PATENT SPECIFICATION (11) 1 572 661

1 572 661

(21) Application No. 15269/77 (22) Filed 13 April 1977
(31) Convention Application No. 4849/76
(32) Filed 15 April 1976
(31) Convention Application No. 7186/76
(32) Filed 8 June 1976 in
(33) Switzerland (CH)
(44) Complete Specification published 30 July 1980
(51) INT CL³ D06P 3/54
(52) Index at acceptance
D1B 2L17 2L18 2L27B 2L29B 2L32A 2L34B 2L3 2L5A1 2L5A 2S 2T

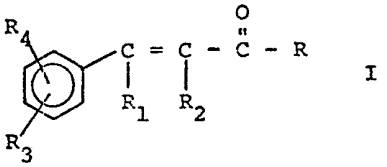


(72) Inventors HANS-PETER BAUMANN
HANS-GEORG KARMANN and
ACHIM WIEDEMANN

(54) PROCESS FOR DYEING IN THE PRESENCE OF A BENZALKETO DERIVATIVE

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a dyeing method effected in the presence of a benzalketo derivative as a dyeing carrier, and, more particularly, provides a method of exhaust dyeing a polyester or polyester blend textile material with a disperse dyestuff characterised in that the dyeing is effected in the presence of a dyeing carrier of formula I,



wherein R is (C_{1-4})alkyl or (C_{1-4})alkoxy,

each of R_1 and R_2, independently, is hydrogen, halogen, methyl or ethyl,

and each of R_3 and R_4, independently, is hydrogen, halogen, hydroxyl, (C_{1-2})alkyl or (C_{1-2})alkoxy,

or a mixture of such dyeing carriers.

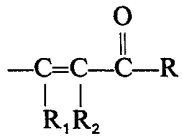
Throughout the specification the term "halogen" means chlorine or bromine, of which chlorine is the preferred halogen.

When R, R_3, or R_4 is alkyl, it is preferably methyl, and when R is alkoxy this is preferably methoxy or ethoxy.

Preferably both of R_1 and R_2, are hydrogen, but when only one of R_1 and R_2 is hydrogen, preferably R_1 is hydrogen.

Preferably either one of R_3 and R_4 is hydrogen while the other is hydrogen, halogen, hydroxyl, (C_{1-2})alkyl or (C_{1-2})alkoxy, or one is halogen while the other is halogen, hydroxyl or (C_{1-2})alkoxy. More preferably each of R_3 and R_4, independently, is hydrogen or halogen, most preferably both being hydrogen.

When both R_3 and R_4 are other than hydrogen, one is preferably *ortho* and the other preferably *para* to the group



Furthermore, when only one of R_3 and R_4 is hydrogen, the substituent signified by the other is preferably *ortho* or *para* to such group.

The preferred compounds of formula I for use in the method of the present invention are benzalacetone and methyl cinnamate.

Many of the compounds of formula I are known and can be produced by known methods. Those not previously known are obtainable in conventional manner from available starting materials.

In the method of the present invention the compounds of formula I are preferably used in association with an emulsifier or mixture of emulsifiers and optionally a solvent or mixture of solvents, and are preferably added to the dyebath prior to dyeing in a formulation containing such extra constituents. The formulations, also provided by the present invention, preferably contain 5 to 95, more preferably 20 to 80 and most preferably 30 to 60 weight percent of one or more compounds of formula I, 5 to 25 and more preferably 10 to

20 weight percent of an emulsifier or mixture of emulsifiers, and 0 to 80, more preferably 0 to 60 and most preferably 20 to 60 weight percent of a solvent or mixture of solvents.

The emulsifiers for use in such formulations may be those conventionally used in disperse dyeing from aqueous dyebaths, anionic ones being preferred. Especially preferred are mono - 2 - ethylhexyl sulphosuccinate, suphonated castor oils and addition products of 1 mole isooctylphenyl with up to 100, preferably 6 to 30 moles ethylene oxide followed by reaction with 1 mole chloroacetic acid to form a terminating group. Mixtures of emulsifiers are preferred.

