

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
24 December 2008 (24.12.2008)

PCT

(10) International Publication Number
WO 2008/155517 A2

(51) International Patent Classification:

C09B 67/22 (2006.01) C09D 11/00 (2006.01)

(21) International Application Number:

PCT/GB2008/001967

(22) International Filing Date:

10 June 2008 (10.06.2008)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0711963.9 21 June 2007 (21.06.2007) GB

(71) Applicant (for all designated States except US): FUJI-FILM IMAGING COLORANTS LIMITED [GB/GB]; PO Box 42, Hexagon Tower, Blackley, Manchester M9 8ZS (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): CORDWELL, Janette [GB/GB]; PO Box 42, Hexagon Tower, Blackley, Manchester M9 8ZS (GB).

(74) Agents: MAYALL, John et al.; Fujifilm Imaging Colorants Limited, Intellectual Property Group, PO Box 42, Hexagon Tower, Blackley, Manchester M9 8ZS (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BI, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

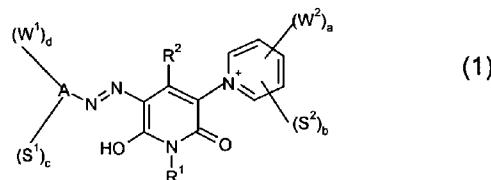
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

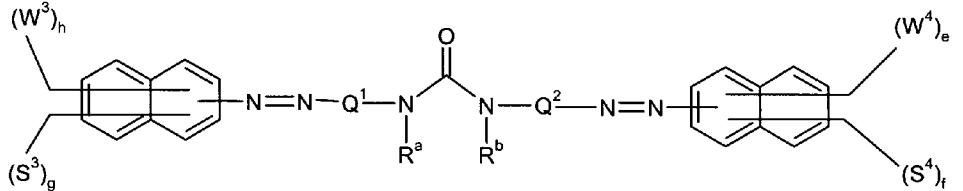
— without international search report and to be republished upon receipt of that report

(54) Title: COLORANT COMPOSITION, INK, PRINTING PROCESS

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(2)



(57) Abstract: A composition comprising a compound of Formula (1) or a salt thereof and compound of Formula (2) or a salt thereof; wherein: A is or comprises an aryl or heteroaryl group; Q¹ and Q² each independently is an optionally substituted phenylene group; R¹, R², R³ and R⁴ each independently is H, optionally substituted alkyl, optionally substituted aryl or optionally substituted arylalkyl; each W¹, W², W³ and W⁴ independently is a -CO₂H, -SO₃H, -PO₃H₂ group or an alky substituted with one or more groups selected from -CO₂H, -SO₃H, -PO₃H₂; each S¹, S², S³ and S⁴ independently is a substituent other than those defined for W¹, W², W³ and W⁴; a and d each independently is from 1 to 5; b and c each independently is from 0 to 4; (a + b) has a value of from 1 to 5; (c + d) has a value of from 1 to 5; e and h each independently is from 1 to 7; f and g each independently is from 0 to 6; (e + f) has a value of from 1 to 7; and (g + h) has a value of from 1 to 7.

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COLORANT COMPOSITION, INK, PRINTING PROCESS

This invention relates to colorant compositions (especially, but not exclusively yellow colorant compositions), to inks containing said colorant compositions and to the use of said inks in ink jet printing ("IJP").

5 Ink jet printing is a non-impact printing technique in which droplets of ink are ejected through fine nozzles onto a substrate without bringing the nozzle into contact with the substrate.

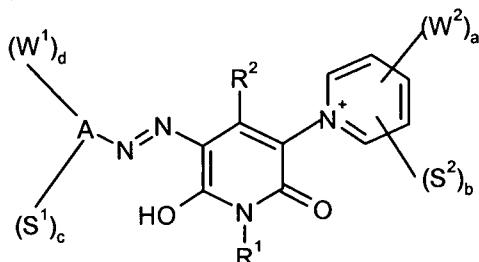
10 There are many demanding performance requirements for colorants and inks used in IJP. For example, they desirably provide sharp, non-feathered images having good water-fastness, light-fastness, ozone-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will tend to reduce print quality and in extreme cases may prevent the printer from printing. The inks are preferably also stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

15 US 6,488,752 discloses several azo containing compounds for use in ink jet printing.

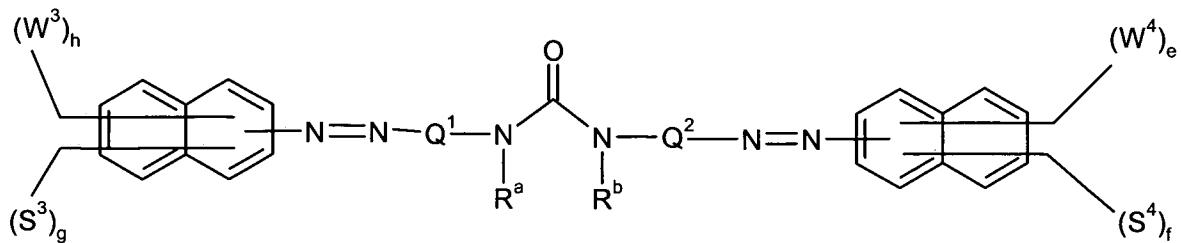
20 For colorants used in ink jet printing inks it is often difficult to simultaneously achieve good chroma, hue, light-fastness and ozone-fastness. Also, it is desirable to provide good performance properties using economically efficient technologies. A further desirable property is that prints should not significantly change hue or colour when stored, exposed to light or when exposed to ozone. For example, a yellow print should preferably stay yellow in colour when exposed to sunlight rather than change to a more red or blue shade.

