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(54) Title: FLUORESCENT DYES FOR PAPER DYEING

(57) Abstract: The present invention relates to an aqueous preparation comprising a fluorescent dyestuff of a specific formula, water, and optionally a dispersing agent, and the use of the aqueous preparation for dyeing cellulose- or polyamide-containing materials.



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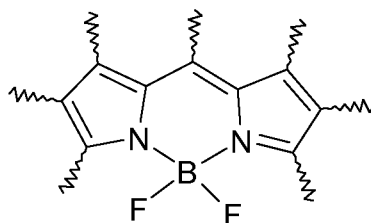
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FLUORESCENT DYES FOR PAPER DYEING

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The present invention relates to an aqueous preparation of a fluorescent dye and its use in dyeing cellulose- or polyamide-containing materials, in particular paper. The dyestuff contains the structural element of a boron dipyrromethene skeleton as shown below.

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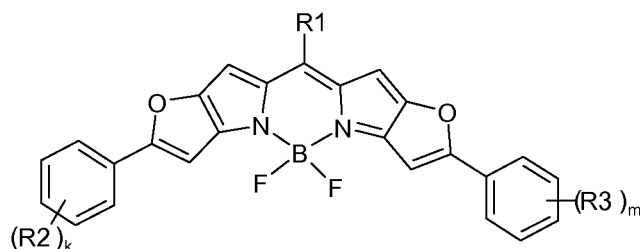


EP 2 022 794 A1 and US 2008/031 1041 A1 disclose molecules with such a boron dipyrromethene skeleton as fluorescent compounds and labeling agents in biological samples. Further, such fluorescent dyes are known from J. Am. Chem. Soc. 2008, 130, 1550-1551, and Chem. Eur. J. 2009, 15, 1096-1 106. The latter article also discloses for two specific dyes an aqueous solution thereof with DMSO.

20 It has now been found that aqueous preparations can be prepared from specific fluorescent compounds with boron dipyrromethene skeleton and used for dyeing, in particular as paper dyes.

Accordingly, the present invention relates to an aqueous preparation containing
25 a compound of formula (1)

- 2 -



(1)

wherein

- 5 R1 represents hydrogen, CN, CF₃, Br, Cl, I; optionally substituted aryl; or optionally substituted alkyl;
- R2 and R3, independently of each other, represent hydrogen; C₁₋₅-alkyl; C₁₋₅-alkoxyl; optionally substituted aryl; optionally substituted phenyl; p-Ci₅-alkoxyphenyl; di(Ci₅-alkyl)amino groups; or -SO₃M, wherein M
- 10 is a cation, preferably hydrogen, alkaline metal, earth alkaline metal, ammonium, or mono-, di-, tri- or tetra-substituted ammonium, in particular mono-Ci₅-alkyl-, di-Ci₅-alkyl-, tri-Ci₅-alkyl-, tetra-Ci₅-alkylammonium, mono-Ci₅-hydroxyalkyl-, di-Ci₅-hydroxyalkyl-, tri-Ci₅-hydroxyalkyl-, tetra-Ci₅-hydroxyalkylammonium, or benzyl-
- 15 tri-Ci₅-hydroxyalkylammonium, or ammonium based on amines derived from nitrogen-containing five- or six-membered saturated heterocycles, such as pyrrolidine, piperidine, morpholine or piperazine or their N-monoalkyl- or N,N-dialkyl-substituted products; wherein R2 and R3 are attached to the aromatic ring at any position;
- 20 k, m are, independently of each other, an integer from 1 to 3, preferably 1 or 2, most preferably 1;

water, and, optionally, a dispersing agent;

- 25 with the proviso that, if the aqueous preparation contains no dispersing agent and R1 is hydrogen, at least one of R2 and R3 is not hydrogen, preferably both R2 and R3 are not hydrogen.

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A preferred proviso is that, if R1 is hydrogen, at least one of R2 and R3 is not hydrogen, preferably both R2 and R3 are not hydrogen.

