

## Description

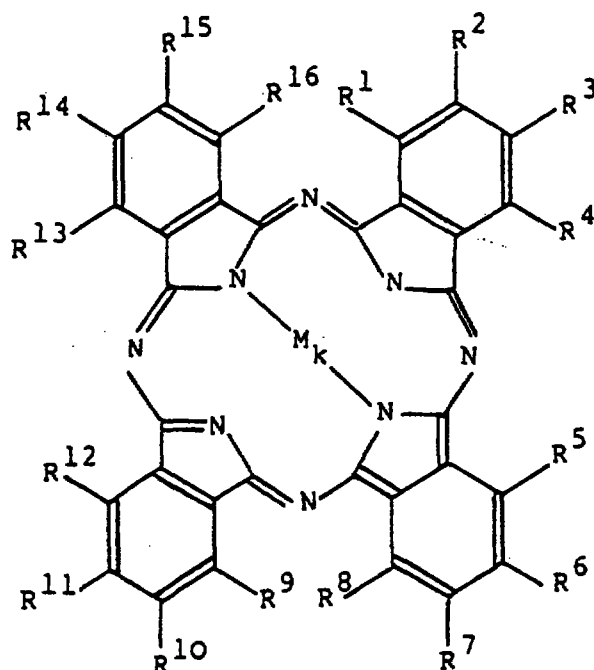
This specification describes an invention relating to certain poly(substituted)phthalocyanine compounds which absorb in the near infra-red region of the electro-magnetic spectrum, e.g. from 750 to 1500 nm, and more especially from 750 to 1100 nm.

Phthalocyanine compounds containing up to sixteen substituents on the peripheral carbon atoms are known in principle from DE-A-2,455,675 but they are reported as pigments. There is no specific disclosure of compounds having more than 4 substituted-thio groups and no indication of the long-wavelength band characteristics of such compounds.

It is known from Zh. Obsh. Khim, 50(10) 2313—8 (1980) that the introduction of phenoxy and phenylthio groups into the phthalocyanine molecule leads to an appreciable shift in the longwave band and its vibrational satellites, the magnitude of which is greater for the phenylthio substituted phthalocyanines than for the corresponding phenoxy derivatives and for the 3-isomers than for the 4-isomer's. There is however, no disclosure of phthalocyanines carrying substituents in the 3 and 6 positions or any indication whether there would be a further bathochromic shift in the long wavelength bands of such phthalocyanines.

A phthalocyanine derivative containing 8 methoxy substituents in the 3,6 positions is known from Materials Science II 1—2 p. 39 (1976) which describes the electrical conductivity and the catalytic activity of the derivative.

According to the present invention there is provided a phthalocyanine compound in which the 16 peripheral carbon atoms carry a substituent,  $R^1$  to  $R^{16}$ , of the following formula:



wherein at least 5 of the groups represented by  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{16}$  are independently  $-X-J$  or  $-X-L-X^1-$ , wherein

J and L are independently an alkyl, an alkenyl, a homo-alicyclic, a phenyl, a phenylene, a naphthyl, a naphthylene or a mono- or bi-valent, mono- or bi-cyclic, heteroaromatic group;

M is H, a metal atom or an oxymetal group;

k is the inverse of half the valency of M;

X is S, Se, Te or NT;

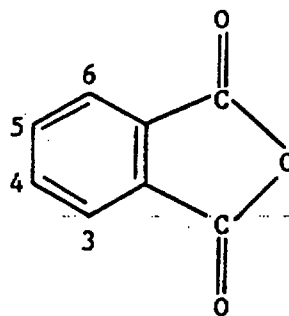
$X^1$  is S, Se, Te, O or NT which is directly attached to the adjacent peripheral carbon atom on the same phthalocyanine nucleus or to a peripheral carbon atom on a different phthalocyanine nuclei;

T is H, alkyl or phenyl; or

when X is NT, J and T together form an aliphatic or aromatic ring;

and the remaining groups from  $R^1$  to  $R^{16}$  are H,  $-O-J$ , halogen or form part of the group  $-X-L-X^1-$ .

The peripheral carbon atoms to which  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{16}$  are attached are hereinafter referred to as the "3,6-carbon atoms" by relation to the equivalent 3,6-positions in the four molecules of phthalic anhydride, see Formule II, from which the phthalocyanine can be derived.



II

It is preferred that each of at least six and, more preferably at least eight, of the 3,6 carbon atoms is linked by a group X to a group J or L.

In a first preferred class of phthalocyanine compound according to the present invention at least five, preferably at least six and more preferably all, of the 3,6-carbon atoms, carry a group X—J. The remaining peripheral carbon atoms may carry other substituents, e.g. halogen atoms, but are preferably unsubstituted, i.e.  $R^2$ ,  $R^3$ ,  $R^6$ ,  $R^7$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{14}$  and  $R^{15}$  are all hydrogen.

In a second preferred class from nine to sixteen of the peripheral carbon atoms, at least five, preferably at least six and more preferably eight, of which are 3,6-carbon atoms, are linked by a group X to a group J or L. The remaining peripheral carbon atoms are preferably unsubstituted or carry halogen atoms i.e. the remaining groups  $R^1$  and  $R^{16}$  are H or halogen. In the second class preferably at least ten, and more preferably at least twelve, of the peripheral carbon atoms is linked by a group X or  $X^1$  to a group J or L. Especially valuable compounds of this second class are those in which fifteen or sixteen of the peripheral carbon atoms are linked to a group J or L by a group X or  $X^1$ .

