CONVENTION

AUSTRALIA

Patents Act 1990

REQUEST FOR A STANDARD PATENT

642270

The Applicant identified below requests the grant of a patent to the nominated person identified below for an invention described in the accompanying standard complete patent specification.

[70,71]Applicant and Nominated Person:

Imperial Chemical Industries PLC
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[54]Invention Title:

ANIONIC COMPOUNDS

[72]Names Of Actual Inventors:

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[31,33,32]

Details of basic application(s):-

9016451.8	UNITED KINGDOM	GB	26 July 1990

The nominated person is not an opponent or eligible person described in section 33-36 of the Act

4 July 1991

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
Imperial Chemical Industries PLC

By: David B Fitzpatrick

Our Ref : 221121

6010

ICI CASE D.35846/AU

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

INSTRUCTIONS
(a) Name of person making statement.

I (a) SUSAN JANE GENTLE

(b) Position of that person.

(b) AUTHORISED OFFICER

(c) Name of applicant

of (c) IMPERIAL CHEMICAL INDUSTRIES PLC

(d) Address of applicant

of (d) IMPERIAL CHEMICAL HOUSE, MILLBANK, LONDON SW1P 3JF, ENGLAND

State the following:-

(e) Delete as necessary

1. The nominated person (applicant) is entitled to the grant of a patent
(e) (i) ~~as assignee of the actual inventor(s)~~
(ii) by contract of employment of the actual inventor(s)
or (iii) (f)

(f) Insert details if not covered by (i) or (ii)

(g) Delete as necessary

2. The nominated person (applicant) is entitled to claim priority from the basic convention application(~~s~~).
(g) (i) as applicants of the said application(~~s~~)
(ii) ~~as the assignee of the applicants of the said application(s)~~
(iii) ~~with the consent of the applicants of the said application(s)~~

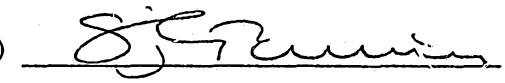
(h) Delete for non-convention applications

3. The basic convention application(~~s~~) was/~~were~~ the first made in a Convention country in respect of the invention the subject of the application. (h)

(i) Insert DATE of signing

Dated (i) 1ST JULY 199,

(j) Signature(s) of person making statement

(j) 

SUSAN JANE GENTLE

Note: No legalization or other witness required

To: The Commissioner of Patents

PHILLIPS ORMONDE AND FITZPATRICK
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Melbourne, Australia

AU9180173

(12) PATENT ABRIDGMENT (11) Document No. AU-B-80173/91
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(54) Title
ANIONIC PHTHALOCYANINE MELANINE DERIVATIVES

International Patent Classification(s)
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(56) Prior Art Documents
AU 53348/86
AU 81420/91
GB 2034739

(57) Claim

1. An anionic phthalocyanine compound which, in the free acid form, has the Formula (1):

$$Pc(SO_3H)_t(SO_2-NR^1-L-NR^2-X-NR^3-G)_q \qquad (1)$$

wherein:

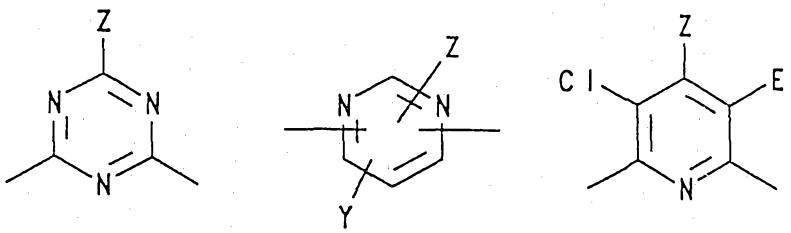
Pc is a metal-containing phthalocyanine nucleus;

R^1, R^2 and R^3 are each independently H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl or substituted aralkyl;

L is a divalent organic linking group;

each X independently is carbonyl or a group of formula (2), (3) or (4):

.../2



(2) (3) (4)

and each Z independently is NR^4R^5, SR^6 or OR^6

each Y independently is H, Cl, Z, SR^7 or OR^7,

each E independently is Cl or CN;

R^4, R^5, R^6 and R^7 are each independently H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl or R^4 and R^5 together with the nitrogen atom to which they are attached form a morpholine or piperidine ring;

G is a colourless organic radical substituted by one or two groups selected from COSH and COOH; and

(t+q) is from 3 to 4 inclusive.

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COMPLETE SPECIFICATION
(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

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Accepted:
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Related Art:

Name of Applicant:

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Invention Title:

ANIONIC COMPOUNDS

Our Ref : 221121
POF Code: 1453/1453

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

6006

ANIONIC COMPOUNDS

This specification describes an invention relating to anionic compounds and particularly to anionic phthalocyanine compounds which are useful as the coloured component of inks, particularly inks used in ink jet printing.

According to the present invention there are provided anionic phthalocyanine compounds which, in the free acid form, have the structure shown in Formula (1):

$$Pc(SO_3H)_t(SO_2-NR^1-L-NR^2-X-NR^3-G)_q \qquad (1)$$

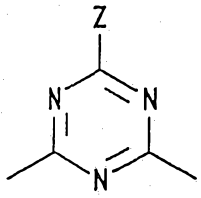
wherein:

Pc is a metal-containing phthalocyanine nucleus;

R^1, R^2 and R^3 are each independently H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl or substituted aralkyl;

L is a divalent organic linking group;

each X independently is carbonyl or a group of formula (2), (3) or (4):



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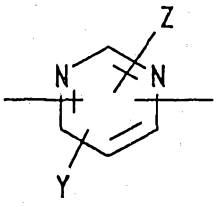

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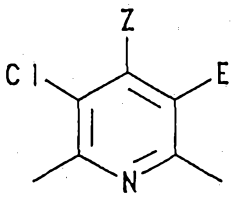


(4)

each Z independently is NR^4R^5, SR^6 or OR^6;

each Y independently is H, Cl, Z, SR^7 or OR^7;

each E independently is Cl or CN;

R^4, R^5, R^6 and R^7 are each independently H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl or R^4 and R^5 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring;

G is a colourless organic radical substituted by one or two groups selected from COSH and COOH; and

(t+q) is from 3 to 4 inclusive.

It is preferred that the compound of Formula (1) contain at least as many groups selected from -COSH and -COOH as $-SO_3H$ groups.

The preferred compounds of Formula (1) are cyan coloured compounds and are useful as dyes.

The metal present in the metal-containing phthalocyanine nucleus may be any of the metals known to be found in complex association with phthalocyanine nuclei, for example Li, Na, K, Mg, Ca, Ba, Al, Si, Sn, Pb or Rh; however it is preferred that the metal is Sc, Ti, V, Cr, Mn, Fe, Co, or Zn, especially Ni or Cu. When the metal is tri- or tetra-valent, one or two Cl atoms may be attached thereto.

R^1, R^3, R^6 and R^7 are preferably each independently selected from H, C_{1-4}-alkyl and hydroxy-C_{1-4}-alkyl, more preferably H, and C_{1-4}-alkyl. It is particularly preferred that R^1 and R^3 are H.

R^2 is preferably H, C_{1-4}-alkyl, or substituted C_{1-4}-alkyl. When R^2 is substituted alkyl it is preferably a hydroxy-C_{1-4}-alkyl.

R^4 and R^5 are preferably each independently H, C_{1-4}-alkyl, and substituted C_{1-4}-alkyl in which the substituents are preferably selected from -COOH, $-SO_3H$ and especially -OH.

When R^4 and R^5 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring, they preferably form a morpholine or piperidine ring.

When X is of Formula (3) it is preferred that Z is attached to the carbon atom between the two ring nitrogen atoms and that Y is para with respect to Z. X is preferably of Formula (2).

Z is preferably NR^4R^5 or OR^6, more preferably $HO(C_{1-4}$-alkylene$)NH$, for example HOC_2H_4NH, or OH.

(t+q) is preferably 4.

It is preferred that the value of q is greater than or equal to the value of t.

The identity of the divalent organic linking group L is not critical providing it does not interfere adversely with the performance of the dye. As examples of divalent organic linking groups represented by L there may be mentioned:

(a) divalent aliphatic radicals, preferably those containing from 2 to 6 carbon atoms, such as ethylene, trimethylene, propylene, tetramethylene, alpha:beta-dimethylethylene and hexamethylene radicals;

(b) divalent aromatic homocyclic radicals in which at least one of the terminal links is through an aliphatic carbon atom, for example as in the benzylene $-C_6H_4.CH_2-$ or the xylylene $-CH_2C_6H_4CH_2-$ group;

(c) divalent monocyclic or fused polycyclic aromatic radicals, for example of the benzene, naphthalene, anthraquinone or fluorene series, such as

1,3- or 1,4-phenylene	2-nitro-1,4-phenylene
3-sulpho-1,4-phenylene	4-methoxy-1,3-phenylene

4-sulpho-1,3-phenylene	4-nitro-1,3-phenylene
2-carboxy-1,4-phenylene	2-chloro-1,4-phenylene
4-carboxy-1,3-phenylene	3,7-disulpho-1,5-naphthylene
2-methoxy-1,4-phenylene;	

(d) divalent radicals wherein the terminal bonds are attached to carbon atoms of two phenyl or naphthalene nuclei which are joined together either through a direct link or through an atom or chain of atoms which may form a homocyclic or heterocyclic ring. Of this type, there may be mentioned as examples divalent radicals derived from

diphenyl	azobenzene
diphenyloxide	diphenyloxadiazole
diphenylamine	benzanilide
diphenylsulphide	diphenylurea
diphenylsulphone	1,2-bis(phenylcarbamyl)ethylene
diphenylmethane	1,4-bis-(phenylcarbamyl)butadiene
diphenylketone	1,2-bis-(phenylcarbamyl)ethane
diphenylethane	1,3-bis-(phenylcarbamyl)propane
diphenylethylene	2,4-dianilino-s-triazine;
3,3'-dichlorobenzidine	3,3'-dicarboxybenzidine

and

(e) nuclear substituted derivatives of the above, for example, containing COOH, COSH, methyl, nitro and/or sulphonic acid and/or chlorine atoms as substituents in the phenyl or naphthalene nuclei.

G is preferably substituted alkyl, especially C_{1-4}-substituted alkyl; substituted aralkyl, especially (C_{1-3}-alkyl)-substituted phenyl; substituted phenyl; and substituted naphthyl wherein at least one of the substituents are selected from B, $-(CH_2)_n-B$, $-O-(CH_2)_n-B$, $-S-(CH_2)_n-B$ and $NR^8(CH_2)_n-B$ in which B is CO_2H or COSH, especially CO_2H, n is an integer from 1 to 6 and R^8 is H or C_{1-4}-alkyl. Preferred examples of G include carboxyphenyl and dicarboxyphenyl.

The group $-NR^3-G$ is derivable from the amino acids of formula GNR^3H, and examples of such amino acids include:

2-aminoisophthalic acid	3-amino-4-fluorobenzoic acid
4-aminoisophthalic acid	3-amino-5-hydroxybenzoic acid

5-aminoisophthalic acid
3-aminophthalic acid
4-aminophthalic acid
2-aminoterephthalic acid
3-aminobenzoic acid
4-aminobenzoic acid
4-(methylamino)benzoic acid
anthranilic acid
4-sulphoanthranilic acid
5-sulphoanthranilic acid
2-amino-4-chlorobenzoic acid
2-amino-5-chlorobenzoic acid
3-amino-4-chlorobenzoic acid
5-amino-2-chlorobenzoic acid
2-amino-5-methylbenzoic acid
2-amino-6-methylbenzoic acid
2-amino-5-bromobenzoic acid
Beta-alanine
Alanine
Asparagine
Cystein
Glutamic acid
Glycine
Hydroxylysine
Isoleucine
Lysine
Phenylalanine
Serine
Tryptophane
Valine

3-amino-4-hydroxybenzoic acid
3-amino-2-hydroxybenzoic acid
2-amino-6-hydroxybenzoic acid
2-amino-4-nitrobenzoic acid
3-amino-5-nitrobenzoic acid
2-nitro-3-aminobenzoic acid
2-nitro-5-aminobenzoic acid
3-nitro-4-aminobenzoic acid
3-acetylamino-5-aminobenzoic acid
3-amino-4-methylbenzoic acid
2-amino-3-methylbenzoic acid
3-amino-4-methoxybenzoic acid
3-amino-4-hydroxybenzoic acid
4-aminosalicylic acid
5-aminosalicylic acid
3-amino-2-naphthoic acid
5-amino-2-naphthoic acid
8-amino-2-naphthoic acid
2-n-butoxy-4-aminobenzoic acid
Arginine
Aspartic acid
Cystine
Glutamine
Glycyl glycine
Hydroxyproline
Leucine
Methionine
Proline
Threonine
Tyrosine

It is to be understood that the present invention relates not only to compounds of Formula (1) but also to mixtures of compounds of Formula (1) and to the salts thereof, particularly the salt with an

alkali metal, ammonia or an amine especially with ammonia or an amine which is volatile at room temperature.

According to a further aspect of the present invention there is provided a process for the preparation of compounds of Formula (1) comprising

(1) halo sulphonation of a metallo phthalocyanine using halo sulphonic acid, especially chlorosulphonic acid;

(2) condensation of the metallo phthalocyanine sulphonyl halide from (1) above with an amine of formula HNR^1LNHR^2;

(3) condensation of one equivalent of an amine of formula $GNHR^3$ with one equivalent of a linking group of formula halo-X-halo in which X is as defined above except that in place of Z there is a halogen radical;

(4) condensation of the product of (3) above with a product of step (2), preferably in the presence of base;

(5) condensation of the product from step (4) above with ZH to give a compound of formula (1);

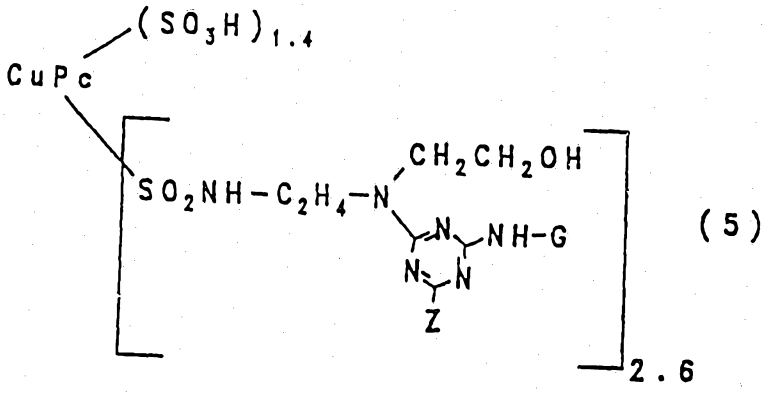
wherein R^1, R^2, R^3, L, X, Z and G are as defined above.

The compounds of Formula (1) are especially useful for the preparation of inks, especially aqueous inks, used in ink jet printing and particularly thermal ink jet printing. The inks can be prepared according to known formulations.

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

Example 1

Preparation of the compound of Formula (5) in which G is 2-carboxyphenyl and Z is $NHCH_2CH_2OH$



(5)

Copper phthalocyanine (45.4g) was added to chlorosulphonic acid (220g) over 1 hour maintaining the temperature below 60°C. It was then heated to 140°C and stirred at this temperature for 3 hours. The mixture was cooled to 45°C and phosphorus trichloride (23.6g) added over 1½ hours at 40-45°C. The mixture was then heated at 90-95°C for 16 hours. After cooling to 25°C the mixture was added to ice/water (3kg) and then filtered and washed with ice/water and pulled dry to give a paste.

The paste was added to 2-aminoethylaminoethanol (32.8g) and water (200ml) at 30°C maintaining the pH at 10-10.5 by addition of sodium hydroxide solution. It was stirred at 38-40°C for 1 hour, the pH adjusted to 8.5 and then filtered, washed with saturated sodium chloride solution and then dried to give a copper phthalocyanine derivative which analysed as $CuPc(SO_3H)_{1.4}(SO_2NHC_2H_4NHC_2H_4OH)_{2.6}$.

Anthranilic acid (2.7g) was stirred in water (150ml) at pH 7.5 and cooled to 0-10°C. A solution of cyanuric chloride (3.6g) in acetone (25ml) was added at 0-10°C maintaining the pH at 7-8 by addition

of 2N sodium hydroxide. The mixture was stirred for ½ hour at 0-10°C to give a dichlorotriazinyl anthranilic acid solution.

The above copper phthalocyanine derivative (7g) and water (250ml) were stirred and the pH adjusted to 11.0. The dichlorotriazinyl anthranilic acid solution was added at 20-25°C and the mixture stirred for 18 hours at pH 9-10. Ethanolamine (12.5g) was then added and the temperature raised to 70°C. The mixture was stirred at 70-75°C for 6 hours, cooled to 25°C, acidified to pH 5 with concentrated hydrochloric acid and the product filtered to give a product paste.

The product paste was slurried in water (400ml) and made alkaline to pH 9 with concentrated ammonium hydroxide. It was then added to a mixture of water (200ml) and concentrated hydrochloric acid (20ml). The product was filtered, reslurried in water (200ml) and the pH adjusted to 9.0 with ammonium hydroxide. The solution was dialysed to remove chloride ion, screened and evaporated to give the ammonium salt of the title compound. Yield 8.3g.

When made into an ink in water/diethylene glycol (92.5/7.5) and printed onto plain paper using a thermal ink-jet printing machine the ammonium salt of the title compound gave bright cyan shades with essentially 100% water fastness. The same water/diethylene glycol mixture was used as the solvent in the inks described in subsequent Examples.

Example 2

Preparation of the compound of Formula (5) in which G is 3-carboxyphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 2.7g of m-aminobenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 3

Preparation of the compound of Formula (5) in which G is 4-carboxyphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 2.7g of p-aminobenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 4

Preparation of the compound of Formula (5) in which G is CH_2CO_2H and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 1.47g of glycine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 5

The procedure described in Example 3 was repeated except that the ammonium hydroxide was replaced by methylamine. The methylammonium salt of the product when made into an ink and printed onto plain paper using a thermal ink jet printing machine gave cyan shades with excellent water fastness.

Example 6

Preparation of the compound of Formula (5) in which G is 4-carboxyphenyl and Z is $N(CH_2CH_2OH)_2$

In place of the 12.5g of ethanolamine used in Example 3 there was used 25.3g of diethanolamine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 7

Preparation of the compound of Formula (5) in which G is 4-carboxyphenyl and Z is OH

In place of the 12.5g of ethanolamine used in Example 3 there was used 390ml of 2N sodium hydroxide solution. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 8

Preparation of the compound of Formula (5) in which G is 3,5-dicarboxyphenyl and Z is $NHCH_2CH_3OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 3.6g of 5-aminoisophthalic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with good water fastness.

Example 9

Preparation of the compound of Formula (5) in which G is 3,5-dicarboxyphenyl and Z is morpholino

In place of the 2.7g of anthranilic acid used in Example 1 there was used 3.6g of 5-aminoisophthalic acid and in place of the 12.5g of ethanolamine there was used 17.8g of morpholine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with good water fastness.

Example 10

Preparation of the compound of Formula (5) in which G is 3-carboxyphenyl and Z is morpholino

In place of the 12.5g of ethanolamine used in Example 2 there is used 17.8g of morpholine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 11

Preparation of the compound of Formula (5) in which G is 4-carboxyphenyl and Z is $NHCH_2CO_2H$

In place of the 12.5g of ethanolamine used in Example 3 there was used 15.4g of glycine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 12

Preparation of the compound of Formula (5) in which G is 4-carboxyphenyl and Z is $NHCH_2CH_2SO_3H$

In place of the 12.5g of ethanolamine used in Example 3 there was used 25.6g of taurine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 13

Preparation of the compound of Formula (5) in which G is 2-methoxy-5-carboxyphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there is used 3.3g of 3-amino-4-methoxybenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 14

Preparation of the compound of Formula (5) in which G is 2-methyl-5-carboxyphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there is used 3.0g of 3-amino-4-methylbenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 15

Preparation of the compound of Formula (5) in which G is 2-carboxy-4-methylphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there is used 3.0g of 2-amino-5-methylbenzoic acid. The ammonium salt of the title produ . when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 16

Preparation of the compound of Formula (5) in which G is 2-methyl-4-carboxyphenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there is used 3.0g of 3-methyl-4-aminobenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 17

Preparation of the compound of Formula (5) in which G is 2-carboxy-5-sulphophenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 3.0g of 2-amino-4-sulphobenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 18

Preparation of the compound of Formula (5) in which G is 2-carboxy-5-sulphophenyl and Z is morpholino

In place of the 12.5g of ethanolamine used in Example 17 there was used 17.8g of morpholine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with excellent water fastness.

Example 19

Preparation of the compound of Formula (5) in which G is 2-carboxy-4-sulphophenyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there was used 4.3g of 2-amino-5-sulphobenzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gave cyan shades with good water fastness.

Example 20

Preparation of the compound of Formula (5) in which G is 3,4-dicarboxy-phenyl and Z is $NHCH_2CH_2OH$

In place of the 3.6g of 5-aminoisophthalic acid used in Example 8 there is used 3.6g of 4-aminophthalic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 21

Preparation of the compound of Formula (5) in which G is 2,5-dicarboxy-phenyl and Z is $NHCH_2CH_2OH$

In place of the 3.6g of 5-aminoisophthalic acid used in Example 8 there is used 3.6g of 2-aminoterephthalic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 22

Preparation of the compound of Formula (5) in which G is 3,5-dicarboxy-phenyl and Z is $n\text{-}C_4H_9$

In place of the 12.5g of ethanolamine used in Example 8 there is used 15.0g of n-butylamine. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 23

Preparation of the compound of Formula (5) in which G is 4-carboxybenzyl and Z is $NHCH_2CH_2OH$

In place of the 2.7g of anthranilic acid used in Example 1 there is used 3.0g of 4-(aminomethyl)-benzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

Example 24

Preparation of the compound of Formula (5) in which G is 3-carboxyphenyl and Z is 4-carboxybenzylamino

In place of the 12.5g of ethanolamine used in Example 2 there is used 10g of 4-(aminomethyl)-benzoic acid. The ammonium salt of the title product when made into an ink and printed onto plain paper using a thermal ink-jet printing machine gives cyan shades with excellent water fastness.

CLAIMS

The claims defining the invention are as follows:

1. An anionic phthalocyanine compound which, in the free acid form, has the Formula (1):

$$Pc(SO_3H)_t(SO_2-NR^1-L-NR^2-X-NR^3-G)_q \qquad (1)$$

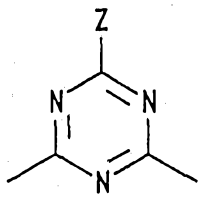
wherein:

Pc is a metal-containing phthalocyanine nucleus;

R^1, R^2 and R^3 are each independently H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl or substituted aralkyl;

L is a divalent organic linking group;

each X independently is carbonyl or a group of formula (2), (3) or (4):



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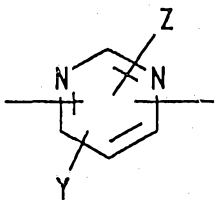

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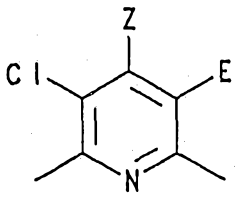

(4)

and each Z independently is NR^4R^5, SR^6 or OR^6

each Y independently is H, Cl, Z, SR^7 or OR^7,

each E independently is Cl or CN;

R^4, R^5, R^6 and R^7 are each independently H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl or R^4 and R^5 together with the nitrogen atom to which they are attached form a morpholine or piperidine ring;

G is a colourless organic radical substituted by one or two groups selected from COSH and COOH; and

(t+q) is from 3 to 4 inclusive.

2. A compound according to claim 1 having at least as many groups selected from -COSH and -COOH as $-SO_3H$ groups.

3. A compound according to claim 1 or claim 2 wherein the phthalocyanine nucleus contains a nickel or copper atom.

4. A compound according to any one of the preceding claims wherein X is a group of Formula (2) and Z is NR^4R^5 or OR^6 wherein R^4, R^5 and R^6 are as defined in claim 1.

5. A compound according to claim 4 wherein Z is $-NH(C_{1-4}$-alkylene$)OH$ or -OH.

6. A compound according to claim 5 wherein Z is $-NHC_2H_4OH$.

7. A compound according to any one of the preceding claims wherein the value of q is greater than or equal to the value of t.

8. A compound according to any one of the preceding claims wherein G is carboxyphenyl and dicarboxyphenyl.

9. A compound according to claim 1 substantially as hereinbefore described with reference to any one of the examples.

DATED: 16 July 1993

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AUSTRALIA 39 PATENT OFFICE

ABSTRACT

Anionic Compounds

Anionic phthalocyanine compounds which, in the free acid form, have the Formula (1):

$$Pc(SO_3H)_t(SO_2-NR^1-L-NR^2-X-NR^3-G)_q \qquad (1)$$

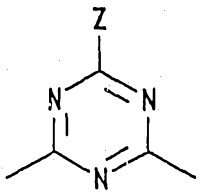
wherein:

Pc is a metal-containing phthalocyanine nucleus;

R^1, R^2 and R^3 are each independently H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl or substituted aralkyl;

L is a divalent organic linking group;

each X independently is carbonyl or a group of formula (2), (3) or (4):



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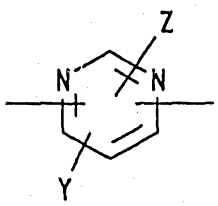

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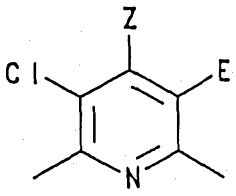

(4)

each Z independently is NR^4R^5, SR^6 or OR^6;

each Y independently is H, Cl, Z, SR^7 or OR^7;

each E independently is Cl or CN;

R^4, R^5, R^6 and R^7 are each independently H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl or R^4 and R^5 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring;

G is a colourless organic radical substituted by one or two groups selected from COSH and COOH; and

(t+q) is from 3 to 4 inclusive.

The compounds are useful for the preparation of inks for use in ink-jet printing.