PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} **:**
C09D 11/00, C09B 69/02, 67/24

A1

(11) International Publication Number: **WO 99/64526**

(43) International Publication Date: 16 December 1999 (16.12.99)

(21) International Application Number: PCT/GB99/01483

(22) International Filing Date: 28 May 1999 (28.05.99)

(30) Priority Data:
9812119.7 5 June 1998 (05.06.98) GB

(71) Applicant *(for all designated States except US)*: AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: WATKINSON, Janette [GB/GB]; Hexagon House, Blackley, P.O. Box 42, Manchester M9 8ZS (GB). LAVERY, Aidan, Joseph [GB/GB]; Felix Schoeller Ltd., Woodburn Green, High Wycombe, Buckinghamshire HP10 0DB (GB). MEYERS, John, Parker [US/US]; Avecia Specialist Colours, Chemical Engineering Labs, 233 Cherry Lane, New Castle, DE 19720 (US).

(74) Agents: MAYALL, John; Avecia Limited, Intellectual Property Group, Hexagon House, Blackley, P.O. Box 42, Manchester M9 8ZS (GB) et al.

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: USE OF LITHIUM SALTS OF ANIONIC DYES TO ENHANCE THEIR LIGHT-FASTNESS

(57) Abstract

The use of lithium as a cation for an anionic dye to enhance the light-fastness of the dye. Also claimed are the lithium salts of certain anionic dyes as defined in the description; mixed lithium/sodium salts of an anionic dye wherein the molar ratio of lithium to sodium is from 1:4 to 99:1 and at least 20 mole % of the total counter ions in the dye are lithium cations; inks containing the dyes; a method of ink jet printing using the inks; a substrate printed with the inks; an ink jet printer cartridge containing the ink and an ink jet printer containing the ink jet printer cartridge.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

USE OF LITHIUM SALTS OF ANIONIC DYES TO ENHANCE THEIR LIGHT–FASTNESS

This invention relates to dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-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 stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

There is a growing demand for wide format prints which are prepared using ink jet printing. Wide format prints are often located outdoors, for example on advertising billboards, where they may be exposed to sunlight for long periods of time. It is therefore desirable that the prints exhibit a high light-fastness to minimise fading.

We have found that lithium salts of anionic dyes exhibit a surprisingly high light-fastness particularly when the dyes are incorporated into inks for use in ink jet printers. We have also found that when lithium is used in conjunction with sodium as cations in anionic dyes, the dyes exhibit a surprisingly high aqueous solubility and a high light-fastness.

According to a first aspect of the present invention there is provided the use of lithium as a cation for an anionic dye to enhance the light-fastness of the dye.

The lithium cation may be used as the sole cation for the anionic dye or in combination with other cations. For example, the lithium cation may be used together with another alkali metal cation (preferably potassium and especially sodium cations), with ammonium or with a quaternary ammonium cation.

The light-fastness of the dye generally increases as the proportion of lithium cations in the total pool of cations increases. Preferably, at least 20 mole %, more preferably at least 50 mole %, still more preferably at least 60 mole % of the cations in the anionic dye are lithium cations. In one embodiment substantially all of the cations in the dye are lithium cations.

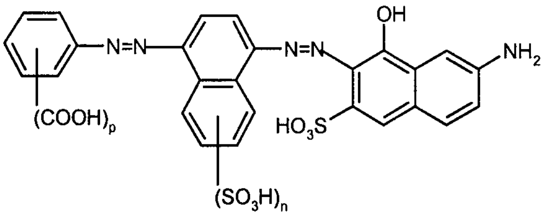
In a second embodiment the lithium is used in combination with sodium as a cations for the anionic dye. We have found that the mixed lithium/sodium salts provide anionic dyes with a high light-fastness and a high aqueous solubility. Preferably the molar ratio of lithium to sodium cations in the anionic dye is from 1:4 to 99:1, more preferably from 1:4 to 3:1 and especially from 1:3 to 1.5:1, more especially from 1:2 to 1:1. This preferred ratio of lithium to sodium cations provides an anionic dye which exhibits an unexpectedly high light-fastness and water-fastness compared to the individual sodium and lithium salts of the dye.

When lithium is used in combination with sodium as the cations for an anionic dye preferably and at least 20 mole% of the total cations in the dye are lithium.

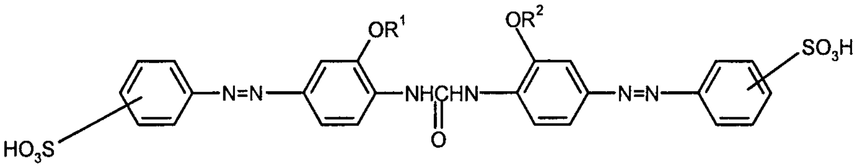
Preferably the anionic dye is a water-soluble anionic dye. Preferred water-soluble anionic dyes are water-soluble anionic direct, reactive and acid dyes, more preferably water-soluble anionic azo, bis azo and tris azo dyes which preferably contain one group, more preferably two or more groups, selected from carboxy, sulpho and phosphono.

It is especially preferred that the water-soluble anionic dye contains at least as many carboxy groups as sulpho groups.

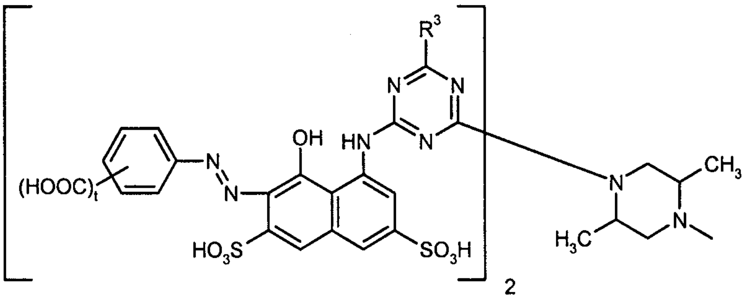
According to a second aspect of the present invention there is provided a dye selected from C.I. Reactive Red 180, C.I. Acid Red 52 and a dye having one of the Formulae (1) to (9), wherein the dye is in the lithium salt form:



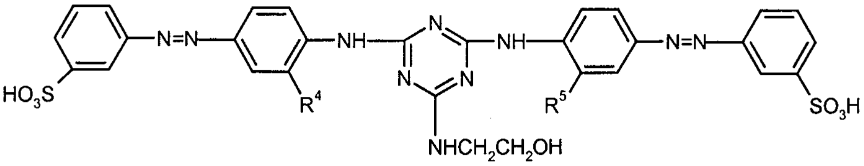
Formula (1)



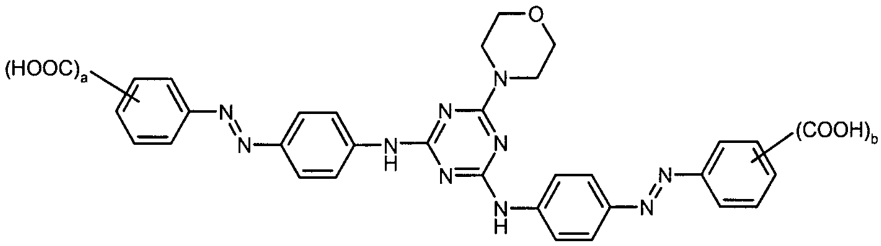
Formula (2)



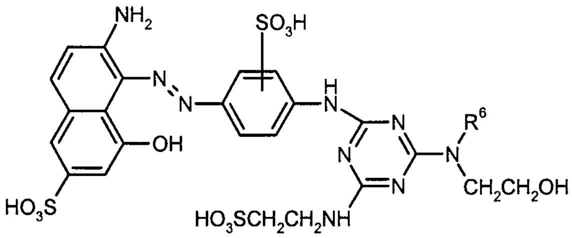
Formula (3)



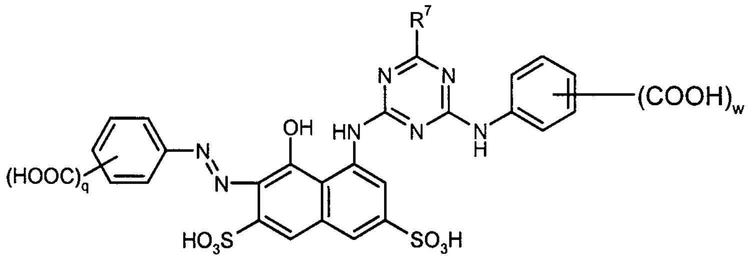
Formula (4)



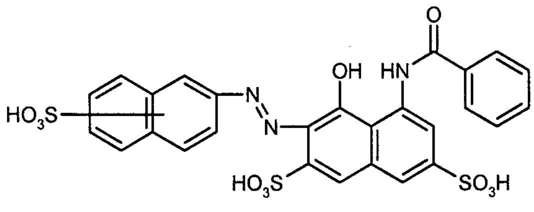
Formula (5)



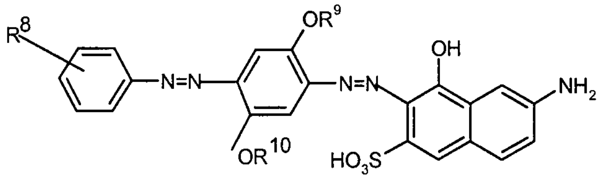
Formula (6)



Formula (7)



Formula (8)



Formula (9)

wherein:

R^1 and R^2	each independently is C_{1-4}-alkyl;
each R^3	independently is alkoxy, -OH, -Cl or amino;
R^4 and R^5	each independently is C_{1-4}-alkoxy;
R^6	is H or hydroxyethyl;
R^7	is -OH, -Cl, or C_{1-4}-alkoxy;
R^8	is -COOH, $-SO_3H$ or $-PO_3H_2$;
R^9 and R^{10}	each independently is methyl or ethyl;
p	is 1 or 2;
n	is 0 or 1;
q and w	each independently is 1 or 2;
a and b	each independently is 1 or 2; and
each t	independently is 1 or 2.

Preferably n is 0.

Preferably p is 2. More preferably p is 2 and each -COOH is meta to the azo group (-N=N-) in Formula (1).

R^1 and R^2 are preferably methyl or ethyl, more preferably methyl. Preferably the $-SO_3H$ groups in Formula (2) are attached at the meta position relative to each azo group.

Preferably each t is 2. More preferably each t is 2 and the -COOH groups are at the 3- and 5- positions in each phenyl group in Formula (3). Preferably R^3 is -OH or C_{1-4}-alkoxy, more preferably -OH or methoxy and especially -OH.

R^4 and R^5 are preferably methoxy.

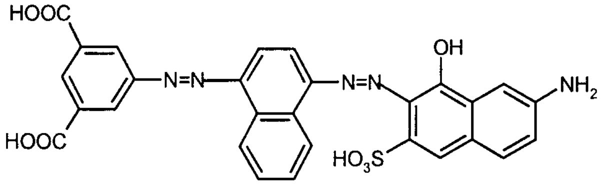
Preferably a and b are 2, more preferably a and b are 2 and each -COOH is attached meta to each azo group (-N=N-) in Formula (5).

Preferably R^6 is hydroxyethyl, more preferably R^6 is hydroxyethyl and the $-SO_3H$ group on the phenyl ring is attached in the ortho position relative to the azo group.

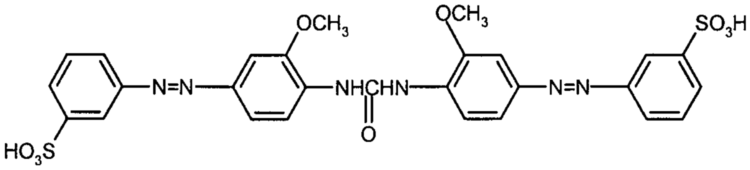
Preferably R^7 is -OH.

Preferably R^8 is -COOH or $-PO_3H_2$. It is especially preferred that R^8 is meta to the azo group in Formula (9).

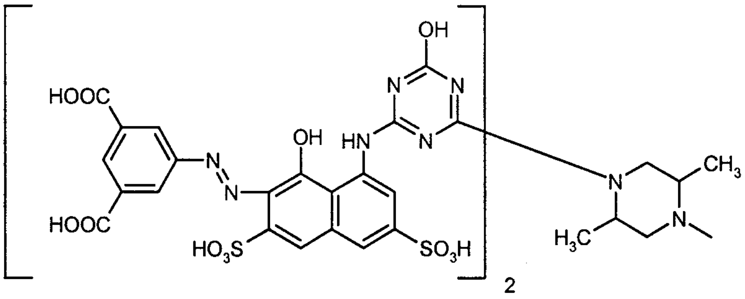
In view of the foregoing preferences, a preferred dye according to the second aspect of the present invention is the lithium salt of a dye having one of the Formulae (10) to (21):



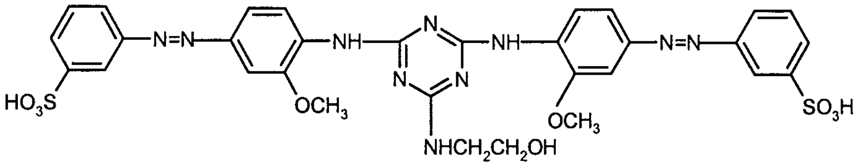
Formula (10)



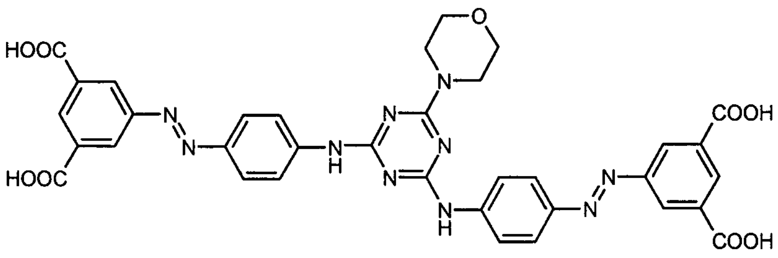
Formula (11)



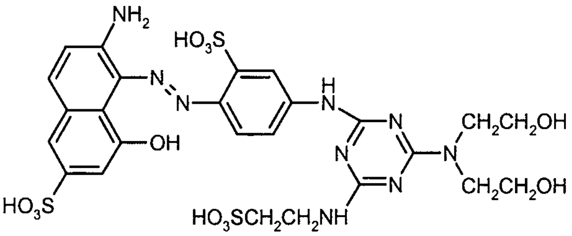
Formula (12)



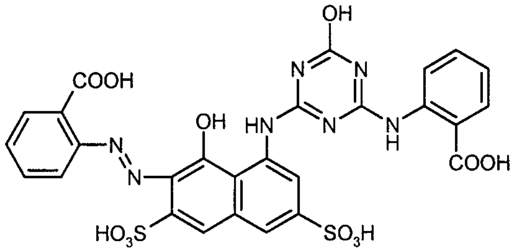
Formula (13)



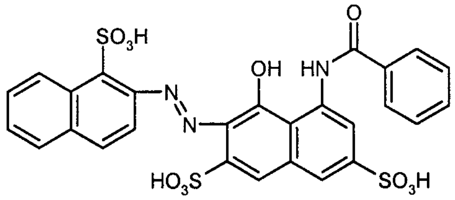
Formula (14)



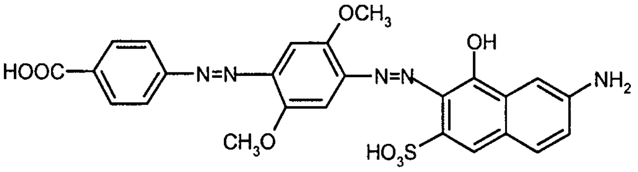
Formula (15)



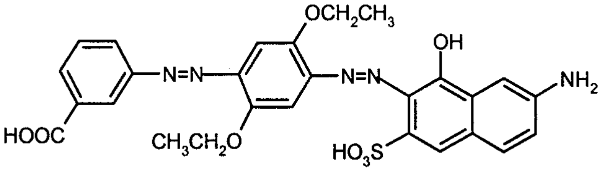
Formula (16)



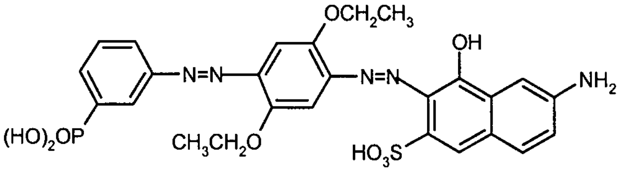
Formula (18)



Formula (19)



Formula (20)



Formula (21)

It is especially preferred that the dye according to the second aspect of the present invention is selected from the lithium salt of a dye of the Formula (10), (11) and (12), because these dyes exhibit a particularly high light-fastness.

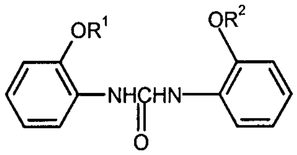
Preferably in this second aspect of the invention substantially all of the -COOH, -SO_3H and -PO_3H_2 groups shown in the dyes of the Formulae (1) to (21) are in the lithium salt form. Accordingly, in the dyes according to the second aspect of the invention preferably all the carboxy groups are present as -COOLi, all the sulpho groups are present as -SO_3Li and all the phosphono groups are present as -PO_3Li_2

The dyes of the Formulae (1) to (21) may be prepared by methods which directly result in the lithium salt. Alternatively the dyes may be prepared in the form of a salt with a cation other than lithium, for example the sodium or potassium salt, followed by conversion into the lithium salt using conventional techniques, preferably, reverse osmosis, nano-filtration, electrodialysis, dialysis, an ion exchange technique or by precipitating the dye in free acid form followed by neutralising with LiOH.

An example of a suitable technique for converting a dye in the form of a salt with a cation other than the lithium into its lithium salt comprises passing a solution of the alternative salt of a dye of Formula (1) to (21) through an acid loaded ion exchange resin to give the free acid form of the dye. A solution/suspension of the free acid form of the dye is then neutralised with a molar excess of lithium hydroxide to give the lithium salt.

The lithium salt of the dyes of Formula (1) may be prepared in the form of their sodium salts using an analogous process to that disclosed in Example 2 of EP 0 356 080. The sodium salt may then be converted to the lithium salt using any of the hereinbefore defined methods.

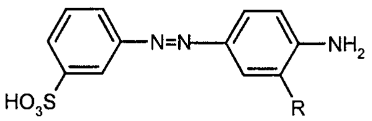
The lithium salt of the dye of Formula (2) may be prepared by diazotising a sulphoaniline (for example using $NaNo_2$ in dilute mineral acid at below 5°C) and coupling with a compound of the formula:



wherein R^1 and R^2 are as hereinbefore defined, followed by conversion to the lithium salt as hereinbefore described. Certain dyes of Formula (2) are commercially available in the form of their sodium salts, for example C.I. Direct Yellow 132.

The lithium salt of the dye of Formula (3) may be prepared using an analogous process to that described in example 3 of PCT publication number WO 94/16021, followed by conversion into the lithium salt.

The lithium salt of the dye of Formula (4) may be prepared by condensing hydroxyethylamine with a chlorotriazine analogue of the compound of Formula (4) in which there is a Cl atom in place of the hydroxyethylamino group, followed by conversion into the lithium salt. The chlorotriazine analogue may be prepared by condensing 2 moles of a compound of Formula (A) with one mole of cyanuric chloride:



Formula (A)

wherein R is as hereinbefore defined for R^4 and R^5.

The compound of Formula (A) may be prepared by diazotising a sulphoaniline and coupling onto aniline substituted by a C_{1-4}-alkoxy group at the 2- position.

Certain dyes of Formula (4) are commercially available as a sodium salt, for example C.I. Direct Yellow 142.

The lithium salt of the dye of Formula (5) may be prepared using an analogous process to that described in example 10 of EP 468 747 followed by conversion into the lithium salt. Certain dyes of the Formula (5) are commercially available in as of their sodium salt, for example CI Direct Yellow 173.

The lithium salt of the dye of Formula (6) may be prepared using conventional techniques, for example by the method described on pages 5 and 6 and Example 1 of PCT publication number WO 96/24636, followed by conversion into the lithium salt.

The lithium salt of the dye of Formula (7) may be prepared using conventional techniques, for example, using the method described on pages 17 and 18 and Example 1 of EP 0 628 088, followed by conversion to the lithium salt as hereinbefore defined.

The lithium salt of the dye of Formula (8) may be prepared by, for example, using the method disclosed in US 5,542,970, cols. 12 to 15, followed by conversion into the lithium salt.

The lithium salt of the dye of Formula (9) may be prepared using conventional techniques, for example the methods disclosed in EP 0 761 771, pages 11 to 16, and US 5,198,022, cols. 3 to 6 followed by conversion into the lithium salt.

C.I Reactive Red 180 and C.I. Acid Red 52 are all commercially available in the free acid form or as salts with sodium. The sodium salt may then be converted to the lithium salt using any of the hereinbefore defined methods.

The dyes may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims.

According to a third aspect of the present invention there is provided an anionic dye in the form of a salt with a mixture of cations wherein:

(i) the cations comprise a mixture of lithium and sodium cations;

(ii) at least 20 mole % of the total cations are lithium cations; and

(iii) the molar ratio of the lithium to sodium cations is from 1:4 to 99:1.

The anionic dye salts according to the third aspect of the invention exhibit surprisingly high light-fastness and good solubility in aqueous media compared to the light-fastness and solubility of the individual sodium and lithium salts of the anionic dye.

Preferably the anionic dye according to the third aspect of the present invention is an anionic direct, reactive or azo dye, more preferably an anionic azo, bis azo, tris azo or xanthene dye, and especially an anionic azo or bis azo dye.

In a first preferred embodiment of the third aspect of the invention the anionic dye is selected from C.I. Direct Black 19, C.I. Reactive Red 180, C.I. Acid Red 52 and a dye having one of the Formulae (1) to (9) as hereinbefore defined in relation to the second aspect of the present invention.