Compounds of especial interest have an absorption peak above 750 nm, especially in the region from 750 to 1100 nm; and those of more especial interest have 90% of their absorption strength at or above 750 nm.

Examples of suitable aromatic and heteroaromatic groups represented by J and L are optionally substituted phenyl, phenylene, naphthyl, especially naphth-2-yl, naphthylene, pyridyl, thienyl, furyl, pyrimidyl and benzothiazolyl. The alkyl and alkenyl groups preferably contain up to 20 carbon atoms, such as vinyl, allyl, butyl, nonyl, dodecyl, octadecyl and octadecenyl. Homoalicyclic groups preferably contain from 4 to 8 carbon atoms, such as cyclohexyl. The divalent group L is attached to an adjacent peripheral carbon atom through the group X or to another phthalocyanine nucleus.

The group represented by J or L may be optionally substituted.

Examples of substituents for the aromatic and heteroaromatic groups J and L are alkyl, alkenyl, alkoxy and alkylthio, and halo substituted derivatives thereof, especially those containing up to 20 carbon atoms, aryl, arylthio, especially phenyl and phenylthio, halogen, nitro, cyano, carboxyl, aralkyl, aryl- or alkyl-sulphonamido, aryl- or alkyl-sulphone, aryl- or alkyl-sulphoxide, hydroxy and primary, secondary or tertiary amino. Examples of substituents for the aliphatic and cycloaliphatic groups J and L are alkoxy, alkylthio, halo, cyano and aryl. In these substituents the alkyl and alkenyl groups preferably contain up to 20, and more preferably up to 4, carbon atoms and the aryl groups are preferably mono- or bi-homo- or hetero-cyclic. Specific examples of substituents are methyl, ethyl, dodecyl, methoxy, ethoxy, methylthio, allyl, trifluoromethyl, bromine, chlorine, fluorine, benzyl, COOH,  $-\text{COOCH}_3$ ,  $-\text{COOCH}_2\text{C}_6\text{H}_5$ ,  $-\text{NHSO}_2\text{CH}_3$ ,  $\text{SO}_2\text{C}_6\text{H}_5$ ,  $\text{NH}_2$ ,  $-\text{NHC}_2\text{H}_5$ , and  $\text{N}(\text{CH}_3)_2$ .

The alkyl group T is preferably  $\text{C}_{1-4}$ -alkyl.

Examples of suitable metals and oxy-metals represented by M are copper, lead, cobalt, nickel, iron, zinc, germanium, indium, magnesium, calcium, palladium, gallium and vanadium.

Suitable compounds according to the first preferred class are those in which each of the 3,6-carbon atoms carries a group  $-\text{X}-\text{R}$  in which R is a phenyl or a naphthyl group and each of the remaining peripheral carbon atoms carries a hydrogen atom.

Throughout this specification the symbols,  $\text{H}_2\text{Pc}$  and  $\text{MPc}$ , in which M is a metal, e.g. Cu, Zn or Pb, will be used to indicate unmetallised and metallised phthalocyanine respectively.

Examples of compounds of the first preferred class are:

- octa-3,6-(4-methylphenylthio)-CuPc
- octa-3,6-(benzylthio)-CaPc
- octa-3,6-(naphth-2-ylthio)-CuPc
- octa-3,6-(4-methoxyphenylthio)-GePc
- octa-3,6-(4-butoxyphenylthio)-CoPc
- octa-3,6-(phenyltelluro)- $\text{H}_2\text{Pc}$
- octa-3,6-(ethylthio)-NiPc
- octa-3,6-(4-*t*-butylphenylthio)-(VO)Pc
- octa-3,6-(hexadecylthio)-CuPc
- octa-3,6-(4-methylthiophenylthio)-CuPc
- octa-3,6-(4-dodecyloxyphenylthio)-CuPc

hepta-3,6-(n-octylthio)-mono-3,6-chloro-CuPc  
 octa-3,6-(3,4-dimethylphenylthio)-H<sub>2</sub>Pc  
 octa-3,6-(pyrid-2-ylthio)-H<sub>2</sub>Pc  
 octa-3,6-(2,4-dimethoxyphenylthio)-CuPc  
 phen-1,4-ylenedithio-bis[hepta-3,6-(4-thiophenylthio)-CuPc]  
 hepta-3,6-(4-butylphenylthio)-mono-3,6-chloro-H<sub>2</sub>Pc  
 octapiperidino-octachloro-H<sub>2</sub>Pc  
 octa(diethylamino)-H<sub>2</sub>Pc  
 octa(ethylamino)-H<sub>2</sub>Pc

Suitable compounds from the second preferred class are those in which (i) from 10 to 16 or R<sup>1</sup> to R<sup>16</sup> are groups —X—R and up to 6 of the remainder are halogen or (ii) up to 14 or R<sup>1</sup> to R<sup>16</sup> are —X—R, from 1 to 8 are —X—Q—X<sup>1</sup> and up to 6 are halogen, in which R is a phenyl or a naphthyl group and Q is a phenylene or a naphthylene group, provided that at least 6 of the groups represented by Q and R are attached through linking groups X, to 3,6-carbon atoms, and the number of X and X<sup>1</sup> groups is from 10 to 16, preferably from 12 to 16 and more preferably 15 to 16.

