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SIMULTANEOUS DYEING OF WOOL AND COTTON FIBROUS MATERIAL WITH CONDENSATION PRODUCT OF FORMALDEHYDE AND MIXTURE OF SULFONES AND HYDROXYBENZENESULFONIC ACIDS

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5 Claims

ABSTRACT OF THE DISCLOSURE

This invention provides a process for the simultaneous dyeing of wool and cellulosic fibrous material with wool- and substantive dyestuffs in the presence of a fibre-affinic wool resisting agent and hexamethylenetetramine. The wool resisting agents used are condensation products of formaldehyde with a mixture of (a) sulfones containing two hydroxybenzene residues linked to the $-\text{SO}_2-$ group and (b) monocyclic hydroxybenzenesulfonic acids. By the present process the deposition of cotton dyestuff on the wool fibre is prevented.

It is known that wool can be advantageously dyed with 30 wool dyes and cellulosic fibres with substantive cotton dyes in one and the same bath, when dyeing is performed in baths that contain in addition to the dyestuffs fibre-affinic wool resisting agents and hexamethylenetetramine and which are of acid reaction at least at the start of the 35 dyeing operation.

It has now been found that particularly valuable results are obtained when the wool resisting agent in the bath is a condensation product of formaldehyde and a mixture of (a) a sulphone containing two monocyclic benzene residues bound to the $-\text{SO}_2-$ groups and further substituted by hydroxyl groups and (b) a monocyclic hydroxybenzenesulphonic acid.

According to this invention wool is dyed simultaneously with cellulosic fibrous material. Suitable cellulosic fibrous materials are regenerated cellulose, such as rayon or spun rayon, as well as native cellulose such as linen or especially cotton. These fibrous materials may be in different stages of their processing, for example loose or mixed yarns or in form of fabrics. They may be present in intimate mixtures, for example in mixed weaves, or the individual types of fibre may form large fibre combinations; this is the case, for example, in fabrics in which warp and weft consist of different types of material, or in carpets in which the pile and the backing are made from different materials. So-called half-wool is specially preferred; it consists of wool and cotton, and this mixture may be intimate or brought about only during the doubling or weaving operation.

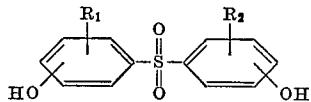
The wool share is dyed with wool dyes which may belong to a variety of types, especially to the group of acid azo dyes or of the acid anthraquinone dyestuffs. Among the azo dyes the monoazo dyes are specially suitable. Advantageous results have been obtained with chromium or cobalt complexes of monoazo dyes that contain more than

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one molecule of dyestuff for every atom of metal bound in complex union, and in which at least one dyestuff molecule is free from sulphonate acid groups and from carboxyl groups not participating in the complex formation. The heavy metal atom may be bound with two different or two identical dyestuff molecules. The complex-forming group of the dyestuffs may be, for example, an ortho-hydroxy-ortho'-aminoazo grouping, an ortho-hydroxy-ortho'-carboxyazo grouping or preferably an ortho, 10 ortho'-dihydroxyazo grouping. A large number of this type of dyestuffs is known.

The cellulose fibres are dyed with substantive cotton dyestuffs which advantageously have as such little affinity for the wool fibre. Otherwise, these dyestuffs may belong 15 to a variety of types. Thus, for example, there may be used azo dyes, especially disazo and polyazo dyes, which may contain metal bound in complex union, preferably copper, or azoxy dyestuffs or sulphonated copper phthalocyanines.

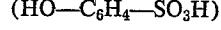
20 The condensation products to be used in the present process are prepared from mixtures of sulphones and sulphonate acids of the kind referred to above. Advantageously, mixtures are used in which the molecular ratio of (a) sulphone to (b) sulphonate acid is from 40:60 to 25 85:15. Both the sulphones and sulphonate acids suitable as relevant starting materials are known. From among the sulphones the dihydroxydiphenylsulphones of the formula



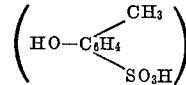
are preferred, in which R₁ and R₂, independently of each other, represent hydrogen atoms or methyl or sulphonate acid groups. As examples the following may be mentioned:

4,4'-dihydroxy-diphenylsulphone,
4,2'-dihydroxy-diphenylsulphone,
4,4'-dihydroxy-3,3'-dimethyl-diphenylsulphone,
4,4'-dihydroxy-diphenylsulphone-3-sulphonate acid
and more especially
4,4'-dihydroxy-3-methyl-diphenylsulphone.

