PATENT SPECIFICATION (11) 1 558 403

1 558 403

(21) Application No. 18448/76 (22) Filed 5 May 1976
(23) Complete Specification filed 4 Aug. 1977
(44) Complete Specification published 3 Jan. 1980
(51) INT CL³ D06P 1/16//C09B 29/36
(52) Index at acceptance
D1B 2C1A6 2C2B 2C2D1A 2C2D1B 2J 2L14 2L15 2L17 2L29A 2L2A 2L3 2L5A 2L6 2L8
C4P 116 120 122 126 1A3B 1F2 1F4

(72) Inventors JOHN GRAY and DAVID RICHARD WARING

(19)

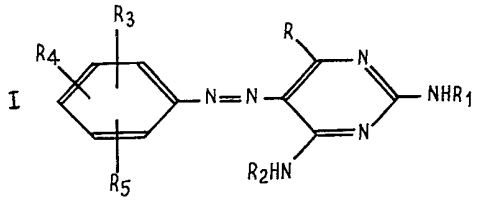
(54) TRANSFER PRINTING

(71) We, KODAK LIMITED, a Company registered under the Law of England, of Kodak House, Station Road, Hemel Hempstead, Hertfordshire, do heaeby 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:—

This invention relates to materials for use in transfer printing, and to methods thereof.

The known techniques of transfer printing are described in an article by D. Burtonshaw, International Dyer and Textile Printer, 335—340, 1971. In the most widely used technique, which is the one to which the present invention relates, a dye capable of sublimation is applied to a non-textile support such as paper or other suitable medium, and the dye is transferred by the action of heat to a contiguous material.

In accordance with the present invention, there is provided a transfer printing sheet comprising a non-textile support bearing a dye having the formula:



I

wherein

R, R_1 and R_2 are each selected from hydrogen, alkyl, substituted alkyl, alkenyl or cyclohexyl; and

R_3, R_4 and R_5 are each selected from hydrogen, alkyl, substituted alkyl, alkenyl, acyl, halogen, cyano, nitro, monofluoromethyl sulphonyl, difluoromethyl sulphonyl and trifluoromethyl sulphonyl.

The substituted alkyl groups from which R, R_1 and R_2 may be selected include, for example, alkyl substituted with alkoxy, halogen, hydroxy, acryloxy and cyano.

The substituted alkyl groups from which R_3, R_4 and R_5 may be selected include trifluoromethyl.

A preferred alkenyl group is allyl.

Preferably, the dye is in a binder, for example a suitable synthetic, semi-synthetic or natural resin. Cellulose esters and ethers may be used as binders.

The non-textile support may be paper, e.g. paper of low porosity, or metal, e.g. an aluminium foil, or a plastics film. All of these supports may be attached to another support on the non-dye-bearing side.

The dye may be applied in a printing ink by the flexographic, gravure, letterpress, silk screen or lithographic process. The dye will usually, although not necessarily, be applied in an imagewise distribution. More than one dye may be applied to the support.

The materials of the present invention may be used to apply a dye or dyes to various polyesters and polyamides, which may be in the form of coatings on other substrates, e.g. metal, leather, cotton or wool. The polyesters or polyamides may be in the form of woven, knitted, bonded or laminated fabrics, or pile fabrics, e.g. carpets.

The materials of the present invention may also be used to apply a dye or dyes to resin-treated cotton and polyester-cotton blends.

Also according to the present invention, there is provided a method of transfer printing a fabric or film of a polyester or polyamide, or a fabric comprising a resin-treated (as herein defined) cellulosic material or a resin-treated (as herein defined) blend of a cellulosic material and a polyester, which comprises placing the dye-bearing side of a transfer printing sheet as defined above in contact with the fabric or film and subjecting the sheet and fabric or film to heat to transfer at least some of the dye from the sheet to the fabric or film.

The transfer of the dye may take place at atmospheric pressure or reduced or increased pressure, or under vacuum, and at a temperature of 180°C to 230°C. The pressure between the sheet and fabric or film may be,

for example, up to 1.5 lb/sq. in. Higher pressures may be used. Apparatus is commercially available for performing transfer printing.

Also according to the present invention, there is provided a fabric or film of a polyester or polyamide, or a fabric comprising a resin-treated cellulosic material or a resin-treated blend of a cellulosic material and a polyester, which has been transfer printed by a method as defined above.

Also according to the present invention, there is provided a printing ink containing a dye having the formula I given above.

By "cellulosic material", we mean natural or regenerated cellulosic material, such as cotton and viscose rayon.

By "resin-treated", we mean that the material has been modified to improve the acceptance of disperse dyes. An example of such a treatment is the application of a cross-linkable urea-formaldehyde or melamine-formaldehyde precondensate, followed by curing or partial curing.

It is found that dyes having the formula I given above used in accordance with the present invention have good sublimation in transfer printing, and give yellow shades on the indicated materials, with generally good fastness to light and to wet treatments. Results are particularly good on polyamides, such as nylon 6.6.

If one or more of R_3, R_4 and R_5 is or are nitro, it is preferred not to use the resulting dyes for printing polyamides or the resin-treated materials because such dyes are less fast to light than other dyes of the formula I.

The preparation of a number of dyes for use in accordance with the invention will now be described.

Examples 1—5.

p-Toluidine (0.01 mole) was dissolved in water (10 ml) and concentrated hydrochloric acid (3 ml). The solution was cooled to 3°C and a solution of sodium nitrite (0.72 g) in water (2 ml) was added at below 5°C. The mixture was stirred for two hours at 0—5°C to complete the diazotisation.

The diazonium solution was then added to a solution of a 2,4-diaminopyrimidine coupler in ethanol or 1:5 (by volume) propionic and acetic acids. After thirty minutes, the dye was filtered off or drowned out into water prior to filtration, depending on its solubility.

The following couplers were used:

Example	Coupler
1	2,4-Dimethylaminopyrimidine
2	2,4-Diethylamino-6-methylpyrimidine
3	2,4-Dibutylamino-6-methylpyrimidine
4	2,4-Dicyclohexylamino-6-methylpyrimidine
5	2,4-Dimethoxyethylamino-6-methylpyrimidine

Examples 6—10.

The procedure of Examples 1—5 was repeated, using the same five 2,4-diaminopyrimidine couplers but with *p*-chloroaniline instead of *p*-toluidine.

Examples 11—25.

The procedure of Examples 1—5 was repeated, using the same five 2,4-dimanopyrimidine couplers but with 3,4-dichloroaniline (Examples 11—15), *p*-trifluoromethylaniline (Examples 16—20) and *p*-acetylaniline (Examples 21—25) respectively instead of *p*-toluidine.

Example 26—30.

Sodium nitrite (0.72 g) was added slowly with stirring to concentrated sulphuric acid (5 ml) at below 70°C. The mixture was warmed to 70°C and then cooled to below 20°C. A mixture of propionic and acetic acids (1:5 by volume, 10 ml) was added drop by drop while the temperature was kept below 20°C. The mixture was cooled to below 5°C and *o*-cyanoaniline (0.01 mole) was added slowly at a temperature below 5°C, followed by the addition of propionic and acetic acids (1:5) at below 10°C. The mixture was stirred for two hours at 0—5°C to complete the diazotisation.

Coupling with the five 2,4-diaminopyrimidines previously listed was carried out as described in Examples 1—5.

Examples 31—35.

The procedure of Examples 26—30 was repeated, using the same five 2,4-diamino-

pyrimidine couplers but with *o*-bromoaniline instead of *o*-cyanoaniline.

The products of Examples 1—35 were used to prepare inks by the following procedure. A sample of each dye (0.5 g) was ball milled with ethyl cellulose (3 g) and a 9:1 (by volume) mixture of ethanol and ethylene glycol (50 g) for 24 hours. The resulting inks were applied to pieces of flexographic transfer printing paper (55 g/sq. m) and allowed to dry. The paper was then used for transfer printing on to polyamide fabric (nylon 6.6) at 200°C for 30 seconds, and on to polyester fabric at 210°C for 30 seconds.

Greenish-yellow prints were produced, having good wash fastness and light fastness.

Samples of a 50:50 polyester/cotton woven blend fabric were impregnated with the following resin formulation to a level of 60—70% wet pick up:

Hexamethylol methyl melamine (type L 5155 supplied by B.I.P. Chemicals Ltd.)	50 g/l
Glyoxal Urea-Formaldehyde precondensate (type BT 333, B.I.P. Chemicals Ltd.)	60 g/l
Monoammonium dihydrogen phosphate	2 g/l
Softener (polyethylene type)	20 g/l

The wet fabric was dried at 110°C for two minutes, then pre-cured at 200°C for 30 seconds.

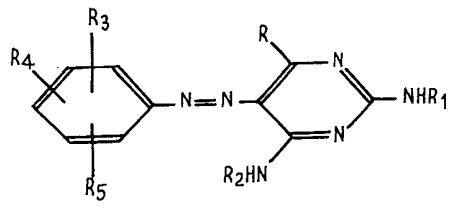
Pieces of transfer printing paper, prepared as described above, were used for transfer printing on to the resin-treated polyester/cotton fabric at 210°C for 30 seconds.

Strong greenish-yellow to yellow prints were produced. The colours had good light fastness, and their fastness to wet treatments was exceptionally good.

WHAT WE CLAIM IS:—

1. A transfer printing sheet comprising a non-textile support bearing dye having the formula:

I



wherein

R, R_1 and R_2 are each selected from hydrogen, alkyl, substituted alkyl, alkenyl or cyclohexyl; and

R_3, R_4 and R_5 are each selected from hydogen, alkyl, substituted alkyl, alkenyl, acyl, halogen, cyano, nitro, and monofluoromethyl sulphonyl, difluoromethyl sulphonyl and trifluoromethyl sulphonyl.

2. A sheet as claimed in Claim 1, wherein R represents hydrogen or alkyl.

3. A sheet as claimed in Claim 2, wherein R represents methyl.

4. A sheet as claimed in Claim 1, 2 or 3, wherein $R_1 = R_2$ = alkyl, substituted alkyl or cyclohexyl.

5. A sheet as claimed in Claim 4, wherein $R_1 = R_2$ = alkyl having 1 to 4 carbon atoms.

6. A sheet as claimed in any one of Claims 1 to 5, wherein R_5 represents hydrogen.

7. A sheet as claimed in Claim 6, wherein R_3 represents hydrogen and R_4 represents 4-methyl, 4-trifluoromethyl, 4-chloro or 4-acetyl.

8. A sheet as claimed in Claim 6, wherein R_3 represents 3-chloro and R_4 represents 4-chloro.

9. A sheet as claimed in Claim 6, wherein R_3 represents 2-cyano and R_4 represents hydrogen.

10. A sheet as claimed in Claim 6, wherein R_3 represents 2-bromo and R_4 represents hydrogen.

11. A sheet as claimed in any one of Claims 1 to 10, wherein the dye is in a binder.

12. A sheet as claimed in any one of Claims 1 to 11, wherein the support is paper.

13. A sheet as claimed in Claim 1 and substantially as hereinbefore described.

14. A method of transfer printing a fabric or film of a polyester or polyamide, or a fabric comprising a resin-treated (as herein defined) cellulosic material or a resin-treated (as herein defined) blend of a cellulosic material and a polyester, which comprises placing the dye-bearing side of a transfer printing sheet as claimed in Claim 1 in contact with the fabric or film and subjecting the sheet and fabric or film to heat to transfer at least some of the dye from the sheet to the fabric or film.

15. A method as claimed in Claim 14, wherein the sheet is as claimed in any one of Claims 2 to 12.

16. A method as claimed in Claim 14 or 15 wherein transfer is effected at a temperature of 180° to 230°C.

17. A method as claimed in Claim 14 and substantially as hereinbefore described.

18. A fabric or film of a polyester or polyamide which has been transfer printed by a method as claimed in Claim 14.

19. A fabric comprising a resin-treated (as herein defined) cellulosic material or a resin-treated (as herein defined) blend of a cellulosic material and a polyester, which has been transfer printed by a method as claimed in Claim 14.

20. A printing ink containing a dye having the formula set out in Claim 1.

21. A printing ink as claimed in Claim 20, wherein the substituents R, R_1 and R_2 of the dye formula have any of the values set out in Claims 2 to 5.

22. A printing ink as claimed in Claim 20 or 21, wherein the substituents R_4, R_5 and R_6 of the dye formula have any of the values set out in Claims 6 to 10.

23. A printing ink as claimed in any one of Claims 20, 21 or 22, also containing a binder.

24. A printing ink as claimed in Claim 20 and substantially as hereinbefore described.

L. A. TRANGMAR, B.Sc., C.P.A.,
Agent 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.