Further, the present invention relates to the use of the aqueous preparation for
5 dyeing or printing materials containing cellulose and/or polyamide, in particular a cellulose-containing material, preferably paper. In a preferred embodiment, the cellulose-containing material is a pulp or a sheet containing cellulosic material. The invention also relates to a process for dyeing or printing materials containing cellulose and/or polyamide, and a product or paper obtained by the process. Fur-
10 ther preferred embodiments of the invention are described hereinafter and in the claims.

In a preferred embodiment, in the dyestuff of formula (1) R2 and R3, independently of each other, represent hydrogen, $\text{Ci}_3\text{-alkoxyl}$, or $-\text{SO}_3\text{M}$ with M being
15 defined as above, in particular R2 or R3 is methoxy, ethoxy, phenoxy, or $-\text{SO}_3\text{M}$, wherein M is ammonium mono-, di- tri- or tetra-substituted by C_{1-4} -alkanolamines, especially monoethanol-, diethanol- and/or triethanolamine. The groups R2 and R3 may be in o-, m- or p-position. Depending on the number of groups, either p-position or the other positions are preferred. If there are two R2 or
20 R3 groups at the aromatic ring (k or m is 2), these are preferably in o- and m-position. In the most preferred embodiment, there is one R2 group and one R3 group at each aromatic ring (k, m is 1) and both are in p-position.

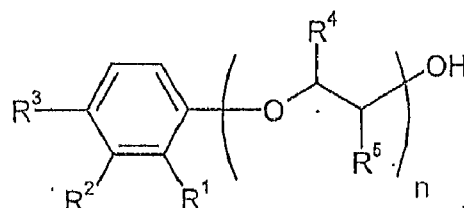
In a further preferred embodiment, in the dyestuff of formula (1) R1 represents
25 hydrogen, CN, or CF_3 .

Possible substituents of the aryl, phenyl, and/or alkyl residues for R1, R2 and R3, respectively, in the compound of formula (1) are $\text{Ci-C}_4\text{-alkyl}$, $\text{Ci-C}_4\text{-alkoxy}$, halogen, hydroxyl, amino, sulfonic, carboxylic, CN or nitro. Preferably, aryl, phenyl
30 and/or alkyl are not substituted.

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In a particularly preferred compound of formula (1), R₁ is H, and R₂ and R₃ are both -SO₃M, with M being defined as above. Further preferred in this embodiment, k and m are 1, and R₂ and R₃ are both in p-position. In a further particularly preferred compound of formula (1), R₁ is H, and R₂ and R₃ are both methoxy. Further preferred in this embodiment, k and m are 1, and R₂ and R₃ are both in p-position

The dispersing agent can be any dispersing agent known from the state of the art, which is suitable for dispersing the compound of formula (1). In a preferred embodiment, the dispersing agent is an alkoxyated aryl compound, preferably an ethoxylated or propoxylated aryl compound, in particular a compound as described in EP 1 285 941 A1 or EP 1 184 402 A2. Preferred dispersing agents have the following formula (2):



(2)

wherein

R¹, R² and R³ are, independently of each other, hydrogen, optionally substituted cyclohexyl or phenyl, wherein at least one of the residues R¹ to R³ is not hydrogen,

R⁴ and R⁵ are, independently of each other, methyl or hydrogen, and

n is an integer from 21 to 40.

Possible substituents of the cyclohexyl or phenyl residues are Ci-C₄-alkyl, C₁-C₄-alkoxy, halogen, CN or nitro. Preferably, phenyl and/or cyclohexyl are not substituted. Preferably, in the compound of formula (2) n is an integer of 26 to 35, most

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preferably $n = 29$ to 31 . Further preferred, R_3 is phenyl. In another preferred embodiment, at least one of R_1 to R_3 is cyclohexyl. In the most preferred dispersing agent, R_3 is phenyl, R_1 , R_2 , R_4 and R_5 are hydrogen, and n is 30 .