Suitable monocyclic hydroxybenzenesulphonate acids 45 are, for example, phenolsulphonate acid



such as 1-hydroxybenzene-4-sulphonate acid and cresol-sulphonate acids



and especially 1 - hydroxy-2-methylbenzene-4-sulphonate acid.

The condensation of the mixtures with formaldehyde is advantageously performed in an aqueous alkaline medium. For example, a mixture of a sulphone and a sulphonate acid of the indicated kind in water may be 60 alkalized with sodium or potassium hydroxide, then formaldehyde is added (for example 0.9 to 1.1 mols per mol of mixture of hydroxyaryl compounds) and the whole is kept for a prolonged time, for example 5 to 6 hours, at an elevated temperature. Mixtures of sulphones and sulphonate acid can also be prepared by reacting a hy-

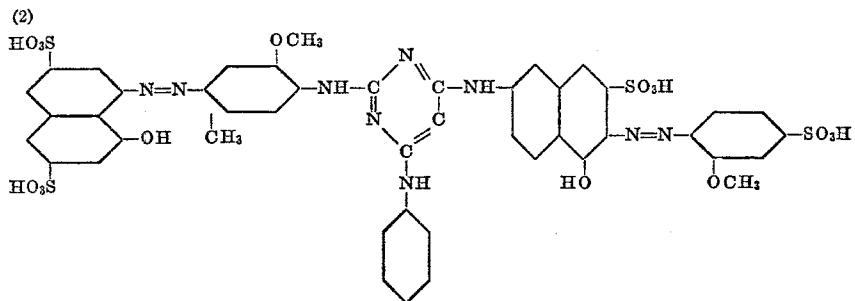
droxybenzene, such as phenol, p-cresol or a xylanol, with concentrated sulphuric acid; then water is added and the alkaline reaction is adjusted by addition of the requisite quantity of alkali metal hydroxide, and without intermediate separation the condensation with formaldehyde is performed.

The amount of the condensation product described above to be added to the dyebath can vary within rather wide limits and may be, for example, from 0.075 to 2%, referred to the weight of the fibrous material to be dyed. The amount of hexamethylenetetramine should be adapted to the amount of condensation product and of acid, but here too there are still rather wide limits within which not only the process can be carried out but even specially good results are obtained. As a general guide rule it may be said that for every part of condensation product at least $\frac{1}{2}$ part and at most 5 parts of hexamethylenetetramine should be used.

The dyebath must have an acid reaction at least at the start of the dyeing operation. The necessary acid reaction is advantageously adjusted by the addition of acetic acid to the dyebath. Since hexamethylenetetramine continuously gives off ammonia during dyeing, the pH value of the dyebath, and incidentally also of the wool, rises in course of time. However, with the quantities of acetic acid conventionally used in dyeing from acid baths it is quite possible to conduct the dyeing process so that even when dyeing takes a relatively long time the pH value never rises substantially above 7 so that it is possible to positively prevent any damage to the wool fibre caused by excess alkalinity.

In the present process the said condensation products prevent the substantive cotton dyestuffs from depositing on the wool. In most instances of dyeing half-wool it is endeavoured to achieve as even a tintorial strength as possible for the two fibres; this is considerably facilitated in dyeing by the present process since the two fibres are dyed at the same time. However, with all types of fibres substantially only the dyestuff intended for the specific fibre deposits on it so that the wool dye is not fixed on the cellulose fibre and the substantive cotton dyestuff is not fixed on the wool.

The present process has the advantage that, even when relatively small quantities of a readily accessible agent



are used, the deposition of the cotton dyestuff on the wool fibre is substantially prevented so that it is possible to obtain from a single bath very clear tone-in-tone or two-tone effects.

