

UNITED STATES PATENT OFFICE

2,517,751

DYEING OF CELLULOSE ACETATE WITH
ACID DYES IN AN AQUEOUS SOLUTION
CONTAINING A MIXTURE OF SWELLING
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1

The present invention relates to an improved method of dyeing cellulose acetate, and to dye-bath compositions suitable for carrying out the dyeing method.

Two general methods are available and widely practiced for dyeing cellulose acetate from aqueous solutions of the acid dyestuffs, namely the "alcohol assistant" method, and the "acid assistant" method. In accordance with the first mentioned method, the dyeing is carried out in the presence of an alcohol, such as ethyl, methyl, or isopropyl alcohol, etc., dissolved in the aqueous solution of the acid dyestuff, while in accordance with the second method, the dyeing is effected in the presence of a mixture of organic and inorganic acids dissolved in the aqueous dyebath.

Of these two methods, the "alcohol assistant" method has the advantage of producing dyeings of superior wash-fastness, while the "acid assistant" method is more economical.

In the case of both the alcohol and acid assistants, the assistants have to be present in the bath in high concentration before their favorable effects on the dyeings obtained are noticeable, which greatly increases the cost of the dyeing operation. For instance, in the case of methyl, ethyl, or isopropyl alcohol, the alcohol has to be present in the bath in concentrations of 60% or more by volume, if deep wash-fast dyeings are to be obtained. The acid assistants must also be present in high concentrations of greater than 5% and approaching the critical concentration at which de-lustering of the cellulose acetate by the acid takes place under normal conditions of dyeing as respects concentration of the dye, time, and temperature. For instance, in the case where the acid assistant consists of a mixture of formic, acetic, and sulfuric acids, each of the acids has to be present in the bath in a concentration of 8.3% by weight, making a total acid concentration of about 25%, which is much higher than is desirable for economical, commercial practice. Further, although satisfactory dyeings on cellulose acetate from aqueous solutions of the acid dyestuffs, containing as dyeing assistant, a mixture of formic, acetic, and sulfuric acids may be obtained, the use of the noxious formic and acetic acids in the open machines preferred by the dyers is prohibited and special apparatus is required for carrying out the dyeing process.

The present dyeing method involves a modification of the aforementioned conventional dyeing procedures whereby all of the advantages of the "alcohol assistant" method and the "acid

2

assistant" method are obtained using aqueous dyebaths containing the acid dyes in normal concentration and an alcohol or acid dyeing assistant in a concentration of less than 1/2 that previously required.

I find that when small amounts of certain hydroxy derivatives of benzene or of poly-hydro-benzene are dissolved in aqueous solutions of the acid dyestuffs, the concentration of alcohol or acid primary dyeing assistant in the bath may be drastically reduced without detriment to the dyeings obtained on cellulose acetate from the baths. Of the available hydroxy benzenes and hydroxy poly-hydro-benzenes, those suitable for the use here contemplated, from the viewpoint of water-solubility, lack of objectionable odor in use, and resistance to oxidation, are resorcinol, phloroglucinol, and cyclohexanol.

Other factors being equal, such as the particular acid dyestuff used, the concentration of the dye in the bath, the duration of the dyeing operation, and the temperature of the bath, all of which factors may be adjusted relatively to each other depending upon the dye used and the depth of shade desired, the dyeings obtained with the dyebaths containing small amounts of resorcinol, phloroglucinol, or cyclohexanol, and materially reduced amounts of alcohol or acid assistants, are equivalent in all respects to the dyeings obtained from baths containing the alcohol or acid assistants in the higher concentrations, and which do not contain the resorcinol, phloroglucinol, or cyclohexanol.

The following examples will illustrate the process of the present invention in comparison with conventional procedures.

Example I

A fabric formed from yarns of cellulose acetate was immersed for eight minutes in a dyebath consisting of water, 30% ethyl alcohol, by volume, and 3% resorcinol, by weight, and having dissolved therein about 0.8% of Brilliant Wool Blue BL (Color Index No. 833). The temperature of the bath was 80° F. The fabric was then withdrawn, partially dried, and washed in a 1% aqueous soap solution, after which it was rinsed and dried.