The solvents or mixtures of solvents used in such formulations may be those conventionally used in disperse dyeing from aqueous dyebaths, and preferably have the properties of carriers for disperse dyestuffs as well as being solvents for the compounds of formula I. Preferred solvents are liquid polyethyleneglycols, i.e. polyethyleneglycols up to a molecular weight of 600, water-soluble alcohols, such as (C_{1-4})alkanols, glycols such as (C_{2-4})glycols, and acetone, and preferred solvents with carrier properties are (C_{1-4})alkyl benzoates and mono-, di- or tri(C_{1-2})alkyl-substituted benzenes, e.g. especially trimethylbenzenes.

The concentration of the compound or compounds of formula I in the dyebath in the method of the invention is preferably 0.4 to 5, or more preferably 0.5 to 2 g/l.

Examples of polyester blend textile materials dyeable according to the method of the invention are those containing polyamides, e.g. wool, or cellulosic materials, e.g. cotton. Polyester-wool blend textile materials are preferably dyed with dyestuffs specially suitable for wool, e.g. C.I. Acid Blue 80 or C.I. Acid Blue 250, while polyester-cotton blend textile materials are preferably dyed with dyestuffs specially suitable for cotton, e.g. direct dyestuffs. According to the kinds of constituents present in the textile material, sufficient suitable dyestuffs can be used in the same dyebath.

The textile material is preferably dyed, in the presence of a compound of formula I, with 0.2 to 8%, more preferably 1 to 4% of its own weight of disperse dyestuff. Suitable disperse dyestuffs for polyesters include those of the anthraquinone or azo dyestuffs series, e.g. C.I. Disperse Orange 25, C.I. Disperse Blue 73, C.I. Disperse Red 73 and C.I. Disperse Blue 16.

An advantage of the method of the present invention is that the dyeing may be effected at temperatures up to 100°C, which is especially desirable when the textile material contains wool as a constituent.

After the dyeing, the textile may be washed, advantageously in the presence of a detergent, and then dried.

The dyeings obtained by the method of the invention are acceptably level and possess a degree of light fastness which would not be expected from pad-dyeings which have been produced at 120—140°C, i.e. at temperatures higher than those normally used in the method of the present invention. The surface of the dyed substrate is not significantly adversely affected, e.g. does not tend to decompose with resultant yellowing.

Furthermore the compounds of formula I do not adversely affect the exhaust of the dyestuffs, so that the dyebath is practically fully exhausted and the dyeings obtained possess notable depth of dyeing.

A further advantage of the method of the invention resides in that the compounds of formula I utilised therein possess a relatively weak and not too irritating smell, and, especially in the case of those not featuring halogen substitution, are relatively non-toxic and easily biologically degradable. Thus their use is acceptable both from the point of view of those engaged in effecting the method and from the ecological standpoint.

In the following Examples, which illustrate the method and formulations of the present invention, the parts and percentages are by weight and the temperatures are in degrees Centigrade.

EXAMPLE 1

5 g of a fabric consisting of a mixture of 55 parts of polyethylene terephthalate fibres and 45 parts of wool are treated in an aqueous dyebath at a temperature of 95° and a goods:liquor ratio of 1:35 for 90 minutes. The dyebath contains 5%, relative to the weight of the fabric, of a mixture of 81.1 parts of a disperse dyestuff mixture consisting of 4% of the dyestuff C.I. Disperse Orange 25, 41.1% of the dyestuff C.I. Disperse Blue 73 and 54.9% of the dyestuff C.I. Disperse Blue 16 and 18.9 parts of the dyestuff mixture for wool consisting of 48.7% of the dyestuff C.I. Acid Blue 80 and 51.3% of the dyestuff C.I. Acid Blue 250, and 2 g per liter of a carrier preparation, which consists of the following constituents in a mixture:

60 parts of benzalacetone
20 parts of a commercial mixture of trimethyl benzenes (mainly 1,2,4 - trimethylbenzene) as solvent serving as carrier
8 parts of mono - 2 - ethylhexyl ester of the sodium salt of sulphosuccinic acid as emulsifier

8 parts of sulphonated castor oil as emulsifier

3 parts of the addition product of 1 mole isooctyl phenol with 6 moles ethyleneoxide units and 1 mole chloroacetic acid as emulsifier

1 part of the addition product of 1 mole isooctyl phenol and 30 moles of ethyleneoxide as emulsifier

A deep marine blue dyeing with good level characteristics is obtained. Both components of the fibre mixture display good level tones. The dyebath is practically fully exhausted.

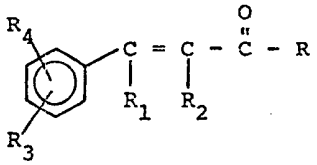
When an equal amount of methyl cinnamate is used in place of benzalacetone, comparable good results are obtained.

EXAMPLE 2

5 g of a polyethylene terephthalate fabric, known commercially under the name "Dacron", (Registered Trade Mark), are treated in a boiling aqueous dye bath at a temperature of about 98° and a goods:liquor ratio of 1:40 for 1 hour. The dyebath contains 1.25% of the disperse dyestuff C.I. Disperse Red 73 and 10% of the carrier preparation used in Example 1, relative to the weight of the fabric. The deep ruby red dyed fabric is washed with the addition of a detergent, hot rinsed, cold rinsed and dried in air.

WHAT WE CLAIM IS:

1. A method of exhaust dyeing a polyester or polyester blend textile material with a disperse dyestuff characterised in that the dyeing is effected in the presence of a dyeing carrier of formula I,



I

wherein R is (C_{1-4})alkyl or (C_{1-4})alkoxy,

each of R_1 and R_2, independently, is hydrogen, halogen, methyl or ethyl,

and each of R_3 and R_4, independently, is hydrogen, halogen, hydroxyl, (C_{1-2})alkyl or (C_{1-2})alkoxy,

or a mixture of such dyeing carriers.

2. A method according to Claim 1, in which R_1 is hydrogen.

3. A method according to Claim 1 or Claim 2, in which R_2 is hydrogen.

4. A method according to any preceding claim, in which one of R_3 and R_4 is hydrogen.

5. A method according to Claim 4, in which one of R_3 and R_4 is hydrogen, and the other is hydrogen, chlorine, hydroxyl, methyl or (C_{1-2})alkoxy.

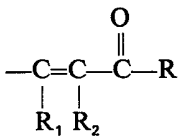
6. A method according to any of Claims 1 to 3, in which one of R_3 and R_4 is halogen, and the other is halogen, hydroxyl or (C_{1-2})alkoxy.

7. A method according to Claim 6, in which one of R_3 and R_4 is chlorine, and the other is chlorine, hydroxyl or (C_{1-2})alkoxy.

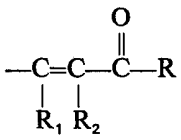
8. A method according to any of Claims 1 to 3, in which each of R_3 and R_4, independently, is hydrogen or halogen.

9. A method according to Claim 8, in which each of R_3 and R_4 is hydrogen.

10. A method according to any of Claims 1 to 3 and 6 to 8, in which one of R_3 and R_4, being a substituent other than hydrogen, is *ortho* and the other, being a substituent other than hydrogen, *para* to the group



11. A method according to any of Claims 1 to 5 and 8, in which one of R_3 and R_4 is hydrogen and the other is a substituent other than hydrogen *ortho* or *para* to the group



12. A method according to Claim 1, in which the dyeing carrier of formula I is benzalacetone or methyl cinnamate.

13. A method according to Claim 1, in which the dyeing carrier of formula I is benzalacetone.

14. A method according to Claim 1, in which the dyeing carrier of formula I is methyl cinnamate.

15. A method according to any preceding claim, in which the concentration of the compound or compounds of formula I in the dyebath is 0.4 to 5 g/l.