To improve its wet fastness the dyed material may, if desired, be after-treated in known manner with an agent that improves wet fastness properties, for example a condensation product of dicyandiamide with formaldehyde.

Instead of adding the condensation product and hexamethylenetetramine separately to the dyebath, the above-mentioned quantities of these substances may be admixed to form stable preparations ready for use and suitable for the performance of the present process. Such preparations are added in an amount from 0.1 to 10%, referred to the weight of the fibrous material to be dyed.

Parts and percentages in the following Manufacturing Instruction and in the example are by weight.

Manufacturing instruction

A mixture of 317 g. of 4,4'-dihydroxy-3-methyl-diphenyl-sulphone and 150.5 g. of 1-hydroxy-2-methylbenzene-4-4-sulphonic acid in 100 ml. of water is rendered alkaline with 463 g. of 30% aqueous sodium hydroxide solution. Then 162 g. of 37% aqueous formaldehyde solution are added and the reaction mixture is stirred for 5 to 6 hours at 100-102° C. The resulting condensation product A may be diluted with water in any desired proportion without any precipitate forming.

Similar condensation products are obtained when

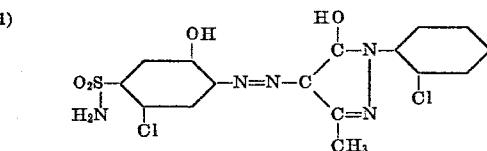
15 4,4'-dihydroxy-diphenylsulphone,
4,2'-dihydroxy-diphenylsulphone,
4,4'-dihydroxy-3,3'-dimethyl-diphenylsulphone,
4,4'-dihydroxy-diphenylsulphone-3'-sulphonic acid or a mixture of these sulphones together with
1-hydroxy-2-methylbenzene-4-sulphonic acid or
20 1-hydroxybenzene-4-sulphonic acid is reacted with formaldehyde in the indicated manner.

Example

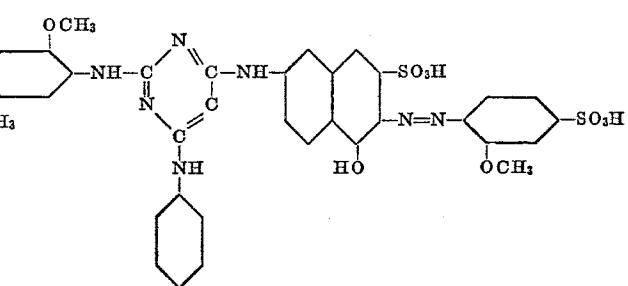
A preparation is manufactured by mixing 1 part of the condensation product A with 2 parts of hexamethylenetetramine.

25 100 parts of half-wool (warp: viscose spun rayon; weft: pure wool boucle yarn) are immersed at 50° C. into a bath containing in 4000 parts of water 40 parts of crystalline sodium sulphate, 2 parts of 40% acetic acid and 1 part of the preparation described above. The bath is kept for 15 minutes at 50° C. and then a solution of the following two dyestuffs in a little water is added:

30 (a) 1:2-chromium complex of the dyestuff of the formula



(b) dyestuff of the formula



60 Within 30 minutes the bath is heated to the boil and the half-wool is dyed for 1 hour at the boil. An even red dyeing is obtained. Shading additions of one or the other of the above dyestuffs may be made at any time in the manner usual in dyeing without the dyeing becoming uneven. Dyestuff (a) has been fixed almost exclusively on the wool and dyestuff (b) almost exclusively on the spun rayon.

65 Instead of the above combination of dyestuffs (a) and (b), the wool dyes shown in column I in combination with the appropriate substantive dyestuffs in column II of the following table may be used in the indicated manner for dyeing half-wool, whereby either on both fibres the same shades (Nos. 1 to 6) or very clean two-tone effects (Nos. 7 to 10) are obtained.

