:

	Dye	Quantity in percent o. w. f.	Shade obtained
a	2-aminophenol-4-sulfonamide ⟶ 8-acetamido-2-naphthol, Cr/2	0.36	Gray.
b	2-aminophenol-4-sulfonamide ⟶ 2-naphthol, Co/2	0.36	Red.
c	4-nitro-2-aminophenol ⟶ 2-napthhol, Cr/2	0.57	Brown.
d	2-amino-5-methoxy-phenol ⟶ 2-naphthol- Cr/2	0.66	Blue.
e	2-aminophenol-4-sulfonamide ⟶ 1-(3-sulfamylphenyl) 3-methyl-5-pyrazolone, Cr/2	0.35	Orange.
f	4-nitro-2-aminophenol ⟶ acetoacetanilide, Co/2	0.12	Yellow.

Example 2

The procedure of Example 1 was repeated with several of the dyes listed in the above table, except that the quantity of auxiliary agent was varied from 0.5% to 2% o. w. f. The observations may be summarized as follows:

When using 0.5% o. w. f. of the auxiliary agent, dyeings were obtained which were much improved as to levelness compared to dyeings made without an auxiliary agent in the dye bath, but not quite so level as those obtained by using 1% o. w. f. of the auxiliary agent (Example 1). Dyeings made with 2% of the agent were as level as in Example 1 but a trace weaker.

Example 3

Simultaneous treatment procedure.—5 parts of wool gabardine were entered into a dye bath, at room temperature, 165 parts of water 0.05 part (1% o. w. f.) of the auxiliary agent and 0.20 part (4% o. w. f.) of ammonium sulfate, and the selected dye from the table in Example 1, in the quantity therein indicated. The bath was heated rapidly to the boil, where it was held for 1.25 hours. The fabric was removed, soaped, rinsed with water and dried.

The above procedure was repeated with each of the dyes tabulated in Example 1, and good, level dyeings of the shades therein indicated were obtained in all cases.

Example 4

When ammonium acetate was substituted for ammonium sulfate in Example 1*b*, a red dyeing was obtained comparing favorably in levelness and penetration to the dyeing obtained in Example 1.

Example 5

Example 1*b* was repeated at 190° F. A red dyeing was obtained equal in levelness to that of Example 1. A longer dyeing period, however, was required to effect good exhaustion.

Example 6

A piece of wool fabric 8 inches wide by 4 feet long was dyed in the Barotor pressure dyeing machine under pressure to attain and maintain a temperature of 225° F. throughout the dyeing cycle. The material was pretreated for 15 min. at 225° F. in 33 parts (o. w. f.) of water containing 0.8% (o. w. f.) of the auxiliary agent above indicated and 5.0% (o. w. f.) of ammonium sulfate.

The dye of Example 1*b* 0.15% (o. w. f.) was dissolved in hot water containing 0.2% (o. w. f.) of the same auxiliary agent, and the solution was added to the treatment bath in the dyeing machine. Dyeing was continued at 225° F. for 1.25 hours; 0.75% (o. w. f.) acetic acid was added, and after 15 minutes longer at 225° F., an additional 0.75% acetic acid was added, and dyeing was continued for 15 minutes longer at 212° F. A more level, well-penetrated dyeing of red shade was obtained, compared with a dyeing by the same procedure without the aid of the assistant.

Example 7

20 yards of wool gabardine piece goods weighing 17 lbs. were dyed in an 18 inch dyeing bath as follows using a 33 to 1 bath ratio: The goods were pretreated with 1% (2.72 oz.) of the auxiliary agent above indicated, and 5% ammonium sulfate (13.6 oz.), by starting cold and raising the temperature to 212° F. as quickly as possible. The bath was boiled 10 minutes. Then the following dye mixture, previously dissolved in 8.0 gals. of hot water was added over a period of 10 minutes: 0.215% (o. w. f.) of the gray dye of Example 1*a* above and 0.062% (o. w. f.) of the sulfonated blue dye of U. S. P. 1,131,516.

The bath was raised back to 212° F. in 5 minutes, and the material was dyed for 1.25 hours. The dyeing obtained was a gray-blue shade and was level and well penetrated.

Example 8

The procedure and dye of Example 1*a* above were applied to wool crepe, and resulted in a well-penetrated gray dyeing.

It will be understood that the details of the above examples may be varied widely without departing from the spirit of this invention.

We claim as our invention:

1. In the process of dyeing wool at a pH of 7.5 to 5.5 with neutral dyeing, metallized complexes of ortho-hydroxyazo dyes which are free of salt-forming acid substituents and whose structure embraces two molecules of a monoazo dye and one atom of a metal selected from the group consisting of chromium and cobalt, the improvement which consists of effecting the dyeing in the presence of an auxiliary agent and of a reagent adapted to generate acid at the dyeing temperature, said auxiliary agent being a poly-oxyalkylene glycol formed by condensing ethylene oxide and polyoxypropylene glycol, said agent having a molecular weight in the range of 7000 to 9000, and said polyoxypropylene component constituting from 10 to 22% by weight of the entire molecule, said auxiliary agent being present in quantity not exceeding 2% by weight of the fiber.

2. A process of dyeing wool, which comprises treat-

ing the same at a pH of 7.5 to 5.5 and at temperatures in the range of 190° to 225° F., with an aqueous solution of an auxiliary agent and with an aqueous dye bath containing a metallized complex of an ortho-hydroxyazo dye whose structure embraces two molecules of a monoazo dye and one atom of a metal selected from the group consisting of chromium and cobalt and which is free of sulfo and carboxy groups, said dye bath containing further a reagent adapted to generate acid at the dyeing temperature, said auxiliary agent being a water-soluble polyoxyalkylene glycol formed by condensing ethylene oxide and polyoxypropylene glycol, said agent having a molecular weight in the range of 7000 to 9000, in which the polyoxypropylene component constitutes from 10 to 22% by weight of the entire molecule, and said acid generating agent being a member of the group consisting of ammonium salts of inorganic acids, ammonium salts of lower aliphatic acids, and lower alkyl esters of water-soluble aliphatic acids, said auxiliary agent being employed in quantity of 0.5 to 2% by weight based on the weight of the fiber, and said acid generating agent being present in quantity of 2 to 7% by weight based on the weight of the fiber.

3. A process as in claim 2, the treatment with said auxiliary agent being applied prior to treatment with the dyestuff.

4. A process as in claim 2, the two treatments being applied simultaneously from a single dye bath.

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U. S. DEPARTMENT OF COMMERCE

PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,835,550 Joseph F. Laucius et al. May 20, 1958

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

Column 4, line 35, for "bath" read -- beck --.

Signed and sealed this 29th day of July 1958.

(SEAL)
Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents