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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C09B 47/00, C09D 11/00, C07D 487/22 // (C07D 487/22, 257:00, 209:00, 209:00, 209:00, 209:00)

A1

(11) International Publication Number: **WO 00/42110**

(43) International Publication Date: 20 July 2000 (20.07.00)

(21) International Application Number: PCT/US00/01206

(22) International Filing Date: 19 January 2000 (19.01.00)

(30) Priority Data:

60/116,315	19 January 1999 (19.01.99)	US
60/121,301	23 February 1999 (23.02.99)	US

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, 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, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, 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.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: NOVEL COLORANTS, COLORANT STABILIZERS, INK COMPOSITIONS, AND IMPROVED METHODS OF MAKING THE SAME

(57) Abstract

The present invention relates to a family of new porphine compounds for use as colorants and/or colorant stabilizers. The new porphine compounds may be used alone as a magenta dye or may be used in combination with one or more colorants to provide light stability to colorants. The present invention further relates to inks containing the new porphine compounds and a method for making the new compounds. The present invention also relates to improved methods of making Cu-meso-tetra-(2-sulfanatophenyl)-porphine (designated o-CuTPPS4). The improved processes allow the production of o-CuTPPS4 at lower cost and higher yields compared to conventional methods of making o-CuTPPS4. The present invention further relates to the use of o-CuTPPS4 as a colorant stabilizer for a variety of colorants, especially magenta colorants. The o-CuTPPS4, according to the present invention, provides a more stable and more "blue" colorant stabilizer compared to known colorant stabilizers, such as Cu-meso-tetra-(p-phenylcarboxylic acid)-porphine.

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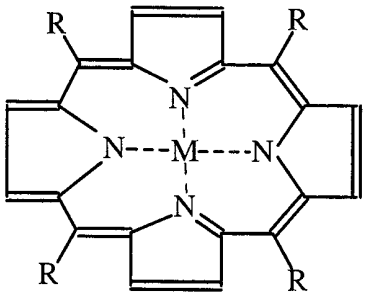
NOVEL COLORANTS, COLORANT STABILIZERS, INK COMPOSITIONS, AND IMPROVED METHODS OF MAKING THE SAME

TECHNICAL FIELD

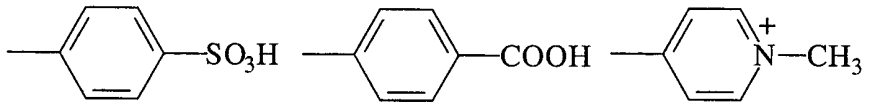
The present invention relates to an improved method for making porphines, and in particular 5,10,15,20-tetraphenyl-21H,23H-porphine-o,o^{1},o^{11},o^{111}-tetrasulfonic acid, tetrasodium salt (designated o-TPPS4). The present invention is also directed to a method of making Cu-meso-tetra-(2-sulfanatophenyl)-porphine (designated o-CuTPPS4) from o-TPPS4. The improved process allows the production of o-CuTPPS4 at lower cost and higher yields compared to conventional methods of making o-CuTPPS4. The present invention further relates to the use of o-CuTPPS4 as a colorant stabilizer for a variety of colorants, especially magenta colorants. The o-CuTPPS4, according to the present invention, provides a more stable and more "blue" colorant stabilizer compared to known colorant stabilizers, such as Cu-meso-tetra-(p-phenylcarboxylic acid)-porphine. The new porphine compounds may be used alone as a magenta dye or may be used in combination with one or more colorants to provide light stability to colorants. The present invention further relates to inks containing the new porphine compounds.

BACKGROUND OF THE INVENTION

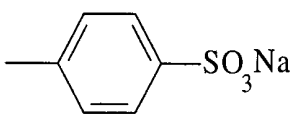
U.S. Patent Application Serial No. 08/757,222 filed November 27, 1996, now U.S. Patent No. 5,782,963; U.S. Patent Application Serial No. 08/788,863 filed January 23, 1997, pending; U.S. Patent Application Serial No. 08/843,410 filed April 15, 1997, now U.S. Patent No. 5,855,655; U.S. Patent Application Serial No. 08/903,911 filed July 31, 1997, now U.S. Patent No. 5,891,229; and U.S. Provisional Patent Applications Serial Nos. 60/055,785 filed August 15, 1997, and 60/062,643 filed October 22, 1997; all of which are assigned to Kimberly Clark Worldwide, Inc., disclose the use of a variety of porphines as colorant stabilizers. Porphines disclosed in the above-referenced applications include, but are not limited to, porphines having the following general structure:



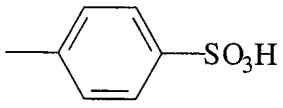
wherein R is any proton-donating moiety and M is iron, cobalt or copper. Desirably, R is SO_3H,



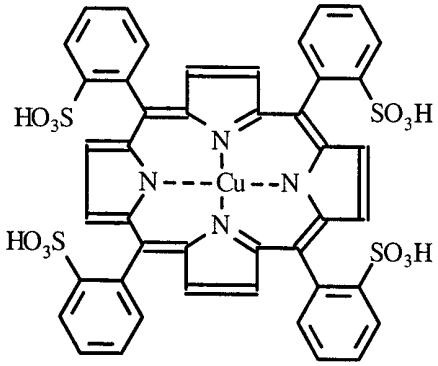
COOH, or R_1COOH wherein R_1 is an alkyl group of from 1 to 6 carbons. R may also be in its corresponding salt form, such as



SO_3Na for SO_3H or

for  .

One such porphine is Cu-meso-tetra-(2-sulfanatophenyl)-porphine (designated o-CuTPPS4) having the following structure:



An attempt to make o-CuTPPS4 is disclosed in Treibs et al., Leibigs Ann. Chem., 718, 183, 1998 (hereafter, "Treibs"). Treibs tried to prepare o-TPPS4 from 2-formylbenzenesulfonic acid, pyrrole, and propionoic acid. However, Treibs could not isolate the resulting product. Treibs reported a yield by GLC analysis of less than about 10 %.

Although porphines provide excellent light stability to colorants, some porphines are relatively unstable and/or tend to "yellow" colorant compositions containing magenta dyes. A more desirable porphine molecule would be one that has less tendency to "yellow" a colorant composition, and moreover, to make the colorant composition more "blue."