A sample of the same cellulose acetate fabric was dyed, under exactly the same conditions, of temperature and immersion time, by immersing it in a bath consisting of the dyestuff, and 75% ethyl alcohol and 25% of water, by volume.

The dyed fabrics obtained using the two different baths were found to be dyed to substan-

3

tially the same deep blue shade, and the dyeings showed equivalent fastness during the scouring step.

Example II

A cellulose acetate fabric was immersed in a dyebath consisting of water, 3% sulfuric acid by weight, and 2.5% of resorcinol, by weight, and having dissolved therein about .25% of Orange II (Color Index No. 151). The fabric was immersed in the bath at a temperature of 90° F.; the temperature then was gradually raised over a period of about one-half hour to 120° F., and held at 120° F. for ½ hour. The fabric was then rinsed, washed in a 1% aqueous soap solution, again rinsed, and dried.

A sample of the same fabric was dyed under identical conditions of temperature and immersion time but from a bath consisting of the dye-stuff, water, and about 8⅓% acetic acid, 8⅓% formic acid and 8⅓% sulfuric acid, by weight.

After dyeing, the fabrics were found to be dyed to substantially the same deep yellow-orange color, and showed equivalent fastness to the scouring treatment.

Example III

A cellulose acetate fabric was immersed in a dyebath consisting of water, 1% resorcinol, by weight, and 2.2% sulfuric acid by weight, and having dissolved therein 0.2% of Anthralan Red BA (Color Index No. not listed) for one hour at a temperature of 175° F. The fabric was thereafter rinsed, washed with a 1% aqueous soap solution, rinsed and dried.

The fabric was dyed to the same clear red shade, and had the same wash-fastness as a similar fabric dyed from an aqueous bath containing 8⅓% acetic acid, 8⅓% formic acid, and 8⅓% sulfuric acid, by weight, under the conditions described in U. S. Patent No. 2,249,607.

The same results, as to similarity of shade and fastness to dyeing were obtained when two samples of cellulose acetate fabric were dyed from aqueous baths having compositions as described in Example II, but containing, as the acid dye-stuff, about 2.5% of Fast Brown R (Color Index No. 175).

The same results were also obtained when two samples of cellulose acetate fabric were dyed from aqueous baths having compositions as described in Example II, but containing about 3.3% of cyclohexanol by volume, and about 2% sulfuric acid, by weight.

Other acid dyestuffs which may be used are:

	Color Index No.
Fast Silk Yellow G.....	145
Amido Yellow E. Pr.....	11
Alizarine Supra Blue A.....	(Not listed)
Artol Brown BL.....	
Artol Green GL.....	
Artol Red BL.....	
Croceine Orange Y.....	26

As will be observed, the presence of about 3% or less of resorcinol or cyclohexanol in the bath permits a reduction in the amount of ethyl alcohol assistant required for effective dyeing from 60% by volume to 30% by volume under the dyeing conditions described. The alcohol concentration may be reduced still further, in some cases and may range from about 10% to about 30% by volume, depending upon the precise dyeing conditions, the lower concentrations being satisfactory, for instance, at somewhat higher

4

temperatures of the bath. In the case of the acid assistant, as is apparent from Example 2, the presence of about 2.5% of resorcinol by weight in the bath permits a reduction in the amount of acid required from 25% by weight to only 3% by weight. Moreover, when the resorcinol is used, excellent dyeings are obtained from a bath containing the inorganic acid only as acid assistant. The possibility of eliminating the noxious formic and acetic acids is most unexpected and highly advantageous. The dyeings obtained from the baths containing resorcinol and sulfuric acid, in the indicated low concentrations, are in every way comparable with those obtained from baths containing a high proportion of the mixed organic and inorganic acids, under the same dyeing conditions, and in the absence of the resorcinol.

As will be understood, the actual proportionate reduction in the amount of the alcohol or acid assistant required for satisfactory dyeings made possible by the presence of the resorcinol, phloroglucinol, or cyclohexanol will vary to some extent depending upon the dyeing conditions.

