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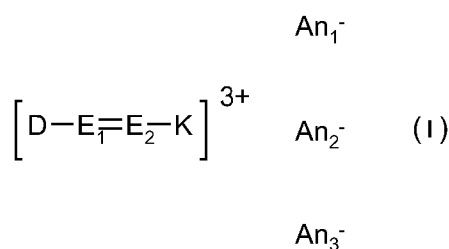
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(57) Abstract: Disclosed are compounds of formula (I); wherein D is an aromatic or a cationic heteroaromatic group, which is optionally substituted by C₁-C₁₄alkyl, C₁-C₁₄alkoxy, hydroxy-C₁-C₁₄alkyl, C₃-C₈cycloalkyl, -CN, NO₂, -NR₃R₄, halogen, C₆-C₁₀aryl, which is optionally substituted or C₁-C₁₄alkyl, or by one or more groups Z; E₁ and E₂ independently from each other are =CH; or =N-; K is an aromatic or heteroaromatic group which is optionally substituted by C₁-C₁₄alkyl, C₁-C₁₄alkoxy, C₃-C₈cycloalkyl, C₆-C₁₀aryl, halogen, hydroxy, NO₂, -NR₃R₄, -N(R₃)(CO)R₄, -SO₂NR₁R₂, -SONR₁R₂ or by one or more Z; or a radical of formula -NR₁R₂; R₁ and R₂ independently from each other are hydrogen; C₁-C₁₄alkyl; cyclo-C₁-C₁₄alkyl; C₆-C₁₀aryl; an aromatic or heteroaromatic group which is optionally substituted by C₁-C₁₄alkyl, C₁-C₁₄alkoxy, C₃-C₈cycloalkyl, C₆-C₁₀aryl, halogen, hydroxy, -NR₅R₆, -N(R₅)(CO)R₅ or by Z; Z is a group of the formula (1 a) *-X₁-Y₁-W₁, wherein X₁ is the direct bond; -NR₇-; -O-; -NR₇(C=O)-; -(CO)NR₇-; -O(C=O)-; -(CO)O-; or -(C=O)-; Y₁ is the direct bond; C₁-C₁₂alkylene, which is optionally interrupted by -O-, -NR₈-, -S-, -(C=O)-, -O(C=O)-, (C=O)O-, -NR₇(C=O)-, -(C=O)NR₇-, and which may substituted by C₁-C₁₄alkyl, hydroxy-C₁-C₁₄alkyl, hydroxy, -NR₉R₁₀ or halogen; or C₆-C₁₀arylene, which may substituted by C₁-C₁₄alkyl, hydroxy-C₁-C₁₄alkyl, hydroxy, amino or halogen; W₁ is a cationic group; and R₃, R₄, R₅, R₆, R₇, R₈, R₉ and R₁₀ independently from each other are hydrogen; C₁-C₁₄alkyl; or Z; and An₁⁻, An₂⁻ and An₃⁻ independently from each other are an anion. The compounds are useful for dyeing of organic materials, such as keratin-containing fibers, wool, leather, silk, cellulose or polyamides, especially keratin-containing fibers, cotton or nylon, more preferably human hair.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/055442

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C09B23/14	C09B26/04	C09B44/00	C09B44/08	C09B44/12
	C09B44/16	C09B55/00	C09B69/00	A61K8/49	A61Q5/10

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 A61K A61Q

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, 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	US 2006/037151 A1 (LAGRANGE ALAIN [FR]) 23 February 2006 (2006-02-23) paragraphs [0001], [0002], [0013] - [0018], [0032] - [0034] paragraphs [0039], [0089] - [0097] claim 1	1-10, 13-21
X	US 2006/021162 A1 (GREAVES ANDREW [FR] ET AL) 2 February 2006 (2006-02-02) paragraphs [0002], [0153] - [0155], [0300], [0301], [0315] examples 1,2 claims 1-37	1-9, 13-21
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Further documents are listed in the continuation of Box C. See patent family annex.

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| <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> | <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> |
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Date of the actual completion of the international search 30 January 2008	Date of mailing of the international search report 22/04/2008
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Name and mailing address of the ISA/ 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	Authorized officer Judele, R
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INTERNATIONAL SEARCH REPORT

International application No
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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.
X	EP 1 219 683 A (CIBA SC HOLDING AG [CH]) 3 July 2002 (2002-07-03) paragraphs [0001], [0025], [0026], [0038] - [0042], [0048] example 6 claims 1-10	1-10,13, 17
X	EP 0 318 294 A (NIPPON CHEMICAL WORKS [JP]) 31 May 1989 (1989-05-31) page 2, lines 8-11 page 3, lines 34-48 example 4 claims 1-9	1-5,9, 11,13,17
A	WO 03/029359 A (CIBA SC HOLDING AG [CH]; ADAM JEAN-MARIE [FR]; BACHER JEAN-PIERRE [FR]) 10 April 2003 (2003-04-10) page 1, paragraph 4 page 26, paragraph 6-page 27, paragraph 3 claims 1,2	1-10, 13-21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2007/055442

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-9 (part), 10 (full) and 13-21 (part)

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9 (part), 10 (full) and 13-21(part)

A tricationic dye having formula (1):
 $[D-N=N-K]_3^+ An_3^-$, wherein E1 and E2 are both =N;
 a composition comprising at least one tricationic dye of formula (1);
 a method of dyeing organic material comprising at least one dye of formula (1) or a composition comprising the said dye;

2. claims: 1-9 (part), 11 (full) and 13-21(part)

compounds of formula (I): $[D-C=C-K]_3^+ An_3^-$, wherein E1 and E2 are both =C;
 a composition comprising at least one tricationic dye of formula (1);
 a method of dyeing organic material comprising at least one dye of formula (1) or a composition comprising the said dye;

3. claims: 1-8 (part) and 13-21(part)

compounds of formula (I): $[D-N=C-K]_3^+ An_3^-$, wherein E1 is =N and E2 is =C;
 a composition comprising at least one tricationic dye of formula (1);
 a method of dyeing organic material comprising at least one dye of formula (1) or a composition comprising the said dye;

4. claims: 1-8 (part) and 13-21(part)

compounds of formula (I): $[D-C=N-K]_3^+ An_3^-$, wherein E1 is =C and E2 is =N and K is an aromatic or heteroaromatic group;
 a composition comprising at least one tricationic dye of formula (1);
 a method of dyeing organic material comprising at least one dye of formula (1) or a composition comprising the said dye;

5. claims: 1-9 (part), 12 (full) and 13-21(part)

compounds of formula (I): $[D-C=N-K]_3^+ An_3^-$, wherein E1 is =C and E2 is =N and K is a radical of formula NR₁R₂;
 a composition comprising at least one tricationic dye of formula (1);
 a method of dyeing organic material comprising at least one dye of formula (1) or a composition comprising the said dye.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2007/055442
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Patent document cited in search report	A1	Publication date	Patent family member(s)	Publication date
US 2006037151	A1	23-02-2006	NONE	
US 2006021162	A1	02-02-2006	NONE	
EP 1219683	A	03-07-2002	NONE	
EP 0318294	A	31-05-1989	CA 1339219 C	05-08-1997
			DE 3852620 D1	09-02-1995
			DE 3852620 T2	04-05-1995
			JP 1138269 A	31-05-1989
			JP 2085181 C	23-08-1996
			JP 7119367 B	20-12-1995
			US 5125930 A	30-06-1992
WO 03029359	A	10-04-2003	BR 0212987 A	17-08-2004
			CN 1556839 A	22-12-2004
			EP 1430102 A1	23-06-2004
			JP 2005520868 T	14-07-2005
			US 2004244127 A1	09-12-2004