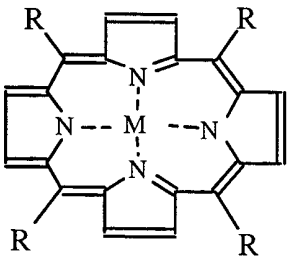
Also, while the above-described porphines provide excellent colorant stability to one or more colorants associated with the porphines, they do not provide an orange/red color to a composition containing the porphines.

Accordingly, there exists a need in the art for a convenient, low cost, high yield method of making o-TPPS4, o-

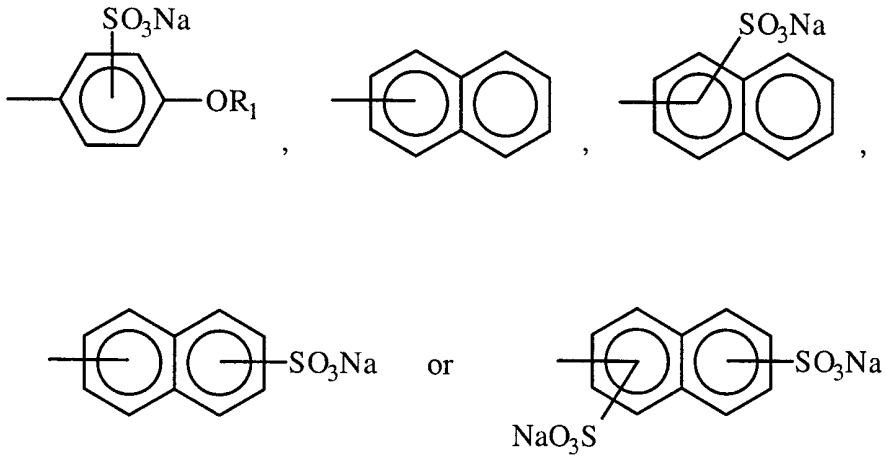
CuTPPS4, and compositions containing o-CuTPPS4. Further, there exists a need for improved porphines, which are capable of providing superior colorant stability while being more stable and without the tendency to "yellow" colorant compositions containing magenta dyes. Finally, there exists a need in the art for a new family of compounds that may be used alone as an orange/red colorant or may be used as a colorant stabilizer for one or more colorants associated with the new compounds.

SUMMARY OF THE INVENTION

The present invention addresses the needs described above by providing a new family of porphine compounds having the following general formula:



where M is iron, cobalt or copper; R represents



and R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group. The porphine compounds may be used as a magenta colorant and/or as a colorant stabilizer for other colorants. The new porphine compounds, when used as a colorant stabilizer, do not "yellow" magenta dyes. Consequently, unstable dyes, such as Acid Red 52, do not need to be used to make a magenta composition. The result is a more "blue" magenta color and a higher porphine to dye ratio, which creates superior light stability.

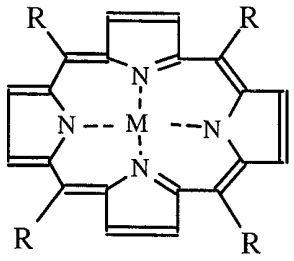
The present invention also addresses the needs described above by providing processes of making o-TPPS4 at a lower cost and higher yields. The present invention also relates to processes of making Cu-meso-tetra-(2-sulfanatophenyl)-porphine (designated o-CuTPPS4), and the use of o-CuTPPS4 as a colorant stabilizer for a variety of colorants, especially magenta colorants. o-CuTPPS4 has excellent stability and provides superior stability to a variety of colorants.

The present invention also relates to colorant compositions having improved stability, wherein the colorant is associated with one or more of the new porphine compounds. The present invention also relates to a process of making the new porphine compounds and the use of the porphine compounds in ink compositions.

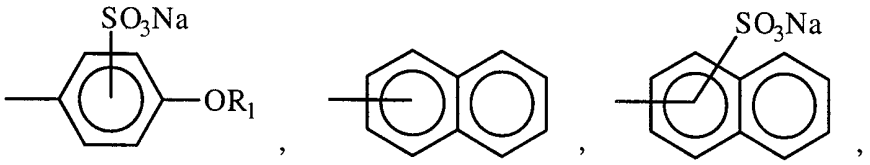
These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

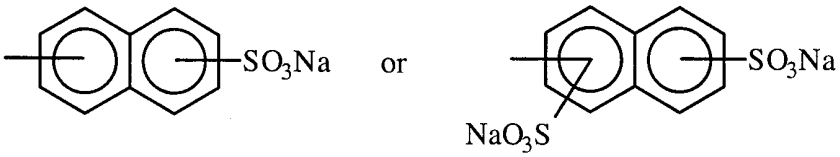
DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a new family of porphine compounds having the following general formula:



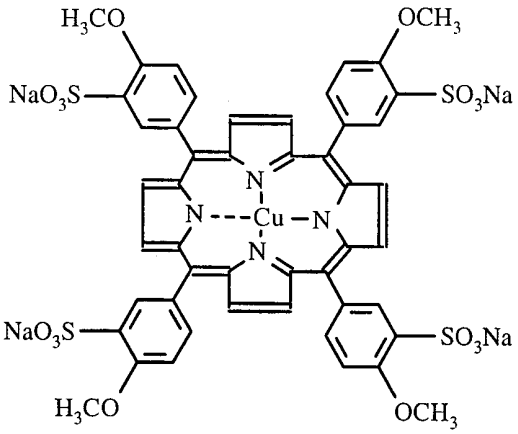
where M is iron, cobalt or copper; R represents



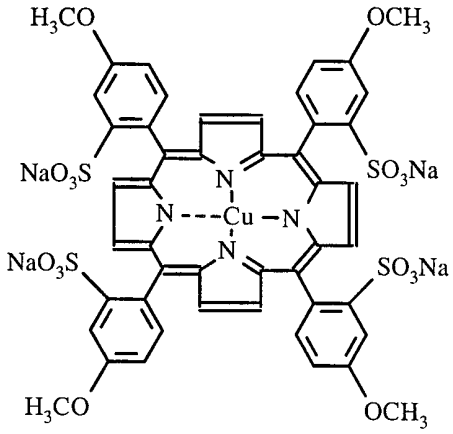


and where R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group. The new compounds may be used alone as a orange/red colorant or may be used as a colorant stabilizer.

In one embodiment of the present invention, the new porphine compound has one of the following structures:



or



The present invention also relates to colorant compositions having improved stability, wherein the colorant is associated with one or more colorant stabilizers comprising the above-described porphine compounds. Desirably, one or more of the new porphine compounds are admixed with a colorant solution. The colorant stabilizer may be one or more of the new porphine compounds alone or in combination with at least one metal or metal salt. Suitable metals and metal salts are disclosed in U.S. Patent No. 5,891,229, assigned to Kimberly Clark Worldwide, Inc., the entirety of which is incorporated herein by reference. Optionally, the new porphine compounds may be

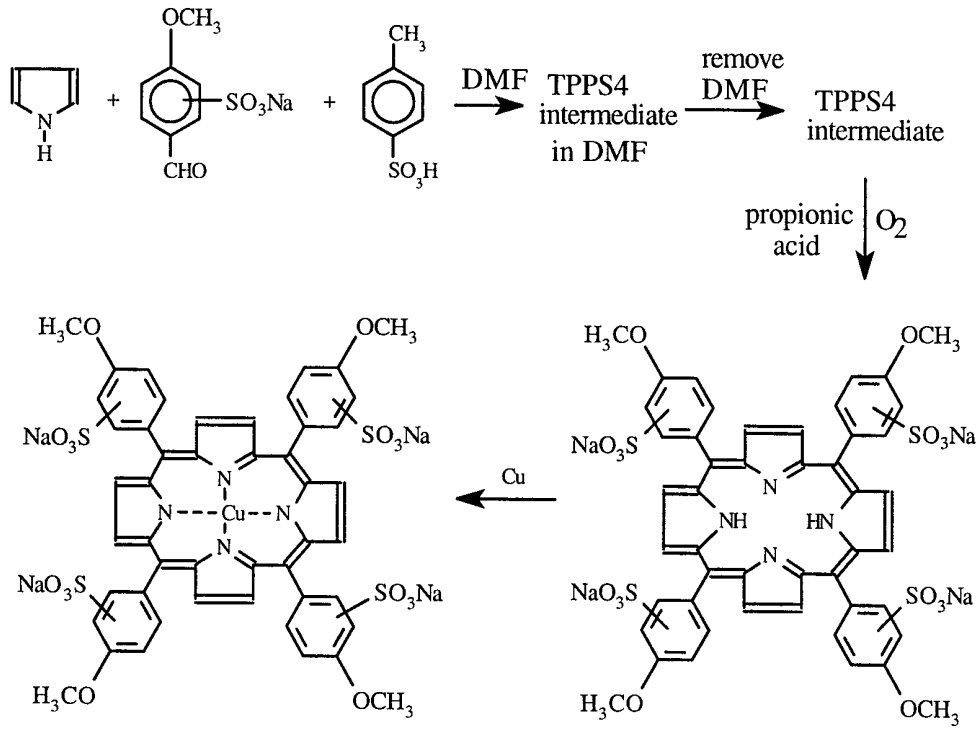
associated with a molecular includant, chelating agent, or other material to improve solubility and/or interaction of the porphine compound and the colorant. Suitable molecular includants, chelating agents, and other composition materials are also disclosed in U.S. Patent No. 5,891,229, assigned to Kimberly Clark Worldwide, Inc., the entirety of which is incorporated herein by reference.

The new porphine compounds may be associated with a variety of dyes or colorants. A suitable dye or colorant, for example, may be an organic dye. Organic dye classes include, by way of illustration only, triarylmethyl dyes, such as Malachite Green Carbinol base {4-(dimethylamino)-_-[4-(dimethylamino)phenyl]-_-phenyl-benzene-methanol}, Malachite Green Carbinol hydrochloride {N-4-[[4-(dimethylamino)phenyl]phenyl-methylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)phenyl]phenylmethylium chloride}, and Malachite Green oxalate {N-4-[[4-(dimethylamino)-phenyl]-phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)-phenyl]phenylmethylium oxalate}; monoazo dyes, such as Cyanine Black, Chrysoidine [Basic Orange 2; 4-(phenylazo)-1,3-benzenediamine monohydrochloride], Victoria Pure Blue BO, Victoria Pure Blue B, basic fuschin and ß-Naphthol Orange; thiazine dyes, such as Methylene Green, zinc chloride double salt [3,7-bis(dimethylamino)-6-nitrophenothiazin-5-ium chloride, zinc chloride double salt]; oxazine dyes, such as Lumichrome (7,8-dimethylalloxazine); naphthalimide dyes, such as Lucifer Yellow CH {6-amino-2-[(hydrazino-carbonyl)amino]-2,3-dihydro-1,3-dioxo-1H-benz[de]iso-quinoline-5,8-disulfonic acid dilithium salt}; azine dyes, such as Janus Green B {3-(diethylamino)-7-[[4-(dimethyl-amino)phenyl]azo]-5-phenylphenazinium chloride}; cyanine dyes, such as Indocyanine Green {Cardio-Green or Fox Green; 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-

sulfobutyl)-1H-benz[e]indolium hydroxide inner salt sodium salt}; indigo dyes, such as Indigo {Indigo Blue or Vat Blue 1; 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one}; coumarin dyes, such as 7-hydroxy-4-methyl-coumarin (4-methylumbelliferone); benzimidazole dyes, such as Hoechst 33258 [bisbenzimide or 2-(4-hydroxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5-bi-1H-benzimidazole trihydro-chloride pentahydrate]; paraquinoidal dyes, such as Hematoxylin {Natural Black 1; 7,11b-dihydrobenz[b]-indeno[1,2-d]pyran-3,4,6a,9,10(6H)-pentol}; fluorescein dyes, such as Fluoresceinamine (5-aminofluorescein); diazonium salt dyes, such as Diazo Red RC (Azoic Diazo No. 10 or Fast Red RC salt; 2-methoxy-5-chlorobenzenediazonium chloride, zinc chloride double salt); azoic diazo dyes, such as Fast Blue BB salt (Azoic Diazo No. 20; 4-benzoylamino-2,5-diethoxy-benzene diazonium chloride, zinc chloride double salt); phenylenediamine dyes, such as Disperse Yellow 9 [N-(2,4-dinitrophenyl)-1,4-phenylenediamine or Solvent Orange 53]; diazo dyes, such as Disperse Orange 13 [Solvent Orange 52; 1-phenylazo-4-(4-hydroxyphenylazo)naphthalene]; anthra-quinone dyes, such as Disperse Blue 3 [Celliton Fast Blue FFR; 1-methylamino-4-(2-hydroxyethylamino)-9,10-anthraquinone], Disperse Blue 14 [Celliton Fast Blue B; 1,4-bis(methylamino)-9,10-anthraquinone], and Alizarin Blue Black B (Mordant Black 13); trisazo dyes, such as Direct Blue 71 {Benzo Light Blue FFL or Sirius Light Blue BRR; 3-[(4-[(4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo]-6-sulfo-1-naphthalenyl)-azo]-1-naphtha-lenyl)azo]-1,5-naphthalenedisulfonic acid tetrasodium salt}; xanthene dyes, such as 2,7-dichloro-fluorescein; proflavine dyes, such as 3,6-diaminoacridine hemisulfate (Proflavine); sulfonaphthalein dyes, such as Cresol Red (o-cresolsulfonaphthalein); phthalocyanine dyes, such as Copper Phthalocyanine {Pigment Blue 15; (SP-4-1)-[29H,31H-phthalocyanato(2-)-N^{29},N^{30},N^{31},N^{32}]copper}; carotenoid dyes, such as trans-ß-carotene (Food Orange 5); carminic acid dyes,

such as Carmine, the aluminum or calcium-aluminum lake of carminic acid (7-a-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracene-carbonylic acid); azure dyes, such as Azure A [3-amino-7-(dimethylamino)phenothiazin-5-ium chloride or 7-(dimethyl-amino)-3-imino-3H-phenothiazine hydrochloride]; and acridine dyes, such as Acridine Orange [Basic Orange 14; 3,8-bis(dimethylamino)acridine hydrochloride, zinc chloride double salt] and Acriflavine (Acriflavine neutral; 3,6-diamino-10-methylacridinium chloride mixture with 3,6-acridine-diamine).

The present invention is further directed to a convenient, fast, low cost, environmental-friendly process of making new porphine compounds. One process of making new porphine compounds proceeds by the following reaction, wherein N,N-dimethylformamide (DMF) is used as the solvent:



The above process produces TPPS4 at yields of greater than 80%, and as high as about 96 to 97%. The TPPS4 is further reacted with Cu to produce one of the porphine compounds of the present invention. The latter reaction proceeds at yields of greater than 90%, and as high as about 96 to 97%.

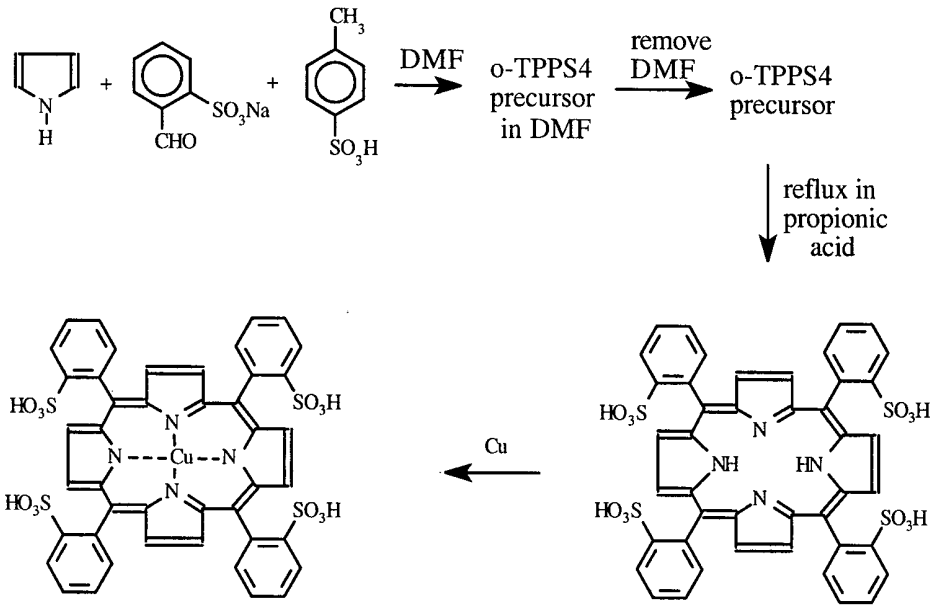
The reaction conditions for the above process may vary. Typically, the reaction may be carried out in a two-step process as follows. The reactants are purified by the following process or a similar purification process. The pyrrole is distilled under argon and a fraction is collected at 130°C. The substituted benzenesulfonic acid, sodium salt reactant is purified by a Dean and Stark method using benzene as the solvent. The solution is filtered at 60°C and the solid pumped in a vacuum oven overnight at room-temperature. The p-toluene sulfonic acid may also be purified by a Dean and Stark method using benzene as the solvent. It should be noted that a variety of substituted benzenesulfonic acid, sodium salt reactants may be used in the above-described reaction. Suitable substituted benzenesulfonic acid, sodium salt reactants include, but are not limited to, 2-formylbenzenesulfonic acid, sodium salt; 3-formylbenzenesulfonic acid, sodium salt; 2-alkoxy-5-formylbenzenesulfonic acid, sodium salt; and 2-formyl-5-alkoxybenzenesulfonic acid, sodium salt; wherein the alkoxy group contains up to about six carbon atoms.

In the first step, the substituted benzenesulfonic acid, sodium salt, N,N-dimethylformamide (DMF) and pyrrole are placed in a reaction vessel and stirred at room-temperature. The mixture is flushed with argon for about five minutes while stirring prior to heating. The mixture is then heated to 100°C for about ten to twelve minutes. The toluene sulfonic acid dissolved in 15 ml of DMF is injected into the reaction mixture. The reaction mixture is heated to 150°C and held at this temperature for about 50 minutes to form a TPPS4 intermediate having an absorption peak at about 210 nm. DMF is removed from the reaction mixture to yield a precipitate.

In the second step, the TPPS4 intermediate is mixed with propionic acid. Air or oxygen is bubbled through the mixture at reflux for a period of time to yield a finished product having an absorption peak at about 412 nm. Conversion of the intermediate to the finished product may be monitored using an UV/VIS spectrometer. Reflux time may vary, but usually the reflux time is up to about 10 hours to convert the TPPS4 intermediate to TPPS4.

The choice of solvent in the first step of the above process may be any solvent, which enables the efficient production of TPPS4 and the new porphine compounds. Suitable solvents include, but are not limited to, DMF, dimethyl sulfoxide (DMSO), and dimethyl acetamide.

In a further embodiment of the present invention, porphine compounds, designated o-CuTPPS4, are produced by the following reaction, wherein DMF is used as the solvent:



The above process produces o-TPPS4 at yields of greater than 90%, and as high as about 96 to 97%.

In this embodiment, the reactants are purified by the following process. The pyrrole is distilled under argon and a fraction is collected at 140°C. The 2-formylbenzenesulfonic acid, sodium salt and p-toluene sulfonic acid may each separately be purified by a Dean and Stark method using benzene as the solvent. The solution is filtered at 60°C and the solid pumped in a vacuum oven overnight at room-temperature.

The reaction in this embodiment is also a two-step reaction. In the first step, the 2-formylbenzenesulfonic acid, sodium salt, N,N-dimethylformamide (DMF) and pyrrole are placed in a reaction vessel and stirred at room-temperature. The mixture is flushed with argon for about five minutes while stirring prior to heating. The mixture is then heated to 100°C for about ten to twelve minutes. The toluene sulfonic acid dissolved in 15 ml of DMF is injected into the reaction mixture. The reaction mixture is heated to 150°C and held at this temperature for about 50 minutes to form a o-TPPS4 precursor having an absorption peak at about 210 nm. DMF is removed from the reaction mixture to yield a precipitate.

In the second step, the o-TPPS4 precipitate is mixed with propionic acid. Air or oxygen is bubbled through the mixture at reflux for a period of time to yield a finished product having an absorption peak at about 412 nm. Conversion of the precursor to the finished product may be monitored using an UV/VIS spectrometer. Reflux time may vary, but usually the reflux time is up to about 10 hours to convert the o-TPPS4 precursor to o-TPPS4.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or scope of the present invention. In the examples, all parts are parts by weight unless stated otherwise.

EXAMPLE 1

Preparation of TPPS4 Intermediate

Tetra-(3-sulfanato-4-methoxyphenyl)-porphine (designated TPPS4) was prepared by mixing the following reactants in DMF solvent: pyrrole; 2-methoxy-5-formylbenzene sulfonic acid, sodium salt; and p-toluenesulfonic acid. Prior to mixing the reactants, pyrrole was distilled under an argon atmosphere with the fraction boiling at 130°C collected. The 2-methoxy-5-formylbenzene sulfonic acid, sodium salt (Aldrich) was purified by a Dean and Stark method using benzene as the solvent. The solution was filtered at 60°C and the resulting solid was pumped in a vacuum oven overnight at room-temperature. The DMF (99.9% anhydrous grade available from Aldrich) was used without further purification. The p-toluenesulfonic acid was purified by a Dean and Stark method using benzene as the solvent.

A mixture of 5.0 g of the pyrrole, 15.6 g of the 2-methoxy-5-formylbenzene sulfonic acid, sodium salt, and 200 ml of the DMF was placed into a 500 ml three-necked, round-bottom flask fitted with a magnetic stir bar, condenser, thermometer, and argon gas bubbler inlet. The reaction mixture was flushed with argon for five minutes with stirring prior to heating. The mixture was then heated to 100°C for about 10-12 minutes at which time 0.76 g of p-toluenesulfonic acid was syringed into the reaction mixture. The p-toluenesulfonic acid was dissolved in 15 ml of DMF. The clear, colorless reaction mixture turned red to blood red to brown red to red black in one to two minutes. The reaction mixture was heated to 150°C and held at this temperature for about 50 minutes.

After about 50 minutes at 150°C, the reaction was cooled in an ice bath for about 20 minutes. The DMF was removed to yield a precipitate. The wet solid was then placed in a vacuum oven overnight at ambient temperature to dry the solid.

EXAMPLE 2

Preparation of TPPS4 in an Argon Atmosphere

Ten grams of the dried powder of Example 1 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux in an argon atmosphere. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the TPPS4 intermediate to TPPS4.

The mixture was refluxed for about 67 hours to yield a small amount of TPPS4 having an absorption peak at 412 nm.

EXAMPLE 3

Preparation of TPPS4 in an Open Air Condenser

Ten grams of the dried powder of Example 1 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux with an open air condenser. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the TPPS4 intermediate to TPPS4.

The mixture was refluxed for about 67 hours. After 10 hours of reflux, conversion to TPPS4 was substantially completed. Full conversion to TPPS4 having an absorption peak at 412 nm was completed at 67 hours.

EXAMPLE 4

Preparation of TPPS4 with Air Bubbled Into the Reaction Mixture

Ten grams of the dried powder of Example 1 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux while air was bubbled into the reaction mixture. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the TPPS4 intermediate to TPPS4.

The mixture was refluxed for 10 hours. Full conversion to TPPS4 having an absorption peak at 412 nm was completed in 10 hours.

EXAMPLE 5

Preparation of CuTPPS4 Colorant Stabilizer

Cu-meso-tetra-(3-sulfanato-4-methoxyphenyl)-porphine (designated CuTPPS4) was prepared by the following reaction. A mixture of 0.31 g of copper, 5.0 g of TPPS4 from Example 4, and 50 ml of water were added to a 200 ml round-bottom flask fitted with a condenser and magnetic stirrer bar. The mixture was heated in reflux for three hours. The hot mixture was evaporated down to about 10 ml and chilled. Acetone was added to the mixture. The precipitate was filtered and washed with hexane and toluene. The precipitate was dried under vacuum to yield 3.9 g of a solid. The yield was about 72%.

TLC showed a clean product of CuTPPS4.

EXAMPLE 6

Preparation of a Magenta Composition Containing CuTPPS4 As the Colorant

A magenta ink was prepared having the following composition wherein the components are given in weight %:

	Red
DI Water	82.69
Borax	1.90
HCL(1N)	1.57
EDTA 2Na	0.10
CuTPPS4 (Example 5)	0.50
EG	5.00
Glycerine	5.00
GIV-GARD DXN®	0.20
COBRATEC® 99	0.10

The ink was prepared using the following components: deionized water; borax; hydrochloric acid as a buffer/pH adjuster; EDTA or sodium salts thereof as a chelating agent; ethylene glycol and glycerine as wetting agents; GIV-GARD DXN® as a biocide; COBRATEC® 99 as a corrosion inhibitor; and CuTPPS4 from Example 5 as the dye.

The magenta composition was printed onto a photoglossy medium to produce a light-stable magenta having color gamut with an enhanced blue component.

EXAMPLE 7

Preparation of a Magenta Composition Containing CuTPPS4 As a Colorant Stabilizer

A magenta ink was prepared having the following composition wherein the components are given in weight %:

	Red
DI Water	81.49
Borax	1.90
HCL(1N)	1.57
EDTA 2Na	0.10
CuTPPS4 (Example 5)	0.50
EG	5.00
Glycerine	5.00
GIV-GARD DXN®	0.20
COBRATEC® 99	0.10
Reactive Red 187	2.89
Acid Red 52	1.20

The ink was prepared using the following components: deionized water; borax; hydrochloric acid as a buffer/pH adjuster; EDTA or sodium salts thereof as a chelating agent; ethylene glycol and glycerine as wetting agents; GIV-GARD DXN® as a biocide; COBRATEC® 99 as a corrosion inhibitor; Reactive Red 187 and Acid Red 52 as dyes; and CuTPPS4 from Example 5 as a colorant stabilizer.

The magenta composition was printed onto a photoglossy medium to produce a light-stable magenta having color gamut with an enhanced blue component.

EXAMPLE 8

Preparation of o-TPPS4 Precursor

Tetra-(2-sulfanatophenyl)-porphine (designated o-TPPS4) was prepared from the following reactants in a DMF solvent: pyrrole; 2-formylbenzene sulfonic acid, sodium salt; and p-toluenesulfonic acid. Prior to mixing the reactants, pyrrole was distilled under an argon atmosphere with the fraction boiling at 140°C collected. The 2-formylbenzene sulfonic acid, sodium salt (Aldrich) was purified by a Dean and Stark method using benzene as the solvent. The solution was filtered at 60°C and

the resulting solid was pumped in a vacuum oven overnight at room-temperature. The DMF (99.9% anhydrous grade available from Aldrich) was used without further purification. The p-toluenesulfonic acid was purified by a Dean and Stark method using benzene as the solvent.

A mixture of 5.0 g of the pyrrole, 15.6 g of the 2-formylbenzenesulfonic acid, sodium salt, and 200 ml of the DMF was placed into a 500 ml three-necked, round-bottom flask fitted with a magnetic stir bar, condenser, thermometer, and argon gas bubbler inlet. The reaction mixture was flushed with argon for five minutes with stirring prior to heating. The mixture was then heated to 100°C for about 10-12 minutes at which time 0.76 g of p-toluenesulfonic acid was syringed into the reaction mixture. The p-toluenesulfonic acid was dissolved in 15 ml of DMF. The clear, colorless reaction mixture turned red to blood red to brown red to red black in one to two minutes. The reaction mixture was heated to 150°C and held at this temperature for about 50 minutes.

After about 50 minutes at 150°C, the reaction was cooled in an ice bath for about 20 minutes. The DMF was removed to yield a precipitate. The wet solid was then placed in a vacuum oven overnight at ambient temperature to dry the solid.

EXAMPLE 9

Preparation of o-TPPS4 in an Argon Atmosphere

Ten grams of the dried powder of Example 8 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux in an argon atmosphere. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the o-TPPS4 precursor to o-TPPS4.

The mixture was refluxed for about 67 hours to yield a small amount of o-TPPS4 having an absorption peak at 412 nm.

EXAMPLE 10

Preparation of o-TPPS4 in an Open Air Condenser

Ten grams of the dried powder of Example 8 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux with an open air condenser. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the o-TPPS4 precursor to o-TPPS4.

The mixture was refluxed for about 67 hours. After 10 hours of reflux, conversion to o-TPPS4 was substantially completed. Full conversion to o-TPPS4 having an absorption peak at 412 nm was completed at 67 hours.

EXAMPLE 11

Preparation of o-TPPS4 with Air Bubbled Into the Reaction Mixture

Ten grams of the dried powder of Example 8 was mixed with 200 ml of propionic acid in a 500 ml three-necked round-bottom flask. The mixture was heated at reflux while air was bubbled into the reaction mixture. The reaction mixture was monitored by a UV/VIS spectrometer to follow conversion of the o-TPPS4 precursor to o-TPPS4.

The mixture was refluxed for 10 hours. Full conversion to o-TPPS4 having an absorption peak at 412 nm was completed in 10 hours.

EXAMPLE 12

Preparation of o-CuTPPS4 Colorant Stabilizer

Cu-meso-tetra-(2-sulfanatophenyl)-porphine (designated o-CuTPPS4) was prepared by the following reaction. A mixture of 0.31 g of copper, 5.0 g of o-TPPS4 from Example 11, and 50 ml of water were added to a 200 ml round-bottom flask fitted with a condenser and magnetic stirrer bar. The mixture was heated in reflux for three hours. The hot mixture

was evaporated down to about 10 ml and chilled. Acetone was added to the mixture. The precipitate was filtered and washed with hexane and toluene. The precipitate was dried under vacuum to yield 3.9 g of a solid. The yield was about 72%.

TLC showed a clean product of o-CuTPPS4.

EXAMPLE 13

Preparation of a Magenta Composition Containing o-CuTPPS4 Colorant Stabilizer

A magenta ink was prepared having the following composition wherein the components are given in weight %:

	Red
DI Water	81.49
Borax	1.90
HCL(1N)	1.57
EDTA 2Na	0.10
o-CuTPPS4 (Example 12)	0.50
EG	5.00
Glycerine	5.00
GIV-GARD DXN®	0.20
COBRATEC® 99	0.10
Reactive Red 187	2.89
Acid Red 52	1.20

The ink was prepared using the following components: deionized water; borax; hydrochloric acid as a buffer/pH adjuster; EDTA or sodium salts thereof as a chelating agent; ethylene glycol and glycerine as wetting agents; GIV-GARD DXN® as a biocide; COBRATEC® 99 as a corrosion inhibitor; Reactive Red 187 and Acid Red 52 as dyes; and o-CuTPPS4 from Example 12 as a colorant stabilizer.

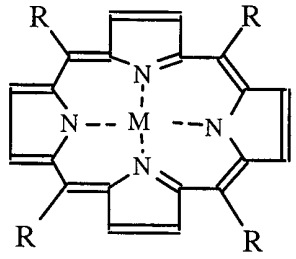
The magenta composition was printed onto a photoglossy medium to produce a light-stable magenta having color gamut with an enhanced blue component.

Having thus described the invention, numerous changes and modifications thereof will be readily apparent to those having ordinary skill in the art, without departing from the spirit or scope of the invention.

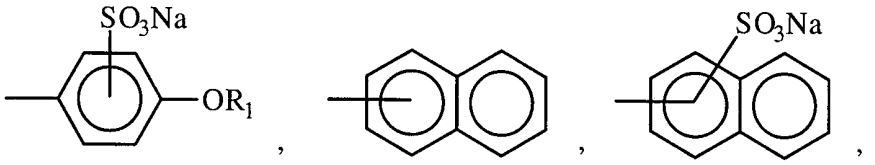
CLAIMS

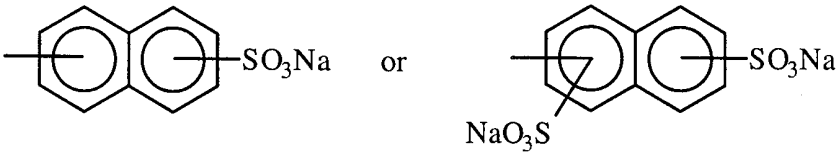
What is claimed is:

1. An ink composition comprising a porphine having the following general formula:



wherein M is iron, cobalt or copper; R represents





and R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group.

2. The ink composition of Claim 1, wherein the composition further comprises one or more colorants.

3. The ink composition of Claim 1, wherein the composition further comprises at least one metal or metal salt.

4. The ink composition of Claim 3, wherein the metal or metal salt comprises a lanthanide or lanthanide salt.

5. The ink composition of Claim 4, wherein the lanthanide or lanthanide salt comprises europium or europium salt.

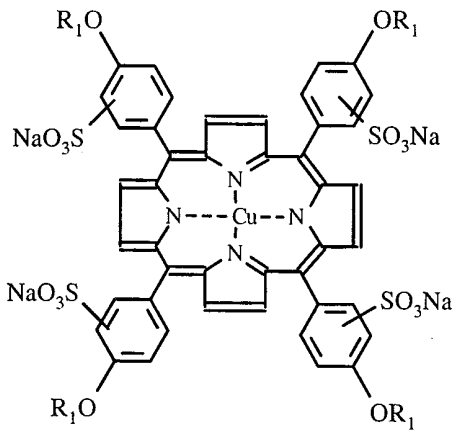
6. The ink composition of Claim 1, wherein the composition further comprises a colorant, a molecular includant, a chelating agent, or a combination thereof.

7. The ink composition of Claim 6, further comprising a molecular includant.

8. The ink composition of Claim 7, wherein the molecular includant is one or more cyclodextrins.

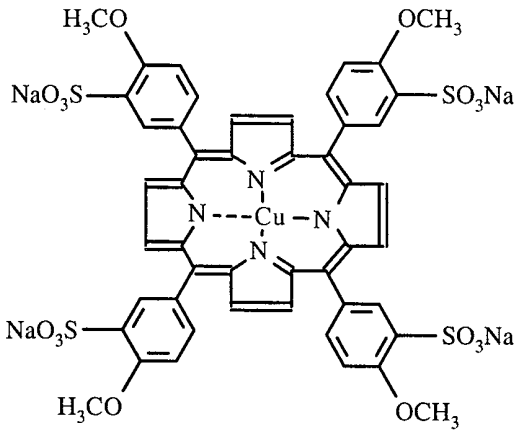
9. The ink composition of Claim 8, wherein the one or more cyclodextrins comprise α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin, δ-cyclodextrin, hydroxypropyl β-cyclodextrin, or hydroxyethyl β-cyclodextrin.

10. The ink composition of Claim 1, wherein the porphine comprises

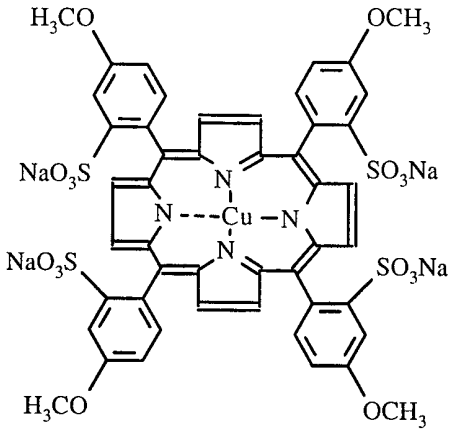


wherein R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group.

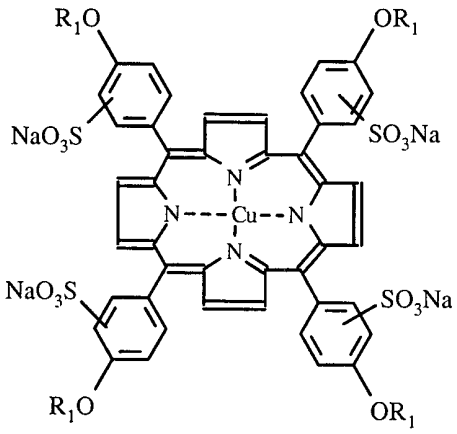
11. The ink composition of Claim 1, wherein the porphine comprises



or

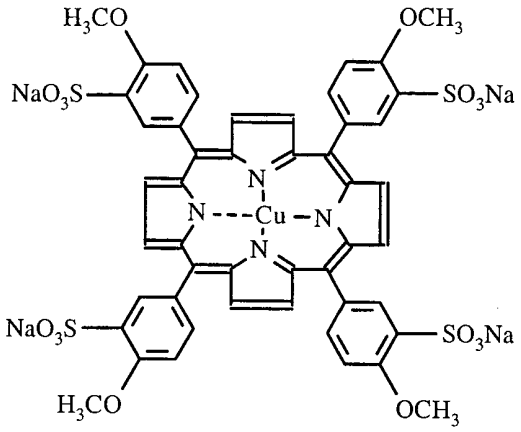


12. A porphine compound having the following structures:

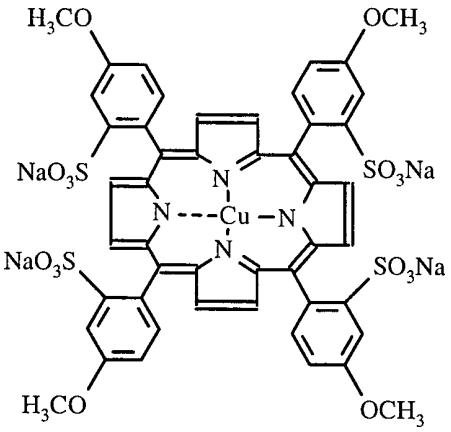


wherein R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group.

13. The compound of Claim 12, wherein the compound has one of the following structures:



or



14. An ink composition comprising the porphine of Claim 11.

15. A method of making a porphine, said method comprising:

forming a first reaction mixture of a substituted benzenesulfonic acid or a sodium salt thereof, pyrrole, a substituted toluene compound, and a solvent;

heating the first reaction mixture to form a porphine precursor;

removing the solvent to yield a precursor precipitate;

mixing the precipitate with propionic acid to form a second reaction mixture;

heating the second reaction mixture at reflux to yield the porphine.

16. The method of Claim 15, wherein the substituted benzenesulfonic acid comprises 2-formylbenzenesulfonic acid, 3-formylbenzenesulfonic acid, 4-formylbenzenesulfonic acid, 2-alkoxy-5-formylbenzenesulfonic acid, 2-formyl-5-alkoxybenzenesulfonic acid, or a salt thereof.

17. The method of Claim 15, wherein the substituted toluene compound is p-toluenesulfonic acid or o-toluenesulfonic acid.

18. The method of Claim 15, wherein the substituted benzenesulfonic acid comprises 2-formylbenzenesulfonic acid and the substituted toluene compound is p-toluenesulfonic acid.

19. The method of Claim 15, wherein the solvent is dimethylformamide, dimethyl sulfoxide, or mixtures thereof.

20. The method of Claim 19, wherein the solvent is dimethylformamide.

21. The method of Claim 15, wherein the first reaction mixture is heated at about 150°C for about one hour in an argon atmosphere.

22. The method of Claim 15, wherein the porphine is further reacted with copper to produce Cu-meso-tetra-(4-sulfanatophenyl)-porphine or Cu-meso-tetra-(2-sulfanatophenyl)-porphine.

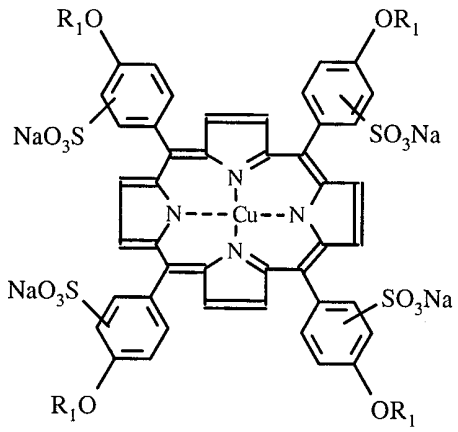
23. The method of Claim 15, wherein the actual yield of the porphine is greater than about 90%.

24. The method of Claim 23, wherein the actual yield of the porphine is about 96%.

25. The method of Claim 15, wherein air is bubbled through the second reaction mixture during reflux.

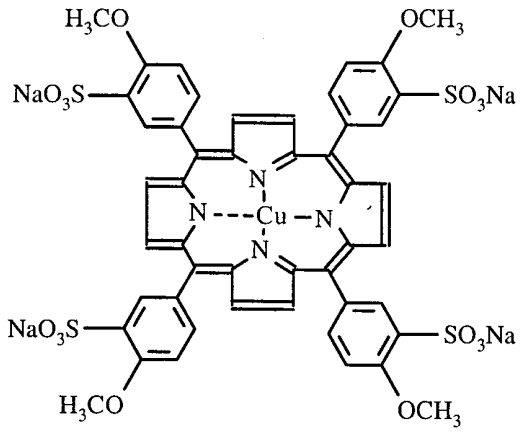
26. The method of Claim 15, wherein oxygen is bubbled through the second reaction mixture during reflux.

27. The method of Claim 15, wherein the porphine comprises:

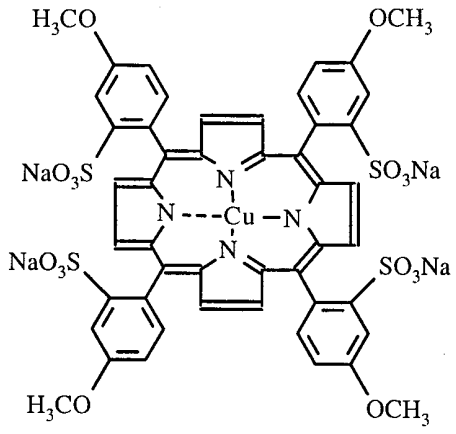


wherein R_1 represents an alkyl group having from 1 to 6 carbon atoms, an aryl group, or a substituted aryl group.

28. The method of Claim 27, wherein the porphine comprises:



or



29. A method of light stabilizing a colorant, comprising associating the colorant with the porphine produced by the method of Claim 15.

30. A method of making an ink comprising mixing a colorant with the porphine produced by the method of Claim 15.

31. A porphine produced by the method of Claim 15.

32. An ink composition comprising a colorant and the porphine produced by the method of Claim 15.

INTERNATIONAL SEARCH REPORT

Inter. ɔnal Application No
PCT/US 00/01206

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B47/00 C09D11/00 C07D487/22 //(C07D487/22,257:00, 209:00,209:00,209:00,209:00)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B C09D C07D

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.
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Y	WO 98 23695 A (KIMBERLY CLARK CO ;NOHR RONALD S (US); BRANHAM KELLY D (US); STOKE) 4 June 1998 (1998-06-04) page 10, last paragraph -page 13, line 26 & US 5 782 963 A cited in the application --- -/--	1-14

[X] Further documents are listed in the continuation of box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 June 2000	28/06/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dauksch, H

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INTERNATIONAL SEARCH REPORT

Interi nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 5 856 515 A (THERIEN MICHAEL J ET AL) 5 January 1999 (1999-01-05) column 5, line 50 -column 8, line 32	15-26

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INTERNATIONAL SEARCH REPORT

Inter. ›nal Application No
PCT/US 00/01206

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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A	J.S. LINDSEY ET AL: " Rothemund and Alder-Longo reactions revisited: synthesis of tetraphenylporphyrins under equilibrium conditions" JOURNALOF ORGANIC CHEMISTRY , vol. 52, 1987, pages 827-836, XP002139600 AMERICAN CHEMICAL SOCIETY. EASTON.; US the whole document -----	15-26

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ›nal Application No
PCT/US 00/01206

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