In general, however, the dyebaths used in accordance with the invention will comprise an aqueous solution of the selected acid dyestuff containing a small amount of resorcinol, phloroglucinol, or cyclohexanol, and as primary dyeing assistant, a lower aliphatic alcohol or acids in an amount equal to less than about ½ the amount of such assistants required to dye cellulose acetate with the acid dyes from aqueous solution by conventional methods under normal conditions of dyeing as regards concentration of the dye, the period of dyeing and the temperature of the bath, and in the absence of the mentioned auxiliary assistants. The amount of resorcinol, phloroglucinol, or cyclohexanol will usually be from about 1 to 4%, but when phloroglucinol is used, it may be desirable to increase the concentration thereof in the bath to about 6%.

The mixture of alcohol or acid with resorcinol, phloroglucinol, or cyclohexanol is more strongly absorbed by the cellulose acetate fibers than is the alcohol or acid assistant alone. Exhaustion trials do not show any appreciable preferential absorption of the alcohol or acid, although the dye exhaustion is approximately 60-80%. It appears that the cellulose acetate fiber-alcohol or acid mixture with resorcinol, phloroglucinol, or cyclohexanol has a greater solvent power for the dye than a cellulose acetate fiber-alcohol or acid system, permitting more rapid and thorough diffusion of the dye through the structure.

That the use of resorcinol, phloroglucinol, or cyclohexanol in combination with the reduced amounts of alcohols or acids as primary dyeing assistants involves a different mechanism or phenomenon in relation to the dyeing of cellulose acetate from aqueous solutions of acid dyestuffs, as compared to the alcohols or acid assistants alone, is evidenced by the different effect which the media have on the physical structure of the cellulose acetate when they are used in excess. If the poly-hydroxy-benzene or hydroxy hexahydro-benzene is not present, and the dyebath contains an excessive amount of alcohol or acid assistant, that is an amount in excess of the critical concentration which causes delustering, the cellulose acetate structure undergoes marked shrinkage or contraction, whereas when the poly-hydroxy-benzene or hydroxy-hexa-hydro-benzene is present, and the alcohol or acid concentration

5

is in excess of the delustering concentration, the cellulose structure expands and is elongated.

Whatever may be the precise explanation for the remarkable effects of small amounts of resorcinol, phloroglucinol, or cyclohexanol in combination with the conventional alcohol or acid assistants, the dyeings obtained in accordance with the present dyeing method compare favorably in all respects with the dyeings obtained from dyebaths in which the alcohol or acid dyeing assistants are used in high concentrations. The results are the more striking inasmuch as it has not been found possible to satisfactorily dye cellulose acetate from aqueous acid dye solutions containing resorcinol, phloroglucinol, or cyclohexanol only, in the absence of the primary dyeing assistant, even when the former are present in increased concentrations.

The invention has been described more particularly in connection with the use of resorcinol, phloroglucinol, or cyclohexanol in combination with alcohols or acids as the primary dyeing assistants, since the alcohols and acids are most commonly used. However, I have also found that very beneficial results are obtained by the addition of a hydroxy benzene or hydroxy-polyhydro-benzene as described herein to aqueous solutions of acid dyes containing, as primary dyeing assistants for cellulose acetate, substances other than the alcohols or acids, such as esters of the alcohols with lower fatty acids, of the type of butyl acetate, butyl formate, ethyl acetate, etc. as well as esters of the type of benzyl acetate. The amount of such esters required for the obtention of excellent dyeings on cellulose acetate from aqueous solutions of the acid dyes is also materially reduced when the bath contains resorcinol, phloroglucinol, or cyclohexanol in the previously stated low concentrations.

The cellulose acetate to be dyed may be in fabric form, in the form of packaged yarn, skeins, etc., or it may be in the form of films, sheets, or the like.

Variations and modifications may be made in carrying out the dyeing procedure described herein, and in the specific composition of the dyebaths without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath consisting of water, and acid dye, from 10 to 35 volume percent of a lower aliphatic alcohol as primary dyeing assistant, and from 1 to 6 percent by weight of an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol.

2. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath containing an acid dye, an ester of an alcohol with an organic acid as primary dyeing assistant, and an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol, the concentration of the ester in the bath being less than one-half the concentration thereof required to facilitate dyeing of the acetate with the acid dye from aqueous solution under corresponding dyeing conditions in the absence of the auxiliary assistant.

3. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath containing an acid

6

dye, an acid as primary dyeing assistant, and an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol, the concentration of the acid dyeing assistant in the bath being less than one-half the concentration thereof required to facilitate dyeing of the acetate with the acid dye from aqueous solution under corresponding dyeing conditions in the absence of the auxiliary dyeing assistant.

4. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath consisting of water, an acid dye, from 10 to about 35% ethyl alcohol, by volume, and from about 1 to 3% of resorcinol by weight.

5. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath consisting of water, an acid dye, about 30% ethyl alcohol by volume, and from about 1 to 3% of resorcinol, by weight.

6. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath containing an acid dye, from about 2 to about 3.5% sulfuric acid, by weight, and from about 1 to about 3% resorcinol, by weight.

7. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath containing an acid dye, from about 10 to 35% ethyl alcohol by volume, and from about 1 to 6% phloroglucinol, by weight.

8. Method of dyeing cellulose acetate with an acid dye comprising the step of treating the acetate with an aqueous dyebath consisting of water, an acid dye, from about 10 to 35% ethyl alcohol and from about 1 to 4% cyclohexanol, by volume.

9. A dyebath for use in dyeing cellulose acetate with acid dyes and consisting of an aqueous solution of an acid dye containing from 10 to 35 volume percent of a lower aliphatic alcohol as a primary dyeing assistant and from 1 to 6 percent by weight of an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol.

10. A composition for use in dyeing cellulose acetate with acid dyes comprising an aqueous solution of an acid dye, an ester of an alcohol with an organic acid as primary dyeing assistant and an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol, the concentration of the ester in the solution being less than one-half the concentration thereof required to facilitate dyeing of the acetate with the acid dye from aqueous solution under corresponding dyeing conditions in the absence of the auxiliary dyeing assistant.

11. A composition for use in dyeing cellulose acetate with acid dyes comprising an aqueous solution of an acid dye containing an acid as a primary dyeing assistant, and an auxiliary dyeing assistant selected from the group consisting of resorcinol, phloroglucinol, and cyclohexanol, the concentration of the acid primary dyeing assistant in the solution being less than one-half the concentration thereof required to facilitate dyeing of the acetate with the acid dye from aqueous solution under corresponding dyeing conditions in the absence of the auxiliary assistant.

12. A dyebath for use in dyeing cellulose acetate with acid dyes consisting of an aqueous solu-

7

tion of an acid dye containing from about 10% to about 35% ethyl alcohol, by volume, and from about 1 to about 3% resorcinol, by weight.

13. A dyebath for use in dyeing cellulose acetate with acid dyes consisting of an aqueous solution of an acid dye containing about 30% ethyl alcohol, by volume, and from about 1 to about 3% resorcinol, by weight.

14. A composition for use in dyeing cellulose acetate with acid dyes comprising an aqueous solution of an acid dye, containing from about 2 to 3.5% sulfuric acid, by weight, and from about 1 to 3% resorcinol by weight.

15. A composition for use in dyeing cellulose acetate with acid dyes comprising an aqueous solution of an acid dye, containing ethyl alcohol as a primary dyeing assistant and from about 1 to 6% by weight of phloroglucinol, the concentration of the primary dyeing assistant in the bath being less than one-half the concentration thereof required to facilitate dyeing of the acetate with the acid dye from aqueous solution under corresponding dyeing conditions and in the absence of the phloroglucinol.

16. A composition for use in dyeing cellulose acetate with acid dyes comprising an aqueous solution of an acid dye containing ethyl alcohol

8

as a primary dyeing assistant and from about 1 to 4% by weight of cyclohexanol, the concentration of the primary dyeing assistant in the bath being less than one-half the concentration required to facilitate dyeing of the acetate with the acid dye from aqueous solution under normal dyeing conditions and in the absence of cyclohexanol.

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