- 5 In another preferred embodiment, the dispersing agent is a polyalkylenepolyimine, in particular such a compound as described in EP 1 555 280 A2. Preferred dispersing agents are polyalkylenepolyimines having alkoxy units and anionic groups, especially those from the group consisting of $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{OSO}_3^-$, $-\text{PO}_3^{2-}$ and $-\text{P}(\text{OR})_2^-$, wherein R represents hydrogen or optionally substituted
10 alkyl, cycloalkyl or aryl.

The aqueous preparation of the dyestuff of formula (1) contains preferably 0.01 to 50% by weight, more preferably 0.5 to 20% by weight, most preferably 1 to 10% by weight, in each case of compound of formula (1). Preferably, the aqueous
15 preparation contains 0 to 10% by weight, more preferably 0.05 to 5% by weight, most preferably 0.1 to 2% by weight, in each case of dispersing agent. The remainder can be water. In an alternative embodiment, the aqueous preparation contains, in addition to the water, further common auxiliaries, such as biocides, UV absorbers, surfactants, urea, or caprolactam. The aqueous preparation contains one
20 or more compounds of formula (1), e.g. 1 , 2 , or 3 formula (1) compounds, preferably one formula (1) compound. The aqueous preparation may also contain one or more other known dyes.

The aqueous preparation is a dispersion or solution, depending on the water solubility of the compound of formula (1). If the compound of formula (1) is not soluble in water, a dispersing agent is added. The aqueous preparation is prepared by dissolving or dispersing the formula (1) compound in water, optionally using the dispersing agent.
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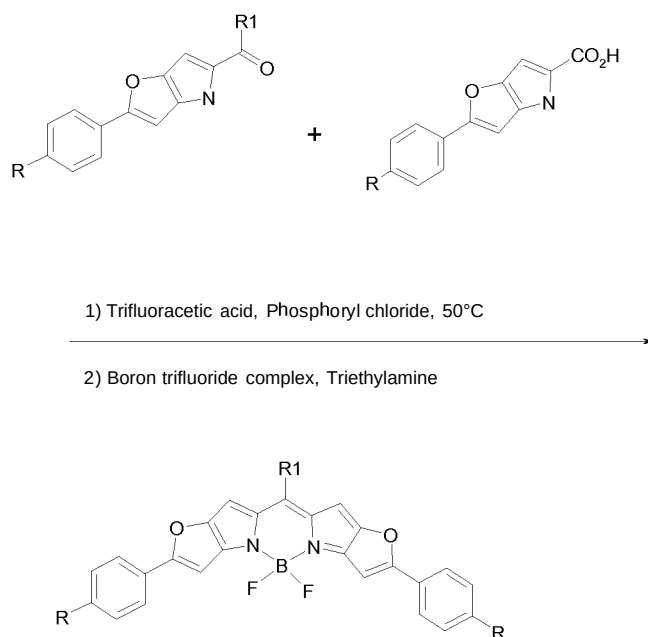
30 The compounds of formula (1) can be synthesized according to methods known in the art, for instance, as described in the literature by K. Suzuki et al, Chem. Eur.

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J. 2009, 15, p. 1096-1 106. Compounds of formula (1) can be, for example, obtained from α -formylated furopyrrole and α -carboxylated furopyrrole in the presence of trifluoroacetic acid and trichlorophosphate with subsequent reaction with boron trifluoride in the presence of trifluoroacetic acid and triethylamine.

5

An exemplary general reaction scheme is:



10

The aqueous preparation can be used for dyeing or printing materials, in particular materials containing cellulose and/or polyamide, preferably cellulose-containing material, in particular paper. In a preferred embodiment, the cellulose-containing material is a pulp or a sheet containing cellulosic material. Preferably, the aqueous preparation is used for dyeing a cellulose-containing material in the pulp, in a size press, and/or by a coating application. In particular, coating application means use of a coating composition or coating colour and/or coating equipment or apparatus. The pulp used may be any wood or plant fiber, e.g. bleached or unbleached, chemical, chemi-mechanical or mechanical pulp, or regenerated cellulosic material, or recycled paper fiber, or any combination thereof. The aforesaid uses can be

20

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applied singly or in a combination of two or more thereof. Further, the aqueous preparation can be used for printing paper, tissue, textile, such as cotton, wool. In addition, the aqueous preparation can be used in dyeing water-based coatings and plastics, such as polyamide. Further, it is also possible to use paper strips containing compounds of the present invention as test strips for labelling reactions. Furthermore, the aqueous preparation can be used for printing of materials, in particular materials containing cellulose and/or polyamide, preferably cellulose.

The invention also relates to a process for dyeing or printing materials containing cellulose and/or polyamide, preferably cellulose-containing material, in particular paper, wherein the material is brought into contact with an aqueous preparation as described above. Suitable materials for the process are the same as the materials described above with respect to the use of the aqueous preparation. Preferably, the contacting of the cellulose-containing material with the aqueous preparation is carried out in the pulp, in a size press, or by a coating application. In case of a coating application, preferably a coating composition or coating colour and/or coating equipment or apparatus is used.

The following Example illustrates the invention without limiting its scope. The Example demonstrates the synthesis of a compound of formula (1) and its use in an aqueous preparation for dyeing paper.

Example

A compound of formula (1), wherein R_2 and $R_3 = OCH_3$ and $R_1 = H$, is synthesized from 2-(4-methoxyphenyl)-4 *H*-furo[3,2- $\frac{3}{4}$]pyrrole-5-carboxylic acid and 2-(4-methoxyphenyl)-4 *H*-furo[3,2- $\frac{3}{4}$]pyrrole-5-carbaldehyde according to the general scheme given above and as described in K. Suzuki et al, Chem. Eur. J. 2009, 15, p. 1096-1106.

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For production of the aqueous preparation, 200 mg of the above formula (1) compound (R2 and R3 = OCH₃ and R1 = H) and 10 mg of a dispersing agent are dissolved in 10 ml deionized water with intensive stirring until a green dispersion is obtained. The dispersing agent used is the reaction product of 1 mole 4-hydroxy
5 biphenyl and 30 moles ethylene oxide according to EP 1 285 941 A1 or EP 1 184 402 A2, e.g. Example 1 thereof.

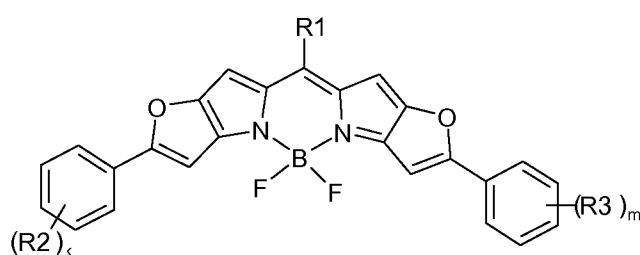
Dyeing process:

7 parts by weight of chemically bleached pinewood sulfite cellulose and 3 parts
10 by weight of chemically bleached birchwood sulfite cellulose are beaten with water in a mixer. 1 part by weight of the liquid dye preparation is added to this stuff followed by mixing for 20 minutes and producing handsheets from that. The obtained paper has a turquoise green color.

15 Thus, the present invention enables the production of paper with brilliant colors.

CLAIMS

- 5 1. An aqueous preparation comprising a compound of formula (1)



(1)

10 wherein

R1 represents hydrogen, CN, CF₃, Br, Cl, I; optionally substituted aryl; or optionally substituted alkyl;

15 R2 and R3, independently of each other, represent hydrogen; Ci₅-alkyl; Ci₅-alkoxyl; optionally substituted aryl; optionally substituted phenyl; p-Ci₅-alkoxyphenyl; di(Ci₅-alkyl)amino groups; or -SO₃M, wherein M is a cation, preferably hydrogen, alkaline metal, earth alkaline metal, ammonium, or mono-, di-, tri- or tetra-substituted ammonium, in particular substituted by C₁₋₅-alkyl and/or Ci₅-hydroxyalkyl, or ammonium based on amines derived from nitrogen-containing five- or six-membered saturated heterocycles, wherein R2 and R3 are attached to the aromatic ring at any position;

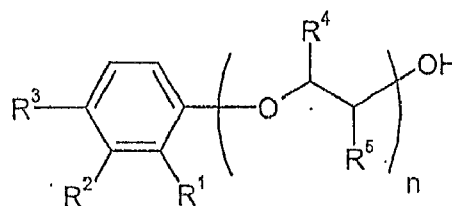
20 k, m are, independently of each other; an integer from 1 to 3;

25 water, and, optionally, a dispersing agent;

- 10 -

with the proviso that, if the aqueous preparation contains no dispersing agent and R¹ is hydrogen, at least one of R² and R³ is not hydrogen.

2. The aqueous preparation of claim 1, wherein R² and R³, independently of each other, represent hydrogen, C₁₋₃-alkoxyl, or -SO₃M.
3. The aqueous preparation of claim 1 or 2, wherein R¹ represents hydrogen, CN or CF₃.
4. The aqueous preparation any of claims 1 to 3, wherein the compound of formula (1) contains one R² group and one R³ group, each in p-position.
5. The aqueous preparation of any of the preceding claims, wherein R¹ is hydrogen, and R² and R³ both are methoxy or -SO₃M.
6. The aqueous preparation of any of the preceding claims, wherein the dispersing agent is a compound of the formula (2):



(2)

wherein

R¹, R² and R³ are, independently of each other, hydrogen, optionally substituted cyclohexyl or phenyl, wherein at least one of the residues R¹ to R³ is not hydrogen,

R⁴ and R⁵ are, independently of each other, methyl or hydrogen, and

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n is an integer from 21 to 40.

7. The aqueous preparation of any of the preceding claims, containing 0.01 to 50% by weight of compound of formula (1), and 0 to 10% by weight of dispersing agent.
5
8. Use of an aqueous preparation according to any of the preceding claims for dyeing or printing materials containing cellulose and/or polyamide.
- 10 9. The use according to claim 8, wherein the cellulose-containing material is pulp or a sheet containing cellulosic material.
10. The use according to claim 8 or 9, wherein the aqueous preparation is used for dyeing the cellulose-containing material in the pulp, in a size press,
15 and/or by a coating application.
11. A process for dyeing or printing materials containing cellulose and/or polyamide, wherein the material is brought into contact with an aqueous preparation as defined in any of claims 1 to 7.
20
12. The process of claim 11, wherein the cellulose-containing material is pulp or a sheet containing cellulosic material.
13. The process of claim 11 or 12, wherein the contacting of the cellulose-containing material is carried out in the pulp, in a size press, and/or by a
25 coating application.
14. A paper or product obtainable by a process according to any of claims 11 to 13.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/059955

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09B67/00 C09B69/00 C07F5/02 D21H21/28
ADD.

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)

C09B C07F D21H

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 , CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEN J ET AL: "4,4-DI FLUOR-4-BORA-3A,4A-DIAZA-S-INDACEN E (BODI PY) DYES MODI FI ED FOR EXTENDED CONJUGATION AND RESTRICTED BOND ROTATIONS", JOURNAL OF ORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCI ETY, EASTON. ; US LNKD- DOI : 10. 1021/J09919270, vol . 65, 1 January 2000 (2000-01-01) , pages 2900-2906, XP000960871 , ISSN : 0022-3263 the whol e document ----- -/-	1

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

14 July 2011

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22/07/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/059955

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	K. UMEZAWA ET AL. : "Bright, Color-Tunable Fluorescent Dyes in the Vis/NIR Region", CHEM. EUR.J., vol. 15, 2009, pages 1096-1106, XP002602607, cited in the application the whole document -----	1