An especially preferred anionic dye in this first preferred embodiment of the third aspect of the present invention has any one of the of the Formulae (10) to (21), more especially of the Formula (11) or (14) as defined in relation to the second aspect of the invention. These preferred anionic dyes have a particularly high aqueous solubility and provide prints which exhibit a good light-fastness when they are in the form of a salt as hereinbefore defined in this third aspect of the invention.

Preferably the molar ratio of lithium to sodium cations in the anionic dye salt according to the third aspect of the invention is from 1:4 to 3:1, more preferably from 1:3 to 1.5:1 and especially from 1:2 to 1:1.

The anionic dye salt according to the third aspect of the invention may have other cations in addition to the sodium and lithium cations. For example the dye may contain sodium, lithium and one or more additional cations selected from potassium, ammonium and quaternary ammonium cations. It is preferred however, that the anionic dye salt according to the third aspect of the invention is substantially free from cations other than sodium and lithium.

The anionic dye salt according to the third aspect of the invention is preferably prepared by mixing the sodium and lithium salts of the anionic dyes to give the required ratio of lithium and sodium ions. Alternatively the anionic dye salt may be prepared by conversion of the sodium salt of the anionic dye to the mixed lithium/sodium salt using a conventional technique, for example by adding an appropriate quantity of LiOH to an aqueous solution of the sodium salt followed by removal of the unwanted inorganic sodium salts, for example by dialysis or reverse osmosis.

Preferably the dyes according to the second and third aspects of the invention are purified to remove impurities, especially di- and trivalent metals, for example calcium and magnesium. It is especially preferred that the dyes contain less than 50, more preferably less than 20 ppm di- and trivalent metals. The dyes may be purified using conventional techniques, for example ultra-filtration, reverse osmosis ion exchange or a combination of such methods.

According to a fourth aspect of the present invention there is provided an ink comprising a liquid medium and a dye according to the second or third aspect of the present invention.

The ink preferably comprises

(a) from 0.01 to 30 parts of a dye according to the second or third aspect of the present invention; and

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

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

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 preferred compounds and compositions in the ink are as hereinbefore defined in relation to the second and third aspects of the invention.

Component (a) of the ink may contain a single dye or a mixture comprising two or more dyes. A preferred mixture comprises a dye of the Formula (10) and a dye of the Formula (2) as defined in relation to the second or third aspect of the invention. Another preferred mixture comprises a dye of the Formula (10) and a dye of the Formula (4) as defined in relation to the second or third aspect of the invention.

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.

Preferably component (a) is completely dissolved in component (b). More preferably component (a) has a solubility in component (b) at 20°C of at least 10% by weight. This allows the preparation of 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.

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

When the 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 solvent(s) are selected from C_{1-6}-alkanols, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol and n-pentanol; cyclic alkanols, for example cyclohexanol and cyclopentanol; diols, preferably diols with 2 to 12 carbon atoms, for example pentane-1,5-diol and hexane-1,6-diol; amides, for example dimethylformamide or dimethylacetamide; amines, for example triethanolamine ethanolamine and diethanolamine; ketones or ketone-alcohols, for example acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; ethers, for example tetrahydrofuran or dioxane; oligo- or poly-alkyleneglycols, for example diethylene glycol, triethylene glycol, hexylene glycol, polyethylene glycol and polypropylene glycol; alkyleneglycols or thioglycols containing a C_2-C_6-alkylene group, for example ethylene glycol, propylene glycol, butylene glycol, pentylene glycol hexylene glycol and thiodiglycol; polyols, for example glycerol and 1,2,6-hexanetriol; C_{1-4}-alkyl-ethers of polyhydric alcohols, for example 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy] ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol, 2-(2-butoxyethoxy)ethanol and ethyleneglycolmonoallylether; cyclic amides, for example 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, for example caprolactone γ-butyrolactone; sulphoxides, for example dimethyl sulphoxide and sulpholane or mixtures containing two or more, especially from 2 to 8, of the aforementioned water-miscible organic solvents, for example thiodiglycol and a second glycol or diethylene glycol and 2-pyrrolidone.

Especially preferred water-miscible organic solvents are 2-pyrrolidone; N-methyl-pyrrolidone; alkylene- and oligo-alkylene-glycols, for example ethyleneglycol, diethyleneglycol, triethyleneglycol; and lower alkyl ethers of polyhydric alcohols, for example 2-methoxy-2-ethoxy-2-ethoxyethanol; and polyethyleneglycols with a molecular weight of up to 500.

A preferred mixture of water and water-miscible organic solvents comprises:

(i) from 60 to 99.5 parts water; and

(ii) from 0.5 to 40 parts in total of one or more solvents selected from diethylene glycol,2-pyrrolidone, N-methylpyrrolidone, cyclohexanol, caprolcatone, caprolactam, pentane-1,5-diol, 2-(2-butoxyethoxy)ethanol and thiodiglycol;

wherein the parts are by weight and the sum of the parts (i) and (ii) = 100.

Examples of further suitable ink media comprising a mixture of water and one or more organic solvent(s) are given in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A which are incorporated herein by reference thereto.

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 CH_2Cl_2; 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 C_{1-4}-alcohols. 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) &/or an alcohol (especially a C_{1-4}-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.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The dyes according to the second and third aspects of the present invention exhibit a high solubility in aqueous media. Accordingly it is preferred that the liquid medium is an aqueous medium, more preferably water or a mixture of water and one or more water-miscible organic solvent(s).

The ink may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

The inks provide prints which exhibit a high light-fastness. Furthermore, the inks are stable and exhibit reduced crusting when they are incorporated into an ink jet printer.

A fifth aspect of the invention provides a process for printing an image on a substrate comprising applying an ink containing a dye according to the second or third aspect of the invention to the substrate by means of an ink jet printer.

The preferred ink used in this process is an ink according to the fourth aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate used in the ink jet printing process is preferably paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, and especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP

201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper.

Preferred textile materials are natural, synthetic and semi-synthetic materials Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

According to a sixth aspect of the present invention there is provided a paper, an overhead projector slide or a textile material printed with an ink according to the fourth aspect of the invention, or by means of a process according to the fifth aspect of the invention.

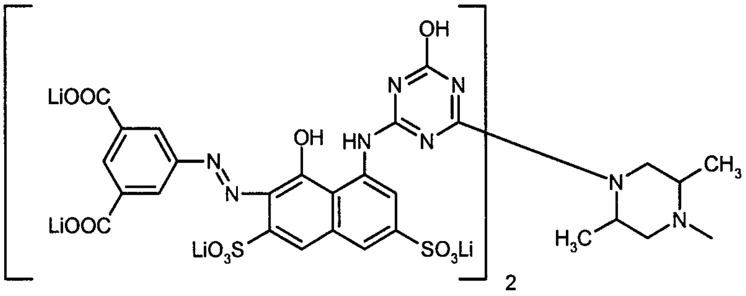
According to a seventh aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and an ink, the ink being present in the chamber and wherein the ink contains a dye according to the second or third aspect of the invention. Preferably the ink is an ink according to the fourth aspect of the present invention.

According to an eighth aspect of the present invention there is provided an ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in the seventh aspect of the present invention.

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

Example 1

Dye (1)



Dye (1)

Dye (1) was prepared as the sodium salt using the method described in Example 3 of PCT publication number WO 94/16021. The sodium salt was converted to the lithium salt using stages (a) and (b) described below:

Stage (a)

The sodium salt of the dye (5g) was dissolved in distilled water (100g) with stirring. Hydrochloric acid (1M) was added to reduce the pH to <2. The mixture was then stirred for 30 minutes to allow complete precipitation. The resulting slurry was filtered through a 0.45µm filter and air dried. The solid was slurried in 0.2M hydrochloric acid (50ml) filtered and air dried. This procedure was repeated three times.

Stage (b)

The product of stage (a) was dispersed in distilled water (100g) and the pH adjusted to 9.5 with lithium hydroxide. The solution was freeze dried to give the title product.

Comparative (1)

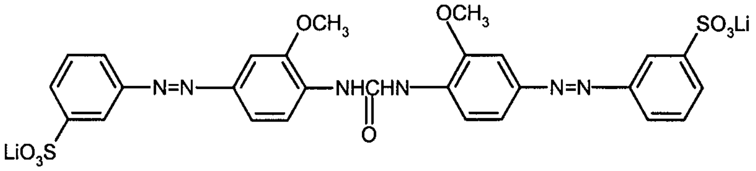
The sodium salt of Dye (1).

Comparative (2)

The ammonium salt of Dye (1).

Comparative (2) was made by converting the sodium salt of Dye (1) to the ammonium salt by the process described in stages (a) and (b) above, except that in stage (b) there was used ammonia in the place of LiOH.

Dye (2)



Dye (2)

The sodium salt of Dye (2) is commercially available from Zeneca Limited as C.I. Direct Yellow 132. The sodium salt was converted to the lithium salt using the process described above for Dye (1).

Comparative (3)

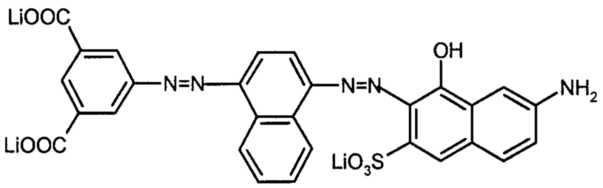
The sodium salt of Dye (2)

Comparative (4)

The ammonium salt of Dye (2).

Comparative (4) was prepared by converting the sodium salt of Dye (2) to the ammonium salt using the process described above for Comparative (2).

Dye (3)



Dye (3)

The sodium salt of Dye (3) was prepared using the process described in Example 2 of EP 0 356 080. The sodium salt was then converted to the lithium salt using the process described above for Dye (1).

Comparative (5)

The sodium salt of Dye (3).

Comparative (6)

The ammonium salt of Dye (3).

Comparative (6) was prepared by converting the sodium salt to the lithium salt using the same process described above for Comparative (2)

Inks

The inks shown in Table 1 comprised:
3.5 parts of the dye shown in the second column of Table 1;
5.0 parts 2-pyrrolidone;
5.0 parts thiodiglycol;
2.0 parts Surfynol 465 (a surfactant available from Air Products Inc.); and
84.5 parts water.

Each ink was prepared by dissolving the Dye shown in the second column of Table 1 (0.35g) in water (8.45g) by adding ammonia and adjusting the pH to 9.5. 2-pyrrolidone (0.5g), thiodiglycol (0.5g) and Surfynol 465 (0.2g) were then added and the mixture was stirred at ambient temperature. The resulting solution was filtered through a 0.45μm filter to give the ink.

Ink Jet Printing

Each ink shown in Table 1 was loaded into a HP 560 ink jet printer and was applied to Xerox Acid paper using the ink jet printer. When the resulting prints had dried a portion of the print was mounted, half covered, and faded in an Atlas Ci35a weatherometer.

The light-fastness of the prints was assessed by measuring the colour difference (ΔE) between the faded and unfaded portions of the print using an X-Rite 939 spectrodensitometer. The time shown in the column marked ΔE in Table 1 refers to the number of hours the print was faded for in the weatherometer.

A low ΔE value indicates a small colour change after fading in the weatherometer and therefore a high light-fastness.

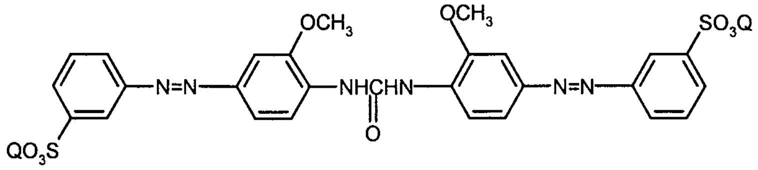
Table 1 clearly show that the lithium salts of the dyes resulted in prints which exhibit a high light fastness compared with sodium and ammonium salts.

Table 1

Ink	Dye	Salt	ΔE (50 hours)	ΔE (64 hours)	ΔE (100 hours)
1	Dye (1)	Li	-	-	18.8
2	Comparative (1)	Na	-	-	19.8
3	Comparative (2)	NH_4	-	-	28.2
4	Dye (2)	Li	8.45	-	-
5	Comparative (3)	Na	10.77	-	-
6	Comparative (4)	NH_4	11.97	-	-
7	Dye (3)	Li	-	4.1	-
8	Comparative (5)	Na	-	4.5	-
9	Comparative (6)	NH_4	-	6.4	-

Example 2

Dye (A)

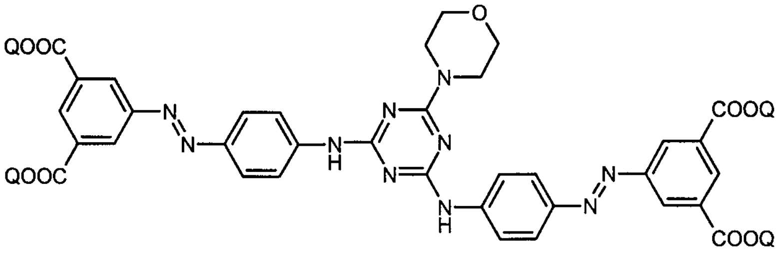


Dye (A)

wherein the cations represented by Q are a mixture of sodium and lithium cations and the molar ratio of lithium:sodium cations is 1:1.5.

Dye (A) was prepared by mixing 60 parts of the sodium salt of Dye (A) (available as C.I. Direct Yellow 132 from Zeneca Limited) with 40 parts of the lithium salt of Dye (A) (i.e. Dye (2) described in Example 1).

Dye (B)



Dye (B)

wherein the cations represented by Q are a mixture of sodium and lithium cations and the molar ratio of lithium:sodium cations is 1:1.5.

The sodium salt of Dye (B) was prepared using the method described in Example 10 of EP 468 747. The sodium salt was then converted to the lithium salt using the process described above for Dye (1).

Dye (B) was prepared by mixing 60 parts of the sodium salt of the dye with 40 parts of the lithium salt of the dye.

Aqueous Solubility

The weight % solubility of Dye (A), Dye (B) and the individual sodium and lithium salts of Dyes (A) and (B) in water at a pH of 9.5 and a temperature of 20°C were measured. The results of the solubility measurements are shown in Table 2.

Light-Fastness

The light -fastness of Dyes (A) and (B) and the individual sodium and lithium salts thereof were measured as described in Example 1; namely by ink jet printing an ink containing the each dye onto Xerox Acid paper and fading the prints using an Xrite Weatherometer. The light-fastness of each dye after 50 hours of fading is shown in Table 2.