Examples of compounds of the second preferred class are:

deca(4-methylphenylthio)-pentachloro-CuPc  
 deca(4-t-butylphenylthio)-pentachloro-CuPc  
 deca(naphth-2-ylthio)-hexachloro-CuPc  
 deca(4-ethylthiophenylthio)-pentachloro-CuPc  
 undeca(4-methylphenylthio)-bromo-CuPc  
 undeca(4-dimethylaminophenylthio)-pentachloro-CuPc  
 dodeca(4-methylphenylthio)-CuPc  
 dodeca(4-t-butylphenylthio)-trichloro-CuPc  
 trideca(4-butoxyphenylthio)-dichloro-InPc  
 pentadeca(n-butylthio)-CuPc  
 pentadeca(4-carboxyphenylthio)-CuPc  
 pentadeca(4-t-butylphenylthio)-CuPc  
 pentadeca(phenylseleno)CuPc  
 pentadeca(naphth-2-ylthio)-MgPc  
 pentadeca(naphth-1-ylthio)-CuPc  
 pentadeca(4-methoxyphenylthio)-CuPc  
 pentadeca(4-dodecyloxyphenylthio)-CuPc  
 pentadeca(4-methylthiophenylthio)-CuPc  
 pentadeca(phenylthio)-CuPc  
 pentadeca(4-butoxyphenylthio)-CuPc  
 pentadeca(n-dodecylthio)-CuPc  
 pentadeca(benzimidazol-2-ylthio)-CuPc  
 hexadeca(4-methylphenylthio)-CuPc  
 hexadeca(4-methylphenylthio)-ZnPc  
 hexadeca-anilino-H<sub>2</sub>Pc  
 hexadeca(4-methylphenylthio)-PbPc  
 hexadeca(4-methylphenylthio)-H<sub>2</sub>Pc  
 hexadeca(4-chlorophenylthio)-NiPc  
 hexadeca(piperidino)-H<sub>2</sub>Pc  
 hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiophenylthio)-CuPc  
 hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiophenylthio)-H<sub>2</sub>Pc  
 octa(phen-1,2-ylenediamino)H<sub>2</sub>Pc  
 hexadeca(diethylamino)H<sub>2</sub>Pc  
 hexadeca(ethylamino)H<sub>2</sub>Pc

Preferred values for, and examples of, the groups represented by R and Q are as given hereinbefore in respect of J and L. Where J and T together form an aliphatic or aromatic ring this may be, for example, pyrid-1-yl, pyrimid-1-yl, piperidin-1-yl, morpholin-1-yl, pyrrol-1-yl or pyrrolidin-1-yl.

The phthalocyanine compounds of the present invention can be prepared by heating a phthalocyanine compound carrying halogen atoms attached to the peripheral carbon atoms to which it is wished attach the group X or X<sup>1</sup> with at least six equivalents of an organic thiol, or an equivalent compound in which the sulphur in the thiol groups is replaced by selenium (selenol), tellurium (tellurol) or NT (amine), in an organic solvent.

The compounds of the first preferred class in which X is sulphur can be prepared by heating an octa-halo-phthalocyanine, in which at least six, and more preferably all, of the halogen atoms are attached to 3,6-carbon atoms, with at least eight equivalents of an organic thiol, J—SH, in an organic solvent.

The compounds of the second preferred class in which X is sulphur can be prepared by heating a phthalocyanine carrying at least nine halogen atoms, at least six of which are attached to 3,6-carbon atoms, with at least nine equivalents of an organic thiol, J—SH, in an organic solvent. If the organic thiol also carries another substituent, such as a second thiol group or a hydroxy or a primary or secondary amino

group, i.e. it is of the form  $HX-L-X'H$  which will react with a halogen atom attached to an adjacent peripheral carbon atom on the phthalocyanine nucleus, the organic radical J of the thiol may become linked to two adjacent peripheral carbon atoms.

Other compounds of the preferred classes may be prepared by using, in place of the thiol, an equivalent compound in which the sulphur is replaced by selenium, tellurium or a group, NT.

The organic solvent, which need not necessarily be a liquid at ambient temperatures and may only partially dissolve the reactants, preferably has a boiling point from 100°C to 300°C and more preferably from 150° to 250°C. The organic solvent is preferably essentially inert although it may catalyse the reaction. Examples of suitable solvents are methylcyclohexanol, octanol, ethylene glycol, and especially benzyl alcohol and quinoline.

Reaction is conveniently carried out under reflux, preferably from 100°C to 250°C and more preferably above 150°C, in the presence of an acid binding agent, such as potassium or sodium hydroxide or sodium carbonate, to neutralise the halo acid formed. The product may be isolated by filtration or by distillation of the organic liquid. The isolated product is preferably purified by repeated recrystallisation from a suitable solvent, such as ethanol, chloroform or pyridine, and/or chromatography, using a silica-filled column and an aromatic solvent, such as toluene or xylene, as eluent.

The phthalocyanine compounds of the present invention can also be prepared by heating an o-phthalic acid derivative, especially o-phthalonitrile (o-PN), carrying substituted-thio, seleno, telluro or NT groups in the 3 & 6 positions. The process may also include an unsubstituted o-PN or an o-PN carrying substituents in other than the 3 & 6 positions, provided the proportion of the o-PN carrying substituted-thio etc groups is sufficient to ensure that there are at least five substituted-thio etc, groups on the 3,6-carbon atoms of the phthalocyanine product. The process is conveniently performed in a solvent in the presence of a base. It may also be promoted by the addition of a catalyst, such as ammonium molybdate.

This process is analogous to the known method for preparing unsubstituted phthalocyanines from ortho-phthalic acid derivatives such as those described in Journal of the Chemical Society, (1938), pp. 1157-63; Advances in Inorganic Chemistry (Radiochemistry), (1965), 7, p 27 & Chemistry of Synthetic Dyes, (1971), 5, pp 241-82.

The solvent preferably has a boiling point from 50°C to 300°C, more preferably from 70°C to 200°C and need not be a liquid at ambient temperatures or completely dissolve the reactants. It is preferably essentially inert though it may interact with the base, catalyse the reaction or even partially replace the substituted-thio groups in the phthalocyanine compound. Preferred solvents are aliphatic alcohols such as iso-amyl alcohol, octanol and benzyl alcohol.

Where an alcohol is employed as solvent it is possible for one or more alcohol residues to replace the substituted thio, etc. groups,  $-X-J$  or  $-X-L-X'$ , attached to the o-PN and become attached to a peripheral carbon atom of the phthalocyanine through an oxygen atoms. Such a phthalocyanine, carrying one or more organic radicals attached through oxygen atoms, provided it also carries at least five groups J or L is attached through a group X to 3,6-carbon atoms is a further feature of the present invention.

The reaction is conveniently carried out between 100°C and 150°C or under reflux in the presence of a base, such as an alkoxide formed between an alkali metal and an alcohol, preferably an aliphatic alcohol. A particularly suitable base is lithium iso-amyl oxide because lithium phthalocyanines are generally soluble in alcohols.

Different metals may be introduced into the phthalocyanine by heating the o-PN with a suitable salt of the appropriate metal or heating lithium phthalocyanine with a solvent soluble compound of the appropriate metal. A metal-free phthalocyanine may be obtained by acidification of the lithium phthalocyanine, in some cases by merely contacting it with an acidic material, such as a silica-gel, or by heating it with a stronger acid, such as p-toluenesulphonic acid.

The phthalocyanine compound in accordance with the present invention is useful for absorbing electro-magnetic energy from an infra-red source and optionally making it available as heat energy. Particular applications where this property can be utilised for practical effect are infra-red inks, liquid crystal displays, infra-red protection systems, such as welding goggles, sun visors, vehicle windscreens and infra-red security systems, e.g. computer-controlled locks and alarms. The position of the absorption maximum depends upon the nature of the compound and the substrate on or in which it is incorporated. Many of the compounds of the present invention exhibit a bathochromic shift of up to 50 mμm when deposited on glass compared with a solution in an organic liquid.

A liquid crystal cell, for the formation of latent images, can be rendered laser-addressable by dissolving a compound in accordance with the present invention in the liquid crystal medium. For example, *Pentadeca(naphth-2-ylthio)-CuPc* has an absorption maximum at 782 mμm and a solubility of 0.5% in the liquid crystal material E7, which is available from BDH Chemicals, of Poole in Dorset, England, and *Hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiophenylthio)-CuPc* has an absorption maximum at 820 mμm and a solubility of 0.3% in the liquid crystal material, E7.

A security card can be rendered opaque to infra-red irradiation by the application to a predetermined area of an ink containing the present compound, for example, by thermal transfer or ink-jet printing. In this way a unique pattern, recognisable by a programmed detector, can be applied to the security card. By suitable choice of compound, a composite pattern absorbing at one or more wavelengths can be formed. For example, *Octa-3,6-(2-aminophenylthio)CuPc* has an absorption maximum at 950 mμm *Octa-3,6-(4-*

*methoxyphenylthio*-CuPc has an absorption maximum at 805 m $\mu$ m and *Pentadeca*-(4-methylphenylthio)-CuPc has an absorption maximum at 775 m $\mu$ m.

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

#### Example 1

A mixture of 3.06 g of 4-methylphenylthiol, 1.26 g of KOH and 10 ml of quinoline was stirred at 130—140°C for 60 minutes and 5.69 g of octa-3,6-chloro-H<sub>2</sub>Pc was added. The mixture was then stirred at 180°C for 1 hour and at 200—210°C for 30 minutes. The mixture was then cooled to 100°C and diluted with 50 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered and dissolved in toluene. The toluene solution was passed through a silica column using toluene as eluent and the main fraction collected and isolated by evaporation to yield 0.26 g of dry octa-3,6-(4-methylphenylthio)-H<sub>2</sub>Pc.

#### Example 2

A mixture of 6.29 g of 4-methylphenylthiol, 3.29 g of KOH and 20 ml of quinoline was stirred at 130—160°C for 90 minutes and 4.16 g of octa-3,6-chloro-CuPc was added. The mixture was then stirred at 180—200°C for 5.5 hour, cooled to 80°C and diluted with 50 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered, washed with ethanol and dissolved in toluene. The toluene solution as passed through a silica column using toluene as eluent and the main fraction collected and isolated by evaporation to yield dry octa-3,6-(4-methylphenylthio)-CuPc.

#### Examples 3 to 17

Further compounds within the scope of the present invention in accordance with the first preferred class were prepared by the methods of Examples 1 and 2, using equimolar quantities of appropriate thiols in place of the thiols described in the Examples, as set out in Table 1. In each product containing less than eight substituted thio groups, the free 3,6-carbon atoms carry chlorine atoms.

Table 1

| Ex | Method | Thiol              | Product                                           |
|----|--------|--------------------|---------------------------------------------------|
| 3  | Ex 1   | 3-methylphenyl     | octa-3,6(3-methylphenylthio)H <sub>2</sub> Pc     |
| 4  | Ex 1   | 4-t-butylphenyl    | hepta-3,6(4-t-butylphenylthio)H <sub>2</sub> Pc   |
| 5  | Ex 1   | 4-t-butylphenyl    | octa-3,6(4-t-butylphenylthio)H <sub>2</sub> Pc    |
| 6  | Ex 2   | 4-t-butylphenyl    | octa-3,6(4-t-butylphenylthio)CuPc                 |
| 7  | Ex 1   | 4-n-nonylphenyl    | hepta-3,6(4-n-nonylphenylthio)H <sub>2</sub> Pc   |
| 8  | Ex 1   | 4-dodecylphenyl    | hepta-3,6(4-dodecylphenylthio)H <sub>2</sub> Pc   |
| 9  | Ex 1   | 3,4-dimethylphenyl | hexa-3,6(3,4-dimethylphenylthio)H <sub>2</sub> Pc |
| 10 | Ex 1   | 4-methoxyphenyl    | octa-3,6(4-methoxyphenylthio)H <sub>2</sub> Pc    |
| 11 | Ex 2   | 4-methoxyphenyl    | octa-3,6(4-methoxyphenylthio)CuPc                 |
| 12 | Ex 2   | 4-butoxyphenyl     | octa-3,6(4-butoxyphenylthio)CuPc                  |
| 13 | Ex 1   | 4-dodecyloxyphenyl | octa-3,6(4-dodecyloxyphenylthio)H <sub>2</sub> Pc |
| 14 | Ex 2   | 4-dodecyloxyphenyl | octa-3,6(4-dodecyloxyphenylthio)CuPc              |
| 15 | Ex 2   | naphth-2-yl        | octa-3,6(naphth-2-ylthio)CuPc                     |
| 16 | Ex 1   | 4-octoxyphenyl     | octa-3,6(4-octoxyphenylthio)H <sub>2</sub> Pc     |
| 17 | Ex 2   | 4-octoxyphenyl     | penta-3,6(4-octoxyphenylthio)CuPc                 |

The octa-3,6-Pcs used in Examples 1 to 17 were made from purified dichlorophthalic anhydride comprising >85% of the 3,6-dichloro isomer. The dichlorophthalic anhydride was purified by centrifugal distillation or fractional crystallisation.

#### Example 18-

A mixture of 12.4 g of 4-methylphenylthiol, 5.6 g of KOH and 20 ml of quinoline was stirred at 140°C for 60 minutes and 5.69 g of tetradecachloromonobromo-CuPc was added. The mixture was then stirred vigorously at 160—180°C for 1 hour, cooled to 100°C and diluted with 50 ml of ethanol (74 OP). After cooling to ambient the solid was filtered, washed with ethanol, water and ethanol and dried to give 7.8 g crude

material. The crude material was passed through a silica column using toluene as eluent and the main fraction collected and isolated by evaporation to yield 5.77 g of dry pentadeca(4-methylphenylthio)-CuPc.

## Example 19

A mixture of 1.65 g of 4-methylphenylthiol, 0.83 g of KOH and 10 ml of quinoline was stirred at 140°C for 30 minutes and 2.8 g of tetradecachloro-monobromo-CuPc was added. The mixture was then stirred at 180—200°C for 5 hours, cooled to 80°C and diluted with 30 ml of ethanol (74 OP). After cooling to 30°C the solid was filtered, washed with ethanol and dried to give 3.6 g crude material. The crude material was passed through a silica column using toluene as eluent and the main fraction collected and isolated by evaporation to yield 0.92 g of dry deca(4-methylphenylthio)-pentachloro-CuPc.

## Examples 20 to 34

Further compounds within the scope of the present invention in accordance with the second preferred class carrying only groups —X—J or chlorine atoms were prepared by the methods of Examples 18 & 19, using equimolar quantities of appropriate thiols or selenols in place of the thiols described in the Examples, as set out in Table 2. In each product having less than fifteen substituted thio groups, the free peripheral carbon atoms carry chlorine atoms.

Table 2

| Example | Thiol/Selenol           | Product                                |
|---------|-------------------------|----------------------------------------|
| 20      | t-butylphenyl           | pentadeca(t-butylphenylthio)CuPc       |
| 21      | 3-methylphenyl          | pentadeca(3-methylphenylthio)CuPc      |
| 22      | 4-methoxyphenyl         | pentadeca(4-methoxyphenylthio)CuPc     |
| 23      | 4-butoxyphenyl          | terdeca(4-butoxyphenylthio)CuPc        |
| 24      | 4-butoxyphenyl          | pentadeca(4-butoxyphenylthio)CuPc      |
| 25      | 4-dodecoxyphenyl        | pentadeca(4-dodecoxyphenylthio)CuPc    |
| 26      | phenyl                  | pentadeca(phenylthio)CuPc              |
| 27      | 2-methoxyphenyl         | tetradeca(2-methoxyphenylthio)CuPc     |
| 28      | 4-methylthiophenyl      | pentadeca(4-methylthiophenylthio)CuPc  |
| 29      | 4-ethylthiophenyl       | deca(4-ethylthiophenylthio)CuPc        |
| 30      | 4-chlorophenyl          | pentadeca(4-chlorophenylthio)CuPc      |
| 31      | 4-(dimethylamino)phenyl | unadeca(4-dimethylaminophenylthio)CuPc |
| 32      | naphth-1-yl             | terdeca(naphth-1-ylthio)CuPc           |
| 33      | naphth-2-yl             | pentadeca(naphth-2-ylthio)CuPc         |
| 34      | phenylselenol           | pentadeca(phenylseleno)CuPc            |

## Example 35

A mixture of 7.75 g of 4-methylphenylthiol, 3.36 g of KOH, and 10 ml of quinoline was stirred at 130°C minutes and 3.18 g of hexadecachloro-PbPc was added. The mixture was then stirred at 180—190°C for 30 minutes, cooled to 50°C and diluted with 30 ml of toluene. The crude material was passed through a silica gel column using toluene as eluent and the main fraction collected. This was isolated by evaporation to give 0.45 g of hexadeca(4-methylphenylthio)PbPc.

## Examples 36 to 40

Further compounds within the scope of the present invention in accordance with the second preferred class carrying only groups —X—J and chlorine atoms were prepared by the method of Example 35 using equimolar quantities of appropriate thiols in place of the 4-methylphenylthiol and equimolar quantities of an appropriate hexadecachloro-Pc in place of the hexadecachloro-PbPc, as set out in Table 3. In each product having less than sixteen substituted thio groups, the peripheral carbon atoms carry chlorine atoms.

Table 3

|    | Example | Thiol          | Product                                       |
|----|---------|----------------|-----------------------------------------------|
| 5  | 36      | 4-methylphenyl | hexadeca(4-methylphenylthio)H <sub>2</sub> Pc |
|    | 37      | 4-methylphenyl | hexadeca(4-methylphenylthio)CuPc              |
|    | 38      | 4-methylphenyl | hexadeca(4-methylphenylthio)ZnPc              |
| 10 | 39      | 4-chlorophenyl | hexadeca(4-chlorophenylthio)CuPc              |
|    | 40      | naphth-2-yl    | deca(naphth-2-ylthio)H <sub>2</sub> Pc        |

## Example 41

15 A mixture of 3.12 g of 4-methylphen-1,2-ylenedithiol, 2.24 g of KOH and 10 ml of quinoline was stirred at 30°C for 30 minutes and 2.13 g of hexadecachloro-H<sub>2</sub>Pc was added. The mixture was then stirred at 80°C for 1 hour, 100°C for 1 hour and 130°C for 1 hour. It was then cooled to 80°C and diluted with 100 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered, washed twice with ethanol and dried. The crude material was passed through a silica column using chloroform as eluent. The main fraction collected, 20 isolated by evaporation and recrystallised from toluene/ether to yield 2.00 g of hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiolphenylthio)-H<sub>2</sub>Pc.

## Examples 42 &amp; 43

25 Further compounds within the scope of the present invention in accordance with the second preferred class carrying groups —X—J, —X—L—X' and chlorine atoms were prepared by the method of Example 42 using equimolar quantities of the appropriate aminothiols in place of the 4-methylphen-1,2-ylenedithiol and/or tetradecachloromonobromo-CuPc in place of the hexadecachloro-H<sub>2</sub>Pc, as set out in Table 4.

Table 4

|    | Example | Thiol                          | Product                                                                    |
|----|---------|--------------------------------|----------------------------------------------------------------------------|
| 35 | 42      | 4-methylphen-1,2-ylene dithiol | hepta(4-methylphen-1,2-dithio-ylene)-mono(4-methyl-2-thiolphenylthio)-CuPc |
| 40 | 43      | 2-aminophenylthiol             | penta(phen-1-amino-2-thio-ylene)-penta(2-aminophenylthio)-CuPc             |

## Example 44

45 A mixture of 7.36 g of tetra(ethylthio)-o-PN and lithium alkoxide (comprising 0.0525 g of lithium in 21 ml of isoamyl alcohol) was stirred at 120—130°C for 2 hours and 130—135°C for a further 1 hour. After cooling to 50°C, 100 ml of methanol was added and the mixture cooled to 20°C. The precipitate which formed was filtered and washed well with methanol before being dissolved in toluene. The toluene solution was passed through a silica column using toluene as eluent. The main fraction was collected and 50 isolated by evaporation to give pentadeca(ethylthio)-monoisoamyloxy-H<sub>2</sub>Pc.

## Example 45

55 A mixture of 3.83 g of tetra(cyclohexylthio)-o-PN and lithium alkoxide (0.023 g of lithium in 7.5 ml of iso-amyl alcohol) was stirred at 120—30°C for 2½ hours. After cooling to 25°C, a solution of 1.79 g of zinc chloride in 25 ml of anhydrous methanol was added. The mixture was then stirred at 25°C for 1 hour and at 120—30°C for 30 minutes. After cooling to 20°C, the precipitate was filtered off and washed with methanol before being dissolved in toluene. The toluene solution was passed through a silica column, using toluene as eluent and the main fraction collected. The product was isolated by evaporation to give hexadeca(cyclohexylthio)-ZnPc.

## Examples 46 to 65

60 Further compounds within the scope of the present invention in accordance with the first and second preferred classes carrying only groups —X—J or groups —X—J and amyloxy groups were prepared by the methods of Examples 44 and 45 using equimolar quantities of appropriate di- or tetra-(substituted-thio)-o-PN in place of the tetra(ethylthio)-o-PN of Example 44 and the tetra(cyclohexylthio)-o-PN of Examples 45 65 and, where appropriate, a metal chloride as set out in Table 5.

Table 5

| Example | Subs-o-PN                                                                 | Product                                                                            |
|---------|---------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| 5       | As in Example 45 (with di- or tetra-(substituted-thio)-o-PN)              |                                                                                    |
|         | 46                                                                        | tetraethyl tetradeca(ethylthio)monoamyloxy-H <sub>2</sub> Pc                       |
|         | 47                                                                        | tetraethyl (ethylthio) <sub>15.3</sub> (amyloxy) <sub>0.7</sub> -H <sub>2</sub> Pc |
| 10      | 48                                                                        | tetra-n-propyl hexadeca(n-propylthio)-H <sub>2</sub> Pc                            |
|         | 49                                                                        | tetra-i-propyl pentadeca(i-propylthio)monoamyloxy-H <sub>2</sub> Pc                |
|         | 50                                                                        | tetra-n-butyl pentadeca(n-butylthio)monoamyloxy-H <sub>2</sub> Pc                  |
| 15      | 51                                                                        | tetra-n-pentyl pentadeca(n-pentylthio)monoamyloxy-H <sub>2</sub> Pc                |
|         | 52                                                                        | tetraethyl/tetrabutyl octa(butylthio)octa(ethylthio)-H <sub>2</sub> Pc             |
|         | 53                                                                        | tetra(ethyl/butyl) octa(butylthio)octa(ethylthio)-H <sub>2</sub> Pc                |
| 20      | (random)                                                                  |                                                                                    |
|         | 54                                                                        | tetracyclohexyl pentadeca(cyclohexylthio)monoamyloxy-H <sub>2</sub> Pc             |
|         | 55                                                                        | tetra-n-octyl hexadeca(n-octylthio)-H <sub>2</sub> Pc                              |
| 25      | 56                                                                        | tetra-s-butyl pentadeca(s-butylthio)monoamyloxy-H <sub>2</sub> Pc                  |
|         | 57                                                                        | tetrabenzyl pentadeca(benzylthio)monoamyloxy-H <sub>2</sub> Pc                     |
| 30      | 58                                                                        | tetraphenyl hexadeca(phenylthio)-H <sub>2</sub> Pc                                 |
|         | 59                                                                        | 3,6-di(iso-propyl) octa-3,6-(isopropylthio)-H <sub>2</sub> Pc                      |
|         | As in Example 46 (with tetra(substituted-thio)-o-PN & CuCl <sub>2</sub> ) |                                                                                    |
| 35      | 60                                                                        | tetra-n-propyl pentadeca(n-propylthio)monoamyloxy-CuPc                             |
|         | 61                                                                        | tetra-n-pentyl pentadeca(n-pentylthio)monoamyloxy-CuPc                             |
|         | 62                                                                        | tetracyclohexyl pentadeca(cyclohexylthio)monoamyloxy-CuPc                          |
| 40      | 63                                                                        | tetra-s-butyl pentadeca(s-butylthio)monoamyloxy-CuPc                               |
|         | 64                                                                        | tetrabenzyl pentadeca(benzylthio)monoamyloxy-CuPc                                  |
|         | As in Example 46 (with tetra(substituted-thio)-o-PN & PbCl <sub>2</sub> ) |                                                                                    |
| 45      | 65                                                                        | tetracyclohexyl pentadeca(cyclohexylthio)monoamyloxy-PbPc                          |

## Example 66

50 A mixture of 0.46 g of dipiperidino-dichloro-o-PN and lithium alkoxide (comprising 0.007 g of lithium and 5 ml of isoamyl alcohol) was stirred at 120–130°C for 20 minutes. After cooling to 20°C, 10 ml of chloroform was added and the mixture passed through a silica column using chloroform as eluent. A fraction was collected and isolated by evaporation to give octapiperidino-octachloro-H<sub>2</sub>Pc.

55 The dipiperidino-dichloro-o-PN was prepared by reacting piperidine with tetra-chloro-o-PN in dimethylformamide and potassium carbonate using the method described in UK 1,489,394.

In all the above preparations structures were confirmed by elemental analysis and the products were characterised by the determination of melting points, absorption maxima and/or extinction coefficients.

## Properties of Infra-red Absorbers

60 The products of the Examples have the properties set out in Table 6. Absorption maxima were measured as solutions in chloroform (Chlor), toluene (Tol) or after deposition on glass (Glass) unless otherwise indicated. Extinction coefficients were determined in toluene or the only solvent in which the absorption maximum was recorded.

65

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Table 6

| <u>Example</u> | <u>Absorption Maxima (m<math>\mu</math>m)</u> |            |              | <u>Extinction</u>  | <u>Melting</u>    |
|----------------|-----------------------------------------------|------------|--------------|--------------------|-------------------|
|                | <u>Chlor</u>                                  | <u>Tol</u> | <u>Glass</u> | <u>Coefficient</u> | <u>Point (°C)</u> |
| 1              | 813                                           | 805        | 828          | 170,000            | >200              |
| 2              | 797                                           | 787        | 797          | 156,000            | >200              |
| 3              | 805                                           | 797        | 818          | 160,000            | >250              |
| 4              | 798                                           | 790        |              | 173,000            | >250              |
| 5              | 793                                           |            | 797          | 152,000            | >250              |
| 6              | 803                                           |            | 797          | 216,000            | >280              |
| 7              | 800                                           |            | 809          |                    | 75                |
| 8              | 789                                           | 787        | 795          |                    | 70                |
| 9              | 807                                           | 803        | 830          |                    | >200              |
| 10             | 799                                           | 792        |              | 161,500            |                   |
| 11             | 805                                           |            | 813          | 155,000            |                   |
| 12             | 800                                           | 786        |              |                    |                   |
| 13             | 818                                           | 808        | 859          |                    | 95                |
| 14             | 807                                           | 794        | 822          |                    | <70               |
| 15             | 799                                           |            | 796          | 136,000            |                   |
| 16             | 816                                           | 806        | 846          |                    | 75                |
| 17             | 775                                           |            |              |                    |                   |
| 18             | 775                                           | 768        | 790          | 169,000            | 120               |
| 19             | 758                                           | 752        | 770          | 174,000            | 148               |
| 20             | 774                                           | 760        | 784          | 142,000            | 128               |
| 21             | 771                                           | 766        | 786          |                    | 95                |
| 22             | 786                                           |            | 801          | 190,000            |                   |
| 23             | 775                                           | 768        | 797          | 158,000            | 140               |
| 24             | 786                                           | 780        | 801          | 182,000            | 100               |

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Table 6 (cont'd)

| <u>Example</u> | <u>Absorption Maxima (m<math>\mu</math>m)</u> |            |              | <u>Extinction</u>  | <u>Melting</u>    |
|----------------|-----------------------------------------------|------------|--------------|--------------------|-------------------|
|                | <u>Chlor</u>                                  | <u>Tol</u> | <u>Glass</u> | <u>Coefficient</u> | <u>Point (°C)</u> |
| 25             | 778                                           | 770        | 792          | 162,000            | 120               |
| 26             | 772                                           | 768        | 794          |                    |                   |
| 27             | 770                                           |            |              |                    |                   |
| 28             | 788                                           | 784        | 810          | 208,500            | 168               |
| 29             | 756                                           | 752        |              |                    |                   |
| 30             | 774                                           |            | 787          | 181,000            | 169               |
| 31             | 782                                           |            | 805          | 118,000            | >200              |
| 32             | 765                                           | 760        |              |                    |                   |
| 33             | 786                                           | 781        | 799          | 197,000            | 143               |
| 34             | 776                                           |            |              |                    |                   |
| 35             | 769                                           |            | 792          |                    | 223               |
| 36             | 769                                           |            |              |                    |                   |
| 37             | 778                                           | 770        | 796          | 220,000            | 142               |
| 38             | 768                                           |            | 791          |                    | 160               |
| 39             | 770                                           |            | 789          | 220,000            |                   |
| 40             | 744                                           |            |              |                    |                   |
| 41             | 800                                           | 797        | 832          | 94,000             | >200              |
| 42             | 790                                           | 787        | 828          | 91,000             | >200              |
| 43             | 909 (in pyridine)                             |            |              |                    |                   |
| 44             | 804                                           | 807        | 827          |                    | >250              |
| 45             | 846                                           | 852        | 860          | 95,000             | 145-150           |
| 46             | 801                                           | 802        |              |                    | >250              |
| 47             | 805                                           | 808        | 830          | 149,000            | >250              |
| 48             | 802                                           | 800        | 819          | 157,600            | 230               |
| 49             | 809                                           |            | 823          | 136,500            | 250               |
| 50             | 807                                           |            | 817          | 147,000            | 95/35             |
| 51             | 802                                           | 802        |              | 162,500            | <30               |
| 52             | 809                                           | 805        | 815          | 129,000            | <30               |
| 53             | 803                                           | 797        | 815          | 115,500            | <30               |
| 54             | