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(71) Applicant *(for all designated States except US)*: **MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA** [IT/IT]; Piazza Kennedy 20, I-00144 Roma (IT).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **SICARDI, Silvio** [IT/IT]; Via Pigafetta, 47bis, I-10129 Torino (IT). **FRIGERIO, Mario** [IT/IT]; Via Zezio, 23, I-22100 Como (IT).

(74) Agents: **GERBINO, Angelo** et al.; Jacobacci & Perani S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).

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(54) Title: A METHOD OF DYEING NATURAL TEXTILE FIBRES WITH A DYEING MEDIUM COMPRISING SUPERCRITICAL CARBON DIOXIDE

(57) Abstract: The method of dyeing natural textile fibres with the use of a dyeing medium comprising supercritical carbon dioxide and a dye provides for the dye to be of the water-soluble, polar type and for the dyeing medium also to comprise a polar cosolvent. The latter is preferably selected from the group consisting of methanol, ethanol, water and mixtures thereof.

A method of dyeing natural textile fibres with a dyeing medium comprising supercritical carbon dioxide

The present invention relates to a method of dyeing textile fibres with the use of a dyeing medium comprising supercritical carbon dioxide and a dye.

Methods of this type have been the subject of considerable interest in recent years, since they are particularly suitable from an ecological/toxicological point of view and are technologically practicable at costs competitive with those of conventional methods which provide for the use of water-based dyeing media.

Supercritical carbon hydroxide has been used with success in methods for dyeing synthetic fibres, for example, polyesters and polyamides, but the results of its use in the dyeing of natural fibres, for example, wool, cotton or silk fibres, have not been so satisfactory.

Disperse dyes, which are normally used for dyeing synthetic fibres, are in fact apolar and soluble in supercritical carbon dioxide, thus permitting vivid and fast dyeing of chemical fibres; these dyes do not, however, have an affinity to natural fibres which are essentially polar.

To obviate this incompatibility, it has been proposed (see, for example, M.L. Colombo et al., "Treatments of cellulosic material with natural products dissolved in SCVF-CO_2" - Proceeding of the 5th Meeting on Supercritical Fluid, March (1998) 357-360) to impregnate the natural fibres with bulking agents such as thiodiglycols and polyethylene glycols before the actual dyeing treatment, but without completely solving the problem. In fact, although this initially achieves a more satisfactory adhesion of the

disperse dye to the fibres, the washings to which the fibres are subsequently subjected nevertheless bring about decolorization thereof.

The object of the present invention is therefore to provide a method of dyeing natural textile fibres with the use of a dyeing medium comprising supercritical carbon dioxide and a dye, which can ensure satisfactory and persistent adhesion of the dye to the fibres.

This object is achieved by means of a method of the type indicated at the beginning of the present description and characterized in that the dye is of the water-soluble, polar type, and in that the dyeing medium also comprises a polar co-solvent.

By virtue of the use of the polar co-solvent, polar dyes can be rendered soluble in supercritical carbon dioxide in which they would otherwise be insoluble, and can thus be brought into contact with the natural fibres for which they have a chemical affinity and on which they can effectively perform their dyeing action which is persistent over time and resistant to washing.

The co-solvent is preferably selected form the group consisting of methanol, ethanol, water and mixtures thereof.

The water-soluble polar dye is preferably of the reactive, direct, cationic, or acid type or the like.

The concentration of the co-solvent in the dyeing medium is advantageously between 2 and 20% and even more preferably between 5 and 10%. These concentrations, as well as all of those given in the remaining part of the present description, in the absence of any indication to the

contrary, should be understood as molar concentrations relative to the moles of CO_2 in the working conditions.

The natural textile fibres which can be dyed by the method of the invention are of substantially any nature, for example, fibres and hair of animal origin, vegetable fibres, and mixtures thereof, particularly wool, cotton and silk fibres.

The general parameters of the dyeing method of the invention are preferably between 70 and 250 bars with regard to pressure, and between 50 and 120°C with regard to temperature.

Further advantages and characteristics of the present invention will become clear from the following examples provided by way of non-limiting indication.

EXAMPLE 1

Dyeing tests were performed in a 1 litre autoclave with a stirrer on samples in the form of small skeins of wool each weighing about 2 g, with a dyeing medium comprising: supercritical CO_2, ethanol as a co-solvent at a molar concentration of about 10% relative to the CO_2, and a quantity of about 1 g, or in any case such as to ensure saturation of the dye bath, of a reactive dye.

The dyeing was carried out for about 2 hours at a pressure of about 200 bars and a temperature of about 90°C. Upon completion of this operation, the autoclave was emptied by depressurization in a single step. The dyed samples were then subjected to rapid washing in running water.

The dyed samples had good colour intensity, good colour-fastness upon washing, and good light-fastness values.

EXAMPLE 2

The tests relating to this example were performed in conditions similar to those of Example 1, with the difference that skeins of cotton were dyed with a direct dye and at about 70°C.

The dyed samples had good colour intensity, reasonable colour-fastness upon washing, and good light-fastness values.

EXAMPLE 3

The tests relating to this example were carried out in similar conditions to those of Example 1 with the difference that a skein of silk was dyed. Moreover, whereas in some tests the same co-solvent was used as in Example 1, in others water at a molar concentration of 2% was used instead.

The dye samples had very good colour intensity, good colour-fastness upon washing, and good light-fastness values.

Naturally, the principle of the invention remaining the same, the details of construction and forms of embodiment may be varied widely with respect to those described purely by way of example, without thereby departing from its scope.

CLAIMS

1. A method of dyeing natural textile fibres with the use of a dyeing medium comprising supercritical carbon dioxide and a dye, the method being characterized in that the dye is of the water-soluble, polar type, and in that the dyeing medium also comprises a polar co-solvent.

2. A method according to Claim 1, characterized in that the co-solvent is selected from the group consisting of methanol, ethanol, water and mixtures thereof.

3. A method according to any one of the preceding claims, characterized in that the dye is selected from the group consisting of reactive, direct, cationic and acid dyes.

4. A method according to any one of the preceding claims, characterized in that the molar concentration of the co-solvent in the dyeing medium is between 2 and 20% and preferably between 5 and 10%.

5. A method according to any one of the preceding claims, characterized in that the natural textile fibres are selected from the group consisting of fibres and hair of animal origin, vegetable fibres, and mixtures thereof.

6. A method according to any one of the preceding claims, characterized in that it is carried out at a pressure of between 70 and 250 bars.

7. A method according to any one of the preceding claims, characterized in that it is carried out at a temperature of between 50 and 120°C.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06P1/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 39 06 724 A (DEUTSCHES TEXTILFORSCHZENTRUM) 13 September 1990 (1990-09-13) column 2, line 38 - line 49 column 3, line 13 - line 15 column 4, line 23 - line 32 column 5, line 1 - line 29; claims 7-9 ---	1-7
A	GB 2 259 525 A (CIBA GEIGY AG) 17 March 1993 (1993-03-17) page 2, last paragraph page 5, line 18 - line 27 ---	1,4-7
A	DE 44 04 839 A (DEUTSCHES TEXTILFORSCHZENTRUM ;JASPER GMBH (DE)) 17 August 1995 (1995-08-17) the whole document ---	1,3-7
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bernardo Noriega, F

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 6 010 542 A (DESIMONE JOSEPH M ET AL) 4 January 2000 (2000-01-04) column 5, line 12 - line 34; claims; example 11 -----	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat' ! Application No
PCT/EP 00/06414

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