Table 2

Dye	Light-Fastness (after 50 hours)	Solubility (wt % in water at pH 9.5))
Dye (A)	7	16
Sodium Salt of Dye (A)	11	11
Lithium Salt of Dye (A)	9	13
Dye (B)	4	19
Sodium Salt of Dye (B)	6	9
Lithium Salt of Dye (B)	5	10

Table 2 clearly shows that the mixed sodium lithium salts represented by Dyes (4) and (5) exhibit a surprisingly high aqueous solubility and light-fastness compared to the solubility and light-fastness of the individual sodium and lithium salts of the respective dyes.

Example 3

Inks

The inks described in Tables 3, 4 and 5 may be prepared wherein the Dye described in the second column is the Dye described below. Numbers quoted in the third column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Tables 3, 4 and 5:

PG = propylene glycol
DEG = diethylene glycol
NMP = N-methyl pyrrolidone
TFP = 2,2,3,3-tetrafluoropropanol
CYC = cyclohexanol
2P = 2-pyrrolidone

P12 = propane-1,2-diol
CET= cetyl ammonium bromide
TBT = tertiary butanol
GLY = glycerol
H - 1,6 = Hexane 1,6-diol
CAP-L = caprolactam
EG = ethylene glycol
UR = Urea
PHO = Na_2HPO_4 and
TDG = thiodiglycol
P-1,5 = Pentane-1,5-diol
CAP = caprolactone
TEA = triethanolamine
BUT = γ-butyrolactone
DEG-MBE = diethylene glycol monobutyl ether
PEG 200 = Polyethylene glycol (average molecular weight of 200)

Dyes (1), (2) and (3) are the dyes described in Example 1;
Dye (4) = the lithium salt of the dye of the hereinbefore defined Formula (13);
Dye (5) = the lithium salt of the dye of the hereinbefore defined Formula (14);
Dye (6) = the lithium salt of the dye of the hereinbefore defined Formula (15);
Dye (7) = the lithium salt of the dye of the hereinbefore defined Formula (16);
Dye (8) = the lithium salt of the dye of the hereinbefore defined Formula (17);
Dye (9) = the lithium salt of the dye of the hereinbefore defined Formula (18);
Dye (10) = the lithium salt of the dye of the hereinbefore defined Formula (19);
Dye (11) = the lithium salt of the dye of the hereinbefore defined Formula (20); and
Dye (12) = the lithium salt of the dye of the hereinbefore defined Formula (21).

TABLE 3

Ink	Dye	Dye Content	Water	PG	DEG	NMP	P-1,5	TEA	CYC	BUT	CAP	EG	CAP-L
10	3	3.0	90		5	4.8		0.2					
11	2	10.0	85	3		3	3			5			
12	4	2.1	91		8							1	1
13	5	3.1	86	5					0.2	4			4.8
14	6	1.1	81			9		0.5	0.5				
15	7	2.5	60	4	15	3	3			6		9	4
16	8	5	65		20		5			10		5	
17	9	2.4	75	5	4		5				6		5
18	10	4.1	80	3	5	2	9.7		0.3				
19	11	3.2	65		5	4	6			5	4		5
20	12	5.1	96								4	6	
21	2	10.8	90	5						5			
22	4	10.0	80	2	6	2	5			1			
23	5	1.8	80		5							4	
24	6	2.6	84			11						15	
25	7	3.3	80	2			10				2	5	6
26	9	12.0	90				7	0.3		2.7			
27	12	5.4	69	2	20	2	1					3	3

TABLE 4

Ink	Dye	Dye Content	Water	GLY	DEG	NMP	CET	TBT	TDG	UR	PHO	2P	PI2
28	1	3.0	80	15			0.2					4.8	
29	2	9.0	90		5						1.2		5
30	3	1.5	85	3.8	5		0.16	4.64	0.2				
31	4	2.5	90		6	3.88					0.12		
32	5	3.1	82	4	8		0.3						5.7
33	6	0.9	85		10					4.8	0.2		
34	7	8.0	90		4.7	5			0.3				
35	8	4.0	70		10	4				1		4	11
36	9	2.2	75	4	10	3				2		6	
37	10	10.0	91			6						3	
38	12	9.0	76		9	7		2.05			0.95	5	
39	11	5.0	78	5	11							6	
40	1	5.4	86			7						7	
41	2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	9.5	
42	1	2.0	90		10								
43	10	2	88			2			10				
44	9	5	78			5			12			5	
45	10	8	70	2		8			15			5	
46	8	10	80						8			12	
47	7	10	80		10								

TABLE 5

Ink	Dye	Dye Content	Water	PEG 200	DEG-MBE	NMP	H-1,6	TEA	TFP	BUT	CAP	EG	CAP-L
48	1	2.0	80	5		6	4					5	
49	2	3.0	90		5	4.8		0.2					
50	2	10.0	85	3		3	3			5		1	
51	4	2.1	91		8								1
52	5	3.1	86	5					0.2	3.8			5
53	6	1.1	81			9		0.5	0.5			9	
54	7	2.5	60	4	15	3	3			6		5	4
55	8	5	65		20					10			
56	9	2.4	75	5	4		5				6		5
57	10	4.1	80	3	5	2	9.7		0.3				
58	11	3.2	70		5	4	6			5	4	6	5
59	12	5.1	96								4		
60	3	10.8	90	5						5			
61	4	10.0	80	2	6	2	5			1		4	
62	5	1.8	80		5							15	
63	1	2.6	84			11						5	
64	7	3.3	80	2			10				2		6
65	8	12.0	90				7	0.3		2.8			
66	9	5.4	69	2	20	2	1					3	3
67	2	6.0	91			4						5	

CLAIMS

1. The use of lithium as a cation for an anionic dye to enhance the light-fastness of the dye.

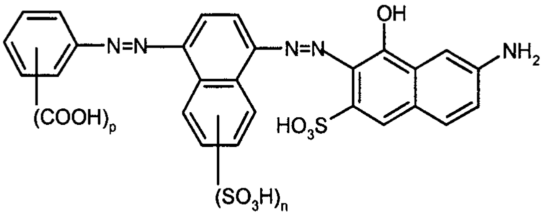
2. The use according to claim 1 wherein at least 20 mole % of the cations in the anionic dye are lithium cations.

3. The use according to either claim 1 or claim 2 wherein lithium is used in combination with sodium as cations for the anionic dye.

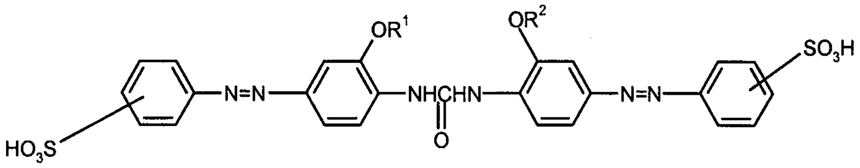
4. The use according to claim 3 wherein the molar ratio of lithium to sodium cations in the anionic dye is from 1:4 to 99:1.

5. The use according to any one of the preceding claims wherein the anionic dye is a water-soluble anionic dye containing at least as many carboxy groups as sulpho groups.

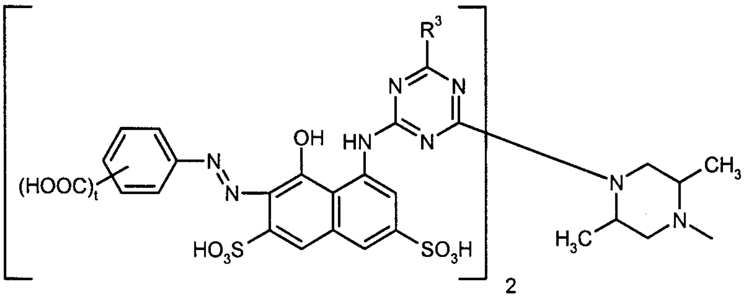
6. A dye selected from C.I. Reactive Red 180, C.I. Acid Red 52 and a dye having one of the Formulae (1) to (9), wherein the dye is in the lithium salt form:



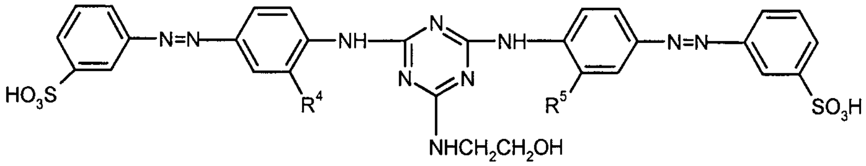
Formula (1)



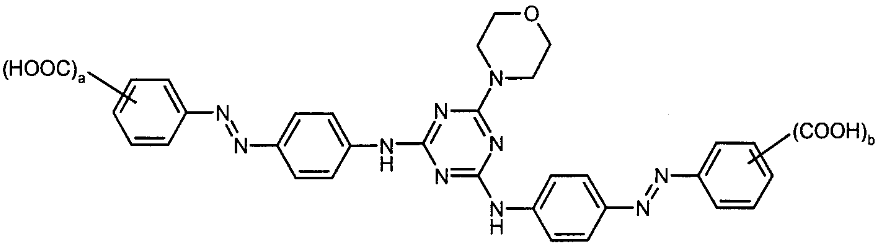
Formula (2)



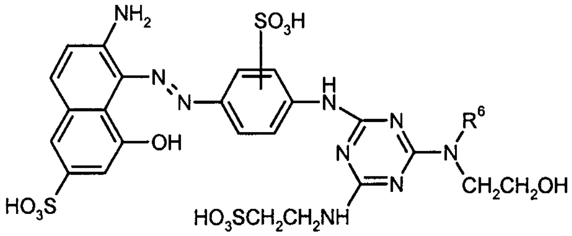
Formula (3)



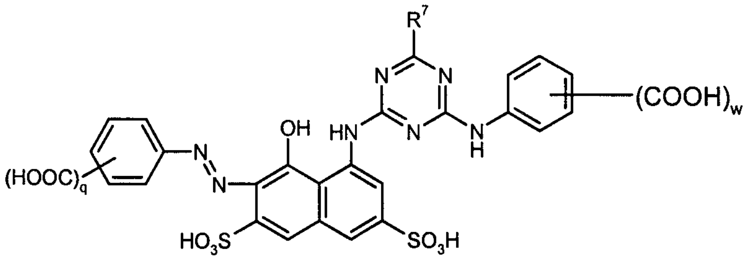
Formula (4)



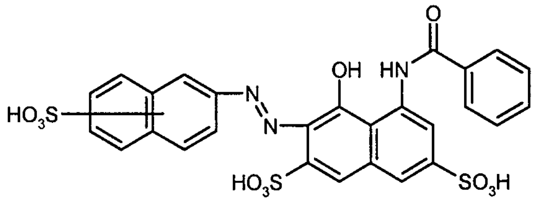
Formula (5)



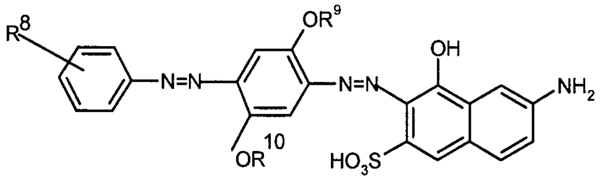
Formula (6)



Formula (7)



Formula (8)

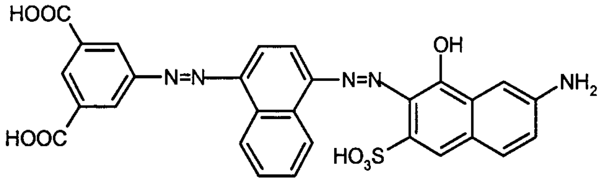


Formula (9)

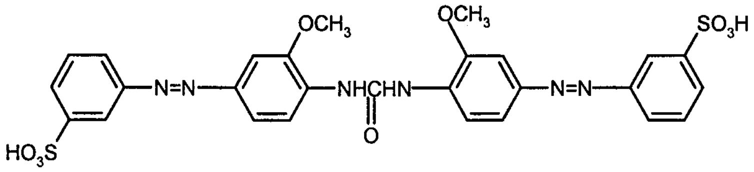
wherein:

R^1 and R^2	each independently is C_{1-4}-alkyl;
each R^3	independently is alkoxy, -OH, -Cl or amino;
R^4 and R^5	each independently is C_{1-4}-alkoxy;
R^6	is H or hydroxyethyl;
R^7	is -OH, -Cl, or C_{1-4}-alkoxy;
R^8	is -COOH, $-SO_3H$ or $-PO_3H_2$;
R^9 and R^{10}	each independently is methyl or ethyl;
p	is 1 or 2;
n	is 0 or 1;
q and w	each independently is 1 or 2;
a and b	each independently is 1 or 2; and
each t	independently is 1 or 2.

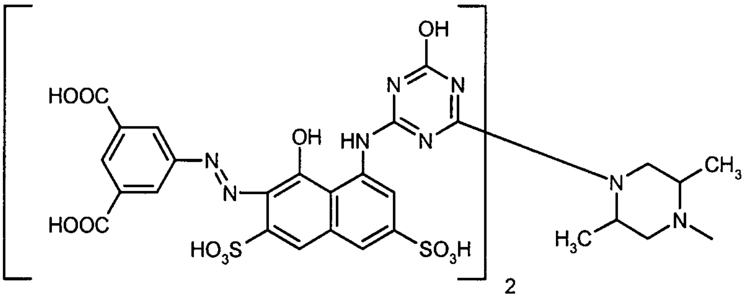
7. A dye according to claim 6 selected from the lithium salt of a dye of the Formula (10), (11) and (12):



Formula (10)



Formula (11)



Formula (12)

8. An anionic dye in the form of a salt with a mixture of cations wherein:

(i) the cations comprise a mixture of lithium and sodium cations;

(ii) at least 20 mole % of the total cations are lithium cations; and

(iii) the molar ratio of the lithium to sodium cations is from 1:4 to 99:1.

9. An anionic dye selected from C.I. Direct Black 19, C.I. Reactive Red 180, C.I. Acid Red 52 and a dye having one of the Formulae (1) to (9) as defined in claim 6, wherein the anionic dye is in the form of a salt according to claim 8.

10. An ink comprising a liquid medium and a dye according to any one of claims 4 to 9.

11. A process for printing an image on a substrate comprising applying an ink containing a dye according to any one of claims 4 to 9 to the substrate by means of an ink jet printer.

12. A paper, an overhead projector slide or a textile material printed with an ink according to claim 10, or by means of the process according to claim 11.

13. An ink jet printer cartridge comprising a chamber and an ink, the ink being present in the chamber and wherein the ink contains a dye according to any one of claims 4 to 9.

14. An ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in claim 13.

INTERNATIONAL SEARCH REPORT

Inter -tional Application No
PC /GB 99/01483

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00 C09B69/02 C09B67/24

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 6 C09D C09B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 635 944 A (LITKE ALVIN C) 18 January 1972 (1972-01-18) column 1, line 37 - line 39; examples 1-3 ---	1-4,8
T	EP 0 183 142 A (HOECHST AKTIENGESELLSCHAFT) 4 June 1986 (1986-06-04) page 4, paragraph 2 ---	8
X	EP 0 246 763 A (ICI PLC) 25 November 1987 (1987-11-25) page 2, line 1 - line 23 page 5, line 45 - line 50 ---	1,2
X	EP 0 014 180 A (CIBA GEIGY AG) 6 August 1980 (1980-08-06) page 2, paragraph 3 examples --- -/--	8

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search 23 September 1999	Date of mailing of the international search report 01. 10. 1999
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 Ketterer, M

1

International Application No
PCT/GB 99/01483

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 318 111 A (ICI LTD) 23 May 1973 (1973-05-23) page 1, line 26 - line 45 ---	8
X	EP 0 357 915 A (BAYER AG) 14 March 1990 (1990-03-14) page 8, line 44 -page 9, line 49 ---	8
X	DE 19 50 097 A (DU PONT DE NEMOURS & CO E I) 9 April 1970 (1970-04-09) page 5, line 8 - line 16 ---	8
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 042 (C-564), 30 January 1989 (1989-01-30) & JP 63 241071 A (MITSUBISHI KASEI CORP;OTHERS: 01), 6 October 1988 (1988-10-06) abstract ---	8,10-14
A	EP 0 425 150 A (HEWLETT PACKARD CO) 2 May 1991 (1991-05-02) cited in the application column 1, line 45 -column 2, line 5 example 6 ---	8,10-14
A	EP 0 415 581 A (HEWLETT PACKARD CO) 6 March 1991 (1991-03-06) claims 1,3 page 3, line 43 - line 44 & US 4 963 189 A cited in the application & US 4 963 189 A cited in the application ---	6,7, 10-14
A	US 5 542 970 A (MIURA KONOE ET AL) 6 August 1996 (1996-08-06) cited in the application formula No.9 on col. 5,6 column 2, line 61 - line 62 ---	1,6,8, 10-14
A	US 4 703 113 A (BOSTOCK STEPHEN B ET AL) 27 October 1987 (1987-10-27) cited in the application column 2, line 49 - line 64 column 3, line 67 -column 4, line 3 column 14, line 14 - line 16 abstract ---	6,8, 10-14
A	US 4 626 284 A (KOBAYASHI MASATSUNE ET AL) 2 December 1986 (1986-12-02) cited in the application Dye No. 21 abstract; claim 6 ---	1,6,8, 10-14
	-/--	

1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01483

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 129 797 A (BASF AG) 2 January 1985 (1985-01-02) page 1	8
A	EP 0 061 025 A (BAYER AG) 29 September 1982 (1982-09-29) examples	8
A	EP 0 284 009 A (HOECHST AG) 28 September 1988 (1988-09-28) page 4, line 44 -page 5, line 9; examples	6,8
A	DE 37 13 052 A (SUMITOMO CHEMICAL CO) 22 October 1987 (1987-10-22) page 6, line 18 - line 19; examples	8

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 99/01483

Box I Observations where certain claims were found unsearchable (Continuation of item 1 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.: 8 (partially)
because they relate to subject matter not required to be searched by this Authority, namely:

Claim 8 covers all possible anionic dyes in combination with a Li-counterion, indepentdent from their structure or use. Therefore a complete search of claim 8 was ot possible, a partial search was carried out focussed vis â vis the examples and claims 6,7,9.

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 II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

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

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

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.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01483

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 3635944	A	18-01-1972	US	3723056	A	27-03-1973
EP 183142	A	04-06-1986	DE	3443305	A	28-05-1986
			BR	8505929	A	19-08-1986
			CA	1253858	A	09-05-1989
			IN	164645	A	29-04-1989
			JP	61130374	A	18-06-1986
			US	4707545	A	17-11-1987
EP 0246763	A	25-11-1987	DE	3775464	A	06-02-1992
			JP	63046260	A	27-02-1988
EP 0014180	A	06-08-1980	AR	225164	A	26-02-1982
			BR	8000270	A	21-10-1980
			CA	1153851	A	20-09-1983
			US	4260391	A	07-04-1981
GB 1318111	A	23-05-1973	NONE			
EP 0357915	A	14-03-1990	DE	3826060	A	01-02-1990
			DE	3833380	A	19-04-1990
			EP	0356681	A	07-03-1990
			JP	2075665	A	15-03-1990
			JP	2075664	A	15-03-1990
			US	5075428	A	24-12-1991
DE 1950097	A	09-04-1970	US	3600376	A	17-08-1971
			US	3701624	A	31-10-1972
JP 63241071	A	06-10-1988	NONE			
EP 0425150	A	02-05-1991	US	5062892	A	05-11-1991
			DE	69018006	D	27-04-1995
			DE	69018006	T	20-07-1995
			HK	117495	A	28-07-1995
			JP	3160070	A	10-07-1991
EP 0415581	A	06-03-1991	US	4963189	A	16-10-1990
			JP	3091577	A	17-04-1991
US 5542970	A	06-08-1996	JP	1483050	C	27-02-1989
			JP	59078273	A	07-05-1984
			JP	60033145	B	01-08-1985
			DE	3338835	A	10-05-1984
			FR	2535333	A	04-05-1984
			GB	2131825	A,B	27-06-1984
			HK	73191	A	13-09-1991
			US	5524571	A	11-06-1996
US 4703113	A	27-10-1987	EP	0176195	A	02-04-1986
			JP	1860242	C	27-07-1994
			JP	5079109	B	01-11-1993
			JP	61062562	A	31-03-1986
			US	5118737	A	02-06-1992
US 4626284	A	02-12-1986	JP	1763008	C	28-05-1993
			JP	4052306	B	21-08-1992
			JP	60081265	A	09-05-1985

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01483

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4626284 A		JP 1594566 C	27-12-1990
		JP 2018711 B	26-04-1990
		JP 60108481 A	13-06-1985
		DE 3436891 A	25-04-1985
		GB 2151250 A,B	17-07-1985
EP 0129797 A	02-01-1985	DE 3322502 A	10-01-1985
EP 0061025 A	29-09-1982	DE 3109351 A	23-09-1982
EP 0284009 A	28-09-1988	DE 3710176 A	13-10-1988
		DE 3867269 A	13-02-1992
		IN 168508 A	13-04-1991
		JP 1870200 C	06-09-1994
		JP 5083103 B	24-11-1993
		JP 63256659 A	24-10-1988
		KR 9601064 B	18-01-1996
		MX 169308 B	29-06-1993
		US 4939242 A	03-07-1990
		US 5011917 A	30-04-1991
DE 3713052 A	22-10-1987	JP 1959230 C	10-08-1995
		JP 6086576 B	02-11-1994
		JP 62246968 A	28-10-1987
		GB 2195350 A,B	07-04-1988
		IT 1205822 B	31-03-1989
		KR 9605660 B	30-04-1996
		US 4832698 A	23-05-1989