16. A method according to Claim 15, in which the concentration is 0.5 to 2 g/l.

17. A method according to any preceding claim, in which the compound or compounds of formula I are used in association with an emulsifier or mixture of emulsifiers and optionally a solvent or mixture of solvents in a formulation added to the dyebath prior to dyeing.

18. A method according to Claim 17, in which the compound or compounds of formula I constitute 5 to 95 weight percent, the emulsifier or mixture of emulsifiers 5 to 25 weight percent, and the solvent or mixture of solvents 0 to 80 weight percent of the formulation.

19. A method according to Claim 17 or Claim 18, in which the emulsifier or mixture of emulsifiers is selected from mono - 2 - ethylhexyl sulphosuccinate, sulphonated castor oils and addition products of 1 mole isooctylphenol with up to 100 moles ethylene oxide followed by reaction with 1 mole chloroacetic acid to form a terminating group.

20. A method according to any of Claims 17 to 19, in which the solvent or mixture of solvents is selected from polyethylene glycols up to a molecular weight of 600, (C_{1-4})alkanols, (C_{2-4})glycols, acetone, (C_{1-4})alkyl benzoates and mono-, di- and tri(C_{1-2})alkyl-substituted benzenes.

21. A method according to any preceding claim, in which the amount of disperse dyestuff used is 0.2 to 8% of the weight of the polyester or polyester blend textile material.

22. A method according to Claim 21, in which the amount of disperse dyestuff is 1 to 4%.

23. A method according to any preceding claim, in which the polyester blend textile material contains wool or cotton.

24. A method according to Claim 1, substantially as described herein with reference to Example 1 or Example 2.

25. A polyester or polyester blend textile material whenever dyed by a method according to any preceding claim.

26. A formulation containing a dyeing carrier or mixture of dyeing carriers of formula I, as defined in Claim 1, an emulsifier or mixture of emulsifiers and, optionally, a solvent or mixture of solvents.

27. A formulation according to Claim 26, containing 5 to 95 weight percent of one or more compounds of formula I, 5 to 25 weight percent of an emulsifier or mixture of emulsifiers, and 0 to 80 weight percent of a solvent or mixture of solvents.

28. A formulation according to Claim 27, containing 20 to 80 weight percent of one or more compounds of formula I, 10 to 20 weight percent of an emulsifier or mixture of emulsifiers, and 0 to 60 weight percent of a solvent or mixture of solvents.

29. A formulation according to Claim 28, containing 30 to 60 weight percent of one or more compounds of formula I, 10 to 20 weight percent of an emulsifier or mixture of emulsifiers and 20 to 60 weight percent of a solvent or mixture of solvents.

30. A formulation according to any one of Claims 26 to 29, in which the emulsifier or mixture of emulsifiers is anionic.

31. A formulation according to Claim 30, in which the emulsifier or mixture of emulsifiers is selected from mono - 2 - ethylhexyl suphosuccinate, sulphonated castor oils and addition products of 1 mole isooctylphenol with up to 100 moles ethylene oxide followed by reaction with 1 mole chloroacetic acid to form a terminating group.

32. A formulation according to any of Claims 26 to 31, in which the solvent or mixture of solvents is selected from polyethylene glycols up to a molecular weight of 600, (C_{1-4})alkanols, (C_{2-4})glycols, acetone, (C_{1-4})alkyl benzoates and mono-, di- and tri(C_{1-2}) alkyl-substituted benzenes.

33. A formulation according to Claim 26, substantially as described herein with reference to Example 1 or Example 2.

34. A method of dyeing according to Claim 1, in which R is (C_{1-4})alkyl.

35. A method of dyeing according to Claim 1, in which R is methoxy or ethoxy.

B. A. YORKE & CO,
Chartered Patent Agents,
98, The Centre,
Feltham.
Middlesex TW13 4EP,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.