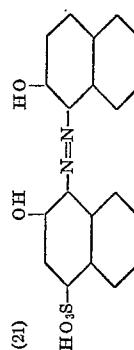
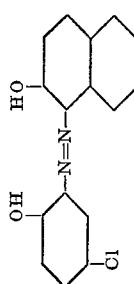
70 If desired, the two constituents of the preparation may be added at the same ratio singly to the dyebath.

| No. | (1) Wool dye | (II) Substantive dyestuff | Shade |
|--------|--------------|---------------------------|--|
| 1..... | (3) | | Blue. |
| 2..... | (5) | | Red. |
| 3..... | (6) | | Yellow. |
| 4..... | (8) | | Mixture of about 83% of the dyestuff of Formula 7 and 17% of the condensation product of 2 mols of dehydrothiophthalein, after-oxidized with hypochlorite. |
| 5..... | (9) | | Mixture of about 75% of the dyestuff of the Formula 10 |
| | | (10) | (10) |
| | | (11) | (11) |
| | | | Mixture of about 25% of the dyestuff of the Formula 11 |
| | | | Violet-brown: |
| | | | |

TABLE—Continued

| No. | (I) Wool dye | | Shade |
|---------|---|--|------------------------------------|
| | (11) Substantive dyestuff | (II) Substantive dyestuff | |
| 6..... | 1:2-cobalt complex of the dyestuff of the formula (12) | Mixture of about 55% of the dyestuff of the formula (13) | Blue-green. |
| 7..... | 1:2-cobalt complex of the dyestuff of the formula (14) | Mixture of about 55% of the dyestuff of the formula 10. (15) | Wool: grey; cellulose: red. |
| 8..... | 1:2-cobalt complex of the dyestuff formula (16) | (17) | Wool: red-brown; cellulose: green. |
| 9..... | 1:2-cobalt complex of the dyestuff of the formula (18) | Dyestuff of the Formula 13..... (19) | Wool: yellow; cellulose: grey. |
| 10..... | 1:2 cobalt complex of the dyestuff of the formula (20) | Condensation product of 2 mols of the dyestuff of the formula and 1 mol of 4,4'-dinitrostilbene-2,2'-disulphonic acid, condensed in NaOH solution under pressure after-oxidized with hypochlorite. | Olive green; cellulose: orange. |

TABLE III—Continued

| No. | (1) Wool dye | (11) Substantive dyestuff | Substantive dyestuff of the composition shown above sub 10/II | Shade |
|------|---|---|---|--------------------------------|
| 11 | Chromium compound in which one molecule each of the dyestuffs | | | Wool: grey; cellulose: orange. |
| (21) |  |  | | Wool: grey; cellulose: red. |

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What is claimed is:

1. The process for the simultaneous dyeing of wool and cotton material, the wool being dyed with wool dyestuffs and the cellulosic fibrous material with substantive cotton dyestuffs, in dyebaths that are of acid reaction at least at the start of the dyeing operation and which contain a fiber-affinic wool resisting agent and hexamethylenetetramine, which process comprises adding as wool resisting agent to the dyebath a condensation product of

5 (1) formaldehyde and

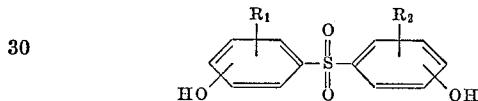
(2) a mixture of

15 (a) sulfones containing two monocyclic benzene residues which are bound with the $-\text{SO}_2-$ group and are further substituted by hydroxyl groups, and

(b) phenolsulfonic acids or cresolsulfonic acids.

20 2. The process according to claim 1, wherein the sulfones (a) are of the formula

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in which R₁ and R₂, independently of each other, represent a member selected from the group consisting of hydrogen atoms, methyl and sulfonic acid groups.

3. The process according to claim 1, wherein the monocyclic hydroxybenzenesulfonic acids (b) are selected from the group consisting of phenolsulfonic acids and cresolsulfonic acids.

4. The process according to claim 1, wherein the condensation products of the indicated kind contain (a) 4,4'-dihydroxy - 3 - methyl-diphenylsulfonic-(1,1') and (b) 1-hydroxy-2-methylbenzene-4-sulfonic acid.

5. The process according to claim 1, wherein the molecular ratio of (a) sulfone to (b) sulfonic acid in the condensation products of the indicated kind is 40:60 to 55 85:15.

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