25 The present invention aims to address, at least in part, one or more of the abovementioned desirable technical goals.

According to a first aspect of the present invention there is provided a composition comprising a compound of Formula (1) or a salt thereof and compound of Formula (2) or a salt thereof:



Formula (1)



Formula (2)

5 wherein:

A is or comprises an aryl or heteroaryl group;
 Q¹ and Q² each independently is an optionally substituted phenylene group;
 R¹, R², R^a and R^b each independently is H, optionally substituted alkyl, optionally substituted aryl or optionally substituted arylalkyl;

10 each W¹, W², W³ and W⁴ independently is a -CO₂H, -SO₃H, -PO₃H₂ group or an alky substituted with one or more groups selected from -CO₂H, -SO₃H, -PO₃H₂;

15 each S¹, S², S³ and S⁴ independently is a substituent other than those defined for W¹, W², W³ and W⁴;

a and d each independently is from 1 to 5;

b and c each independently is from 0 to 4;

(a + b) has a value of from 1 to 5;

20 (c + d) has a value of from 1 to 5;

e and h each independently is from 1 to 7;

f and g each independently is from 0 to 6;

(e + f) has a value of from 1 to 7; and

(g + h) has a value of from 1 to 7.

25 In Formula (1), b and c are preferably each independently 0, 1 or 2, more preferably 0 or 1.

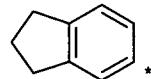
In Formula (1) a and d are preferably each independently 1, 2, or 3, more preferably 1 or 2.

30 Preferably (a+b) has a value of 1, 2 or 3, more preferably 1 or 2. Preferably (c+d) has a value of 1, 2 or 3, more preferably 2 or 3.

The compound of Formula (1) or a salt thereof is preferably a mono azo compound (i.e. containing only one azo (-N=N-) group).

In one embodiment A is an aryl group, more preferably a naphthyl or phenyl group and especially a phenyl group.

In another embodiment A is an indanyl group, more preferably A is an indanyl group of the Formula (1a):



5 Formula (1a)

wherein the asterisk represents the point of attachment to the azo group in the compound of Formula (1).

10 Preferably each W¹ and each W² independently is -CO₂H, -SO₃H, -PO₃H₂ or C₁₋₁₀alkyl (more preferably C₁₋₆-alkyl) substituted by one, two or three (more preferably one) groups selected from -CO₂H, -SO₃H, and -PO₃H₂.

More preferably each W¹ and each W² independently is -CO₂H, -SO₃H or C₁₋₆-alkyl substituted by -CO₂H or -SO₃H.

15 It is especially preferred that each W¹ independently is -CO₂H or -SO₃H.

It is especially preferred that each W² is -CO₂H.

Preferably at least one W¹ is attached in an ortho position relative to the azo group (-N=N-).

20 Preferably S¹ and S² are each independently optionally substituted aryl, optionally substituted aralkyl, halogen (especially F and Cl), nitro, cyano, -CF₃, -OR³, -NR⁴R⁵, -SR⁶, -C(O)R⁷, -C(O)OR⁸, -SO₂R⁹, -SOR¹⁰, alkyl optionally substituted by a group other than -SO₃H, -CO₂H or -PO₃H₂ or a group of Formula (1b):

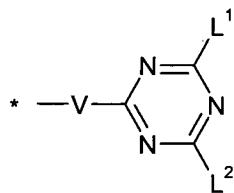
wherein:

25 R³ and R⁶ each independently is H, optionally substituted alkyl or optionally substituted aryl;

R⁴ and R⁵ each independently is H, optionally substituted alkyl, optionally substituted aryl, -CO(C₁₋₆-alkyl), -CONH₂, or R⁴ and R⁵ together with the nitrogen to which they are attached form a 5- or 6- membered ring;

30 R⁷, R⁸, R⁹ and R¹⁰ each independently is optionally substituted alkyl or optionally substituted aryl;

the group of Formula (1b) is:



Formula (1b)

wherein

L¹ and L²

each independently is -OR¹¹, -SR¹² or -NR¹³R¹⁴;

R¹¹ and R¹²

each independently is H, optionally substituted aryl or optionally substituted alkyl; and

R¹³ and R¹⁴

each independently is H, optionally substituted aryl, optionally substituted alkyl, -CO(C₁₋₆-alkyl), -CONH₂ or R¹³ and R¹⁴ together with the nitrogen to which they are attached form an optionally substituted morpholine or piperazine ring;

V

is -N (R¹⁵)- or -S-;

R¹⁵

is H, optionally substituted alkyl or optionally substituted aryl; and

the asterisk (*) represents the point of attachment to the group represented by A.

In a preferred embodiment S¹ and S² are each independently optionally substituted aryl, optionally substituted aralkyl, halogen (especially F and Cl), nitro, cyano, -CF₃, -OR³, -NR⁴R⁵, -SR⁶, -C(O)R⁷, -C(O)OR⁸, -SO₂R⁹, -SOR¹⁰ or alkyl optionally substituted by a group other than -SO₃H, -CO₂H or -PO₃H₂; wherein R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are as hereinbefore defined.

Preferably R⁷, R⁸, R⁹ and R¹⁰ are each independently optionally substituted alkyl.

When any of S¹ and S² is optionally substituted alkyl it is preferably optionally substituted C₁₋₁₀-alkyl, more preferably C₁₋₆-alkyl optionally substituted by -OH, nitro, cyano, halogen (especially F or Cl), amino, -NH(C₁₋₄-hydroxyalkyl) or -NH(C₁₋₄-alkyl).

When any one of R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ is optionally substituted alkyl it is preferably optionally substituted C₁₋₁₀-alkyl, more preferably optionally substituted C₁₋₆-alkyl. Preferred optional substituents are -OH, nitro, cyano, amino and halogen (preferably F or Cl), more especially Cl and -OH.

When one any of R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ is optionally substituted aryl it is preferably optionally substituted phenyl or optionally substituted naphthyl, especially optionally substituted phenyl. Preferred optional substituents are C₁₋₄-alkoxy, (C₁₋₄-hydroxyalkoxy)-C₁₋₄-alkoxy-, -OH, -CO₂H, -SO₃H, -CF₃, amino, -NH(C₁₋₄-alkyl), -NH(C₁₋₄-hydroxyalkyl), -NH(-CO(C₁₋₄-alkyl)), halogen

(especially F or Cl), nitro, -CO(C₁₋₄-alkyl), -SO₂(C₁₋₄alkyl) and C₁₋₄-alkyl optionally substituted by -OH, -CO₂H and -SO₃H.

When R⁴ and R⁵ together with the nitrogen to which they are attached form a 5 or 6 membered ring, the ring is preferably optionally substituted morpholine or optionally substituted piperazine.

Preferred optional substituents on the rings which may be formed by R⁴ and R⁵, and R¹³ and R¹⁴, together with the nitrogen to which they are attached are selected from -OH, -CO₂H, -SO₃H, C₁₋₄-alkoxy and C₁₋₄-alkyl optionally substituted by -OH, -CO₂H or -SO₃H.

R⁷, R⁸, R⁹ and R¹⁰ are preferably each independently C₁₋₄-alkyl, more preferably methyl or ethyl.

When any one of S¹ and S² is aralkyl it is preferably optionally substituted phenyl-(alkylene)- or optionally substituted naphthyl-(alkylene)-, more preferably optionally substituted phenyl-(C₁₋₆-alkylene)- or optionally substituted naphthyl-(C₁₋₆-alkylene)-. Preferred optional substituents on the aralkyl groups are those listed above for the aryl groups, more preferably C₁₋₄-alkyl, C₁₋₄-alkoxy, -SO₃H, -CO₂H, amino, nitro, F or Cl.

Preferably each S¹ and each S² is has no -CO₂H, -SO₃H and -PO₃H₂ groups.

Preferably each S¹ and S² independently is C₁₋₄-alkyl or C₁₋₄ alkoxy.

Preferably, c is from 0 to 3, more preferably c is 0.

Preferably, b is from 0 to 3, more preferably b is 0.

Preferably R¹ is H, optionally substituted C₁₋₁₀-alkyl, optionally substituted phenyl or optionally substituted phenyl-(C₁₋₆-alkylene)-, more preferably H, phenyl, C₁₋₆-alkyl optionally substituted by -OH, -SO₃H or -CO₂H, especially H or C₁₋₄-alkyl, more especially H.

Preferably R² is optionally substituted C₁₋₁₀-alkyl, optionally substituted phenyl, more preferably phenyl, or C₁₋₆-alkyl optionally substituted by -OH, -CO₂H or -SO₃H, especially C₁₋₄-alkyl, more especially methyl or ethyl. Most preferably R² is methyl.

In a preferred compound of Formula (1) or salt thereof:

A is as hereinbefore defined;

each W¹ and each W² independently is -CO₂H, -SO₃H or a C₁₋₆ alkyl substituted by -CO₂H or -SO₃H;

each S¹ and S² independently is C₁₋₆ alkyl, phenyl, nitro, halo (especially F and Cl), cyano, -CF₃, -NH₂, C₁₋₆ alkoxy, -SC₁₋₆ alkyl, -C₁₋₆ alkyl substituted by -OH or -NHC(O)C₁₋₆ alkyl;

R^1 is H or C_{1-6} -alkyl optionally substituted by $-OH$, $-SO_3H$ or $-CO_2H$;

R^2 is C_{1-4} alkyl;

5 a and d each independently is 1 or 2;
b and c each independently is 0, 1 or 2.

Preferably, W^2 is $-CO_2H$.

Preferably, each W^1 independently is $-CO_2H$ or $-SO_3H$.

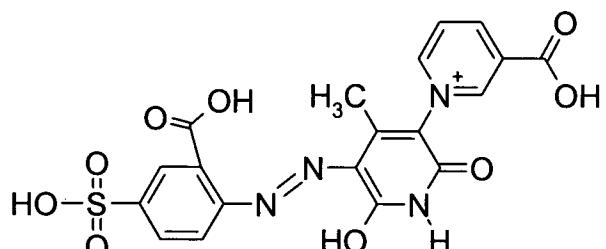
Preferably, R^1 is H or C_{1-4} alkyl, more preferably H.

Preferably, R² is methyl or ethyl, more preferably methyl.

10 It is especially preferred that a is 1 and W^2 is $-\text{CO}_2\text{H}$ which is attached to the pyridinium ring in the 3- position.

Preferably, A is phenyl or indanyl

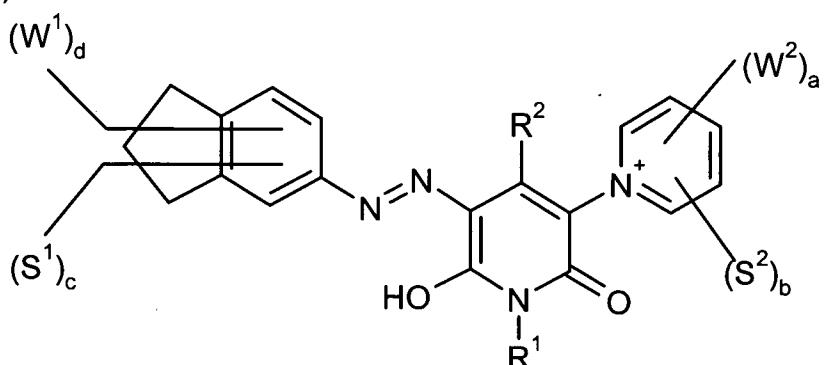
A particularly preferred compound of Formula (1) or a salt thereof is of Formula (3) or a salt thereof:



Formula (3)

The compound of Formula (3) has a particularly bright yellow colour and high chroma, it also exhibits especially good light-fastness.

20 In one embodiment the compound of Formula (1) or a salt thereof is of
Formula (1c) or a salt thereof:



Formula (1c)

25 **wherein:**

W^1, W^2, S^1, S^2, R^1 and R^2 a, b, c and d are as hereinbefore defined.

Preferably, d is from 1 to 3, c is from 0 to 3 and (c + d) is from 1 to 3. In this embodiment all the groups represented by each W^1 and each S^1 are preferably attached to the benzyl ring present in the compound of Formula (1c).

Preferably each S^1 independently is C_{1-6} -alkyl or C_{1-6} -alkoxy each of which is optionally substituted by -OH.

In Formula (1c) c is preferably 0. Preferably d is 1 or 2. It is especially preferred in Formula (1c) that c is 0, a is 1 or 2 and at least one W^1 is ortho relative to the azo group in Formula (1c).

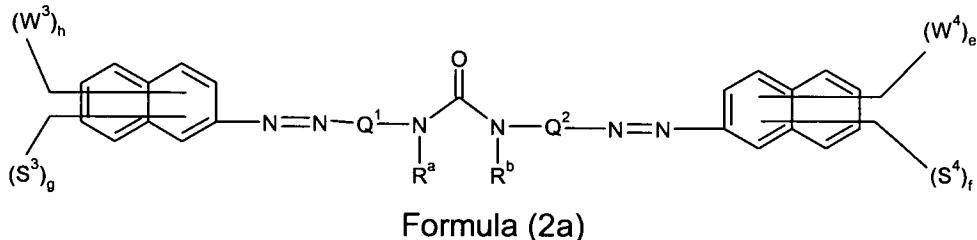
The compound of Formula (1) or a salt thereof may be prepared by the synthetic methods as described in US Patent number 6,488,752 at column 5.

The compound of Formula (3) or a salt thereof may be prepared by the method described in US Patent number 6,488,752, Example 1, beginning at column 10.

The compound of Formula (2) or a salt thereof preferably contains only two azo groups.

Preferably, one or both of the naphthyl groups present in the compound of Formula (2) or a salt thereof are attached to the relevant azo group present in the compound of Formula (2) in the 2-naphthyl position.

Accordingly, a preferred compound of Formula (2) or a salt thereof is of Formula (2a) or a salt thereof:



wherein Q^1 , Q^2 , W^3 , W^4 , S^3 , S^4 , R^a , R^b , e, f, g and h are as hereinbefore defined.

Q^1 is preferably a phenylene group which is para connected to the $-N=N-$ group and the $-NR^a-$ group present in the compound of Formula (2).

Similarly, Q^2 is preferably a phenylene group which is para connected to the $-N=N-$ group and the $-NR^b-$ group present in the compound of Formula (2).

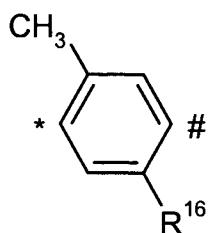
Q^1 and Q^2 may optionally be substituted with from 1 to 4 groups (more preferably 1 or 2 groups) each independently selected from any of those as defined above for W^1 and S^1 .

Preferably, Q^1 and Q^2 do not contain any $-CO_2H$, $-SO_3H$ and $-PO_3H_2$ groups.

Preferably, Q¹ and Q² are each independently substituted with 1 or 2 groups selected from C₁₋₆ alkyl, C₁₋₆ alkoxy, -C(O)OC₁₋₆ alkyl and -C(O)NHC₁₋₆ alkyl groups.

5 Preferably, Q¹ and Q² are substituted with at least one C₁₋₆ alkyl, more preferably at least one methyl group. Preferably, a C₁₋₆ alkyl group is present in Q¹ and Q² in a position which is ortho relative to the relevant azo (-N=N-) group in the compound of Formula (2).

Preferably, Q¹ is of the Formula (2b):



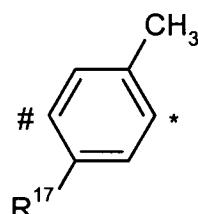
Formula (2b)

wherein

R¹⁶ is H or methyl;

15 the asterisk (*) symbol represents the point of attachment to the azo group and the hash (#) symbol represents the point of attachment to the -NR^a- group present in the compound of Formula (2).

Similarly, Q² is preferably of Formula (2c):



20 Formula (2c)

wherein

R¹⁷ is H or methyl;

25 the asterisk (*) symbol represents the point of attachment to the azo group and the hash (#) symbol represents the point of attachment to the -NR^b- group present in the compound of Formula (2).

R^a and R^b may each independently be any of the groups as hereinbefore defined for R¹.

Preferably, R^a and R^b are each independently H or C₁₋₆ alkyl optionally substituted with from one to three (especially just one) -CO₂H, -OH or -SO₃H groups.

Preferably, R^a and R^b are H.

5 Preferably, h is 1, 2 or 3, more preferably 2.

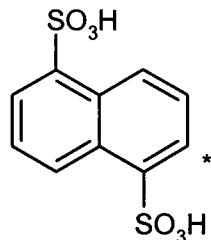
Preferably, e is 1, 2 or 3, more preferably 2.

Preferably, both h and e are 2.

When W³ or W⁴ is an alkyl group substituted with one or more groups selected from -CO₂H, -SO₃H and -PO₃H₂, the alkyl group is preferably a C₁₋₆ alkyl group

10 Preferably, W³ and W⁴ are each independently -CO₂H, -PO₃H₂ or -SO₃H, more preferably, W³ and W⁴ are -SO₃H.

Preferably, one or both of the naphthyl groups present in the compound of Formula (2) or a salt thereof are of Formula (2d):



15 Formula (2d)

wherein the asterisk (*) represents the point of attachment to the relevant azo groups in the compound of Formula (2).

Preferably, f is 0, 1 or 2, more preferably 0.

20 Preferably, g is 0, 1 or 2, more preferably 0.

Preferably, f and g are both 0.

S³ and S⁴ may each independently be any of the groups as previously described for S¹.

In a preferred compound of Formula (2) or a salt thereof:

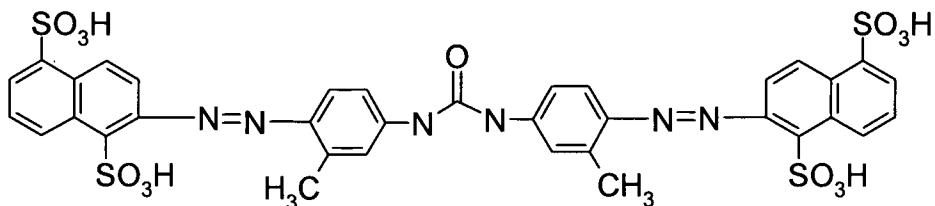
25 each W₁ and W₂ independently is -CO₂H, -PO₃H₂ or -SO₃H;

each S₃ and S₄ independently is C₁₋₄ alkyl or C₁₋₄ alkoxy;

e and h each independently is 1, 2 or 3;

f and g each independently is 0, 1 or 2.

30 Most preferably the compound of Formula (2) or a salt thereof is of Formula (4) or a salt thereof:



Formula (4).

The compound of Formula (4) is commercially available as C.I. Direct 5 Yellow 50.

The compound of Formula (2) or a salt thereof may be prepared by well established diazotisation chemistry.

In a preferred synthetic route a substituted amino naphthylene is diazotised and coupled to an optionally substituted aniline compound. The product of this 10 diazotisation reaction is preferably coupled together using phosgene (COCl₂).

In the present invention the compounds of Formula (1) and Formula (2) may be in the form of the free acid (i.e. the protonated form) or in the form of a salt or a mixture thereof. Accordingly, any acidic groups such as -CO₂H, -SO₃H and -PO₃H₂ present in the compounds of Formula (1) or (2) may be in the form of the 15 free acid or a salt or a mixture thereof.

Preferably, the compounds of Formula (1) and Formula (2) are in the form of a salt.

Preferred salts are alkali metal salts, ammonium and substituted ammonium salts.

Preferred metal salts are the alkali metal salts, preferably lithium, sodium, 20 potassium salts and especially sodium salts.

Preferred ammonium and substituted ammonium salts are ammonia, organic amines and quaternary organic amines (e.g. (CH₃)₄N⁺). The organic amines may be substituted with for example hydroxy groups (e.g. alkanolamines).

Preferably, the compound of Formula (1) or a salt thereof and of Formula 25 (2) or a salt thereof are each independently in the form of a salt selected from the group consisting of metal, ammonium and substituted ammonium salts or a mixture thereof.

Preferably, the compounds of Formulae (1) and (2) are both in the form of the same salt.

The compounds of Formulae (1) and (2) in the form of the free acid may be converted into salts using known techniques. For example, the compound of Formula (1) in the form of the free acid may be neutralised with base such as an alkali metal hydroxide or an amine. Normally such neutralisation is performed in 30 an aqueous liquid medium.

The salt form can be exchanged by known techniques. For example, a compound of Formula (1) or (2) in the form of an alkali metal salt can be converted into an ammonium salt by ultrafiltration with an ammonia solution or by means of an ammonium ion-exchange resin.

5 Preferably, both of the compounds of Formulae (1) and (2) or salts thereof are soluble in water. More preferably, both compounds are soluble in water at a concentration of at least 5% by weight of the compound.

10 Preferably, both of the compounds of Formulae (1) and (2) or salts thereof are yellow, orange or brown in colour. More preferably, both compounds are yellow in colour when at a concentration of 5% by weight in water.

In a preferred composition, the compound of Formula (1) or a salt thereof and/or the compound of Formula (2) or a salt thereof are purified by dialysis, reverse osmosis, ultrafiltration, ion exchange or a combination thereof. This purification may be before and/or after the preparation of said composition.

15 The compound of Formula (1) or a salt thereof and the compound of Formula (2) or a salt thereof may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention and its claims.

20 In a preferred embodiment the compound of Formula (1) or a salt thereof is of Formula (3) or a salt thereof and the compound of Formula (2) or a salt thereof is of Formula (4) or a salt thereof.

The compound of Formula (4) and salts thereof are known as C.I. Direct Yellow 50.

25 Whilst the composition according to the first aspect of the present invention may comprise a compound of Formula (1) or salt thereof and a compound of Formula (2) or a salt thereof in any proportions relative to each other we have found that certain weight ratios offer even more desirable hue, ozone-fastness and light-fastness.

30 Preferably, the weight ratio of the compound of Formula (1) or a salt thereof to the compound of Formula (2) or a salt thereof is from 5:95 to 95:5, more preferably from 50:50 to 95:5 and especially from 70:30 to 90:10. Among other things, these ratios provide an excellent yellow shade for the yellow ink of a trichromatic (cyan, magenta and yellow) printing ink set.

35 The compositions according to the first aspect of the present invention may be prepared by simply adding a compound of Formula (1) or a salt thereof to a compound of Formula (2) or a salt thereof. More preferably, the two compounds are mixed so as to form a homogenous mixture. The mixing may be by dry blending using for example, a shaker mixer, roller mixer, tumbler mixer or the like.

More preferably, mixing of the compound of Formula (1) or a salt thereof and the compound of Formula (2) or a salt thereof is achieved by wet blending (i.e. mixing the compounds together with a liquid). Preferably, the liquid is or comprises water. It is especially preferable that both the compound of Formula (1) and (2) are dissolved into a liquid medium, especially an aqueous liquid medium.

5 According to a second aspect of the present invention there is provided an ink comprising a composition according to the first aspect of the present invention and a medium.

In a preferred embodiment the ink comprises:

10 (a) from 0.01 to 30 parts of a composition according to the first aspect of the present invention; and

(b) from 70 to 99.99 parts of a medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

15 The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

The medium may be a low melting point solid but is preferably a liquid medium (preferably a liquid at 25°C).

20 Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 5%, more preferably at least 10% by weight. This allows the preparation of stable inks and concentrates which may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

25 In one embodiment the liquid medium is or comprises water (i.e. the ink is aqueous).

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

30 When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether

ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₄-alkyl ethers of diols, preferably mono-C₁₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Examples of further suitable ink media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include ketones and alcohols (especially methyl ethyl ketone and C₁₄ alkanols). In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C₁₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic

solvents.. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

When the liquid medium is an organic solvent free from water the compounds of Formula (1) and (2) are preferably in the form of a salt with a 5 lipophilic amine. Preferred lipophilic amines contain at least one C_{4-20} alky group, more preferably at least one C_{6-20} alkyl group.

Inks in which component (b) is an organic solvent free from water are particularly useful where fast drying times are required and particularly when 10 printing onto hydrophobic and/or non-absorbent substrates, for example plastics, metal and glass.

Preferably, the low melting point solid is solid at 25°C and melts at a temperature above 50°C. More preferably, the low melting point solid has a melting point in the range from 60°C to 125°C.

Suitable media which melt in this temperature range include long chain fatty 15 acids, long chain sulfonamides or long chain alcohols, preferably those having C_{18-24} chains. The compound of Formula (1) or a salt thereof and the compound of Formula (2) or a salt thereof may be dissolved in the low melting point solid or they may be finely dispersed in it.

Inks according to the second aspect of the present invention may be 20 prepared by adding together a compound of Formula (1) or a salt thereof, a compound of Formula (2) or a salt thereof and a medium.

Preferably, the medium is a liquid medium. When the liquid medium is or 25 comprises water, it is preferred that the water used to prepare the ink has a relatively low conductivity.

Preferably, the water used to prepare the ink has a conductivity of less than 50 μ S/cm, more preferably less than 10 μ S/cm and especially less than 2 μ S/cm. Water having these conductivity values can be prepared by known methods such as deionization, reverse osmosis and distillation.

Preferably, the above components used to prepare the ink are mixed 30 together so as to fully dissolve the compounds and to homogenise the ink.

The inks according to the second aspect of the present invention may also contain additional components suitable for use in ink jet printing inks. Inks may contain for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants.

Preferably, the ink has been filtered through a filter having a mean pore size 35 of less than 10 μ m, more preferably less than 5 μ m, especially less than 2 μ m, more especially less than 1 μ m. In this way particulate matter is removed which could otherwise block the fine nozzles used in ink jet printers.

Preferably, the ink has a viscosity of less than 50mPa.s, more preferably less than 20mPa.s, especially less than 10mPa.s at a temperature of 25°C.

Preferably, the ink has a concentration of halide ions of less than 500 parts per million and more preferably less than 100 parts per million. It is especially preferred that the ink has less than 100, more preferably less than 50 parts per million in total of divalent and trivalent metals. Parts per million refer to parts by weight of the relevant ions or metals relative to the total weight of the ink. Any suitable means to remove halide ions and/or di and trivalent metals may be employed, e.g. ion exchange and ultra-filtration.

Preferably, the ink is aqueous and has a conductivity of less than 50 μ S/cm. Preferably, the conductivity of the ink is measured at a temperature of 25°C. Low conductivities are preferably achieved by, for example, dialysis, ion exchange or ultra-filtration.

Preferably, the ink is yellow, more preferably the ink is yellow in colour when the total amount of the compound of Formula (1) or a salt thereof and the compound of Formula (2) or a salt thereof is 5% by weight relative to the ink.

According to a third aspect of the present invention there is provided a process for printing an image on a substrate comprising applying thereto an ink according to the second aspect of the present invention.

Preferably, the printing is performed by means of an ink jet printer.

The image may be in the form of a picture, text, graph, photograph or the like without any particular limitation.

According to a fourth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and an ink, wherein the ink is present in the chamber and the ink is according to the second aspect of the present invention.

According to a fifth aspect of the present invention there is provided a substrate printed with an ink according to the second aspect of the present invention.

Preferred substrates include paper, transparent plastic or textile materials.

Preferred substrates are those having a receptor layer for the ink. The receptor layer may be porous or non-porous.

According to a sixth aspect of the present invention there is provided the use of a composition according to the first aspect of the present invention for preparing an ink jet printing ink comprising water and said composition, wherein the ink has a conductivity of less than 50 μ S/cm.

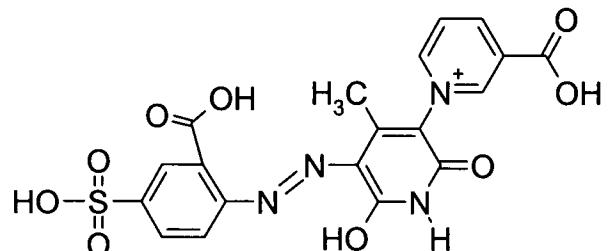
In the description of the present invention the words "a" or "an" are frequently used to mean one or more where such meaning is appropriate and unless otherwise stated. Thus for example, "a compound of Formula (1) or a salt thereof" means one or more compound of Formula (1) or salts thereof. For 5 example, the composition according to the first aspect of the present invention might comprise a compound of Formula (1) in the form of the free acid and the compound of Formula (1) in the form of a salt in combination with a compound of Formula (2) in the form of a salt. Similarly, a substrate means one or more substrates, a chamber means one or more chambers and an image means one or 10 more images.

The invention is further illustrated by the following Examples in which all parts, percentages and ratios are by weight unless otherwise stated.

Example 1

Dye (1)

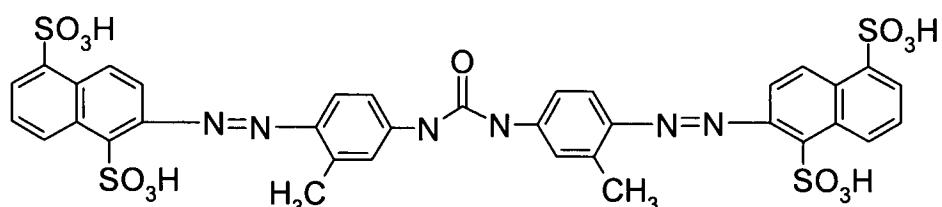
Dye (1) was prepared and purified according to US 6,488,752, column 10, line 1 to column 11, line 14. Dye (1) was compound of Formula (3), namely:



20 in the form of the sodium salt.

Dye (2)

Dye (2) was obtained from Abbey Color Inc under the tradename ABCOLTM Direct Yellow RLSW. Dye (2) was a compound of Formula (4), namely:



25 in the form of the sodium salt.

Compositions according to the present invention may be prepared by dissolving Dye (1) in the amounts indicated in Table 1, column 1 and Dye (2) in

the amounts indicated in Table 1, column 2 in sufficient deionized water to make the total composition up to 100 parts by weight.

Table 1

5

Dye (1) parts	Dye (2) parts	Ratio of amount Dye (1): Dye (2)
2	2	1:1
2	1	2:1
3.66	1	3.66:1
4	1	4:1
2	0.4	5:1
2	0.2	10:1

Ink jet printing inks

10 The compositions described in Table 1 may be used to prepare ink jet printing inks by adding one or more suitable additives. In particular, ink jet printing inks may be prepared containing 2-pyrrolidone (5 parts), thiodiglycol (5 parts), Surfynol™ 465 (1 part from Air products) the amounts of Dyes (1) and (2) as indicated in Table 1 and deionized water so as to make the total up to 100 parts.

Example 2 - Further Inks

15 The further inks described in Tables I and II may be prepared wherein the first column indicates the amount of Dye (1) in parts, the second column indicates the amount of Dye (2) in parts and the third column indicates the ratio of the amounts of Dye (1) to Dye (2). All of the further inks in Tables I and II are made up to 100 parts with deionized water. The numbers quoted in the fourth column onwards refer to the number of parts of the relevant ingredient and all parts and ratios are by weight. The further inks may be applied to paper by thermal or piezo ink jet printing.

20 The following abbreviations are used in Tables I and II:

PG = propylene glycol

25 DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

30 2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

5 PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = urea

TABLE I

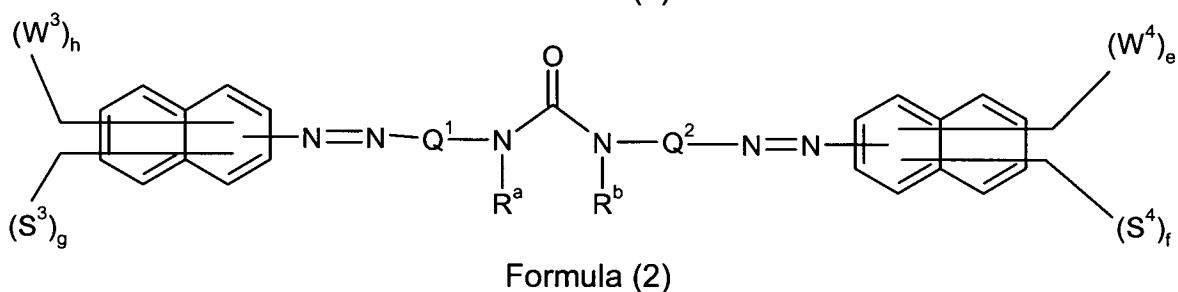
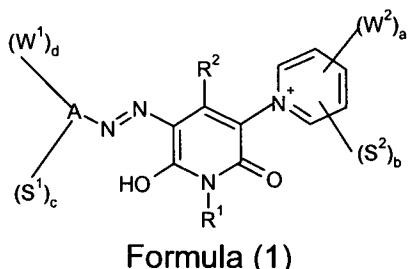
Dye (1)	Dye (2)	Ratio of Dye (1) : Dye (2)	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
5	0.5	10:1	5	6	4	0.2			5	1	1	5
4	0.5	8:1		5	5							
3	1	3:1		3	3							
2	2	1:1		8								
6	3	2:1		5								
4	1	4:1			9	0.5	0.2	4	9	5	4	5
4.7	1.3	3.6:1	4	15	3	3	0.5	0.5	6	10	5	4
3.7	2.3	1.6:1		20					10	6	5	5
4.2	1.8	2.3:1	5	4	5	5	0.2	4	6	6	5	5
4	2	2:1	3	5	2	10	0.3	5	4	6	6	5
3	3	1:1		5	4	6						
2	0.5	4:1										
1.67	0.83	2:1	5									
1.87	0.63	3:1	2	6	2	5						
2.08	0.42	5:1		5								
2.25	0.25	9:1			11							
2.3	0.2	11.5:1	2									
1.25	1.25	1:1										
2	0.5	4:1	2	20	2	7	0.3	3	2	3	3	5
2.08	0.42	5:1			4	1						

TABLE II

CLAIMS

1. A composition comprising a compound of Formula (1) or a salt thereof and compound of Formula (2) or a salt thereof:

5



10

wherein:

A

is or comprises an aryl or heteroaryl group;

Q¹ and Q²

each independently is an optionally substituted phenylene group;

15

R¹, R², R³ and R⁴

each independently is H, optionally substituted alkyl, optionally substituted aryl or optionally substituted arylalkyl;

each W¹, W², W³ and W⁴

independently is a -CO₂H, -SO₃H, -PO₃H₂ group or an alky substituted with one or more groups selected from -CO₂H, -SO₃H, -PO₃H₂;

20

each S¹, S², S³ and S⁴

independently is a substituent other than those defined for W¹, W², W³ and W⁴;

a and d

each independently is from 1 to 5;

b and c

each independently is from 0 to 4;

25

(a + b)

has a value of from 1 to 5;

(c + d)

has a value of from 1 to 5;

e and h

each independently is from 1 to 7;

f and g

each independently is from 0 to 6;

(e + f)

has a value of from 1 to 7; and

30

(g + h)

has a value of from 1 to 7.

2. A composition according to claim 1 wherein in the compound of Formula (1) or a salt thereof:

each W^1 and W^2 independently is $-CO_2H$, $-SO_3H$ or a C_{1-6} alkyl substituted by $-CO_2H$ or $-SO_3H$;

5 each S^1 and S^2 independently is C_{1-6} alkyl, phenyl, nitro, halo, cyano, $-CF_3$, $-NH_2$, C_{1-6} alkoxy, $-SC_{1-6}$ alkyl, $-C_{1-6}$ alkyl substituted by $-OH$ or $-NHC(O)C_{1-6}$ alkyl;

R^1 is H or C_{1-6} -alkyl optionally substituted by $-OH$, $-SO_3H$ or $-CO_2H$;

10 R^2 is C_{1-4} alkyl;

a and d each independently is 1 or 2;

b and c each independently is 0, 1 or 2; and

in the compound of Formula (2) or a salt thereof:

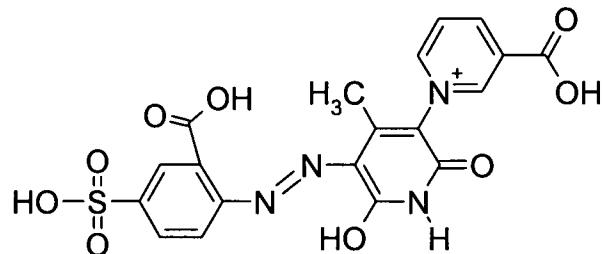
15 each W_1 and W_2 independently is $-CO_2H$, $-PO_3H_2$ or $-SO_3H$;

each S_3 and S_4 independently is C_{1-4} alkyl or C_{1-4} alkoxy;

e and h each independently is 1, 2 or 3;

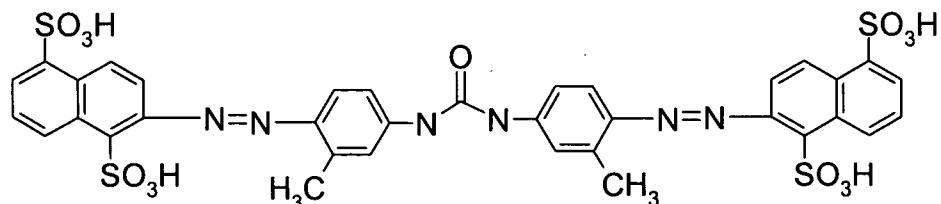
f and g each independently is 0, 1 or 2.

20 3. A composition according to any one of the preceding claims wherein the compound of Formula (1) or a salt thereof is of Formula (3) or a salt thereof and the compound of Formula (2) or a salt thereof is of Formula (4) or a salt thereof:



25

Formula (3)



Formula (4).

4. A composition according to any one of the preceding claims wherein the weight ratio of the compound of Formula (1) or a salt thereof to the compound of Formula (2) or a salt thereof is from 5:95 to 95:5.

5 5. A composition according to any one of claims 1 to 3 wherein the weight ratio of the compound of Formula (1) or a salt thereof to the compound of Formula (2) or a salt thereof is from 50:50 to 95:5.

10 6. A composition according to any one of claims 1 to 3 wherein the weight ratio of the compound of Formula (1) or a salt thereof to the compound of Formula (2) or a salt thereof is from 70:30 to 90:10.

15 7. A composition according to any one of the preceding claims wherein the compound of Formula (1) or a salt thereof and of Formula (2) or a salt thereof is in the form of a salt selected from the group consisting of metal, ammonium and substituted ammonium salts or a mixture thereof.

20 8. A composition according to any one of the preceding claims wherein the compound of Formula (1) or a salt thereof and/or a compound of Formula (2) or a salt thereof are purified by dialysis, reverse osmosis, ultrafiltration, ion exchange or a combination thereof, before and/or after preparation of said composition.

25 9. An ink comprising a composition according to any one of the preceding claims and a medium.

10. An ink according to claim 9 comprising:
(a) from 0.01 to 30 parts of the composition according to any one of claims 1 to 8; and
(b) from 70 to 99.99 parts of a medium;
30 wherein all parts are by weight and the sum of the parts (a) + (b) = 100.

11. An ink according to claim 9 or 10 wherein the medium is a liquid medium.

12. An ink according to claim 11 wherein the liquid medium is or comprises water and the water used to prepare the ink has a conductivity of less than 35 50 μ S/cm.

13. An ink according to claim 11 or 12 wherein the liquid medium comprises a mixture of water and an organic solvent.
- 5 14. An ink according to any one of claims 11 to 13 having a viscosity of less than 50mPa.s at a temperature of 25°C.
- 10 15. A process for printing an image on a substrate comprising applying thereto an ink according to any one of claims 9 to 14.
- 15 16. A process according to claim 15 wherein the printing is performed by means of an ink jet printer.
17. An ink jet printer cartridge comprising a chamber and an ink, wherein the ink is present in the chamber and the ink is according to any one of claims 9 to 14.
18. A substrate printed with an ink according to any one of claims 9 to 14.
19. Use of a composition according to any one of claims 1 to 8 for preparing an ink jet printing ink comprising water and said composition, wherein the ink has a conductivity of less than 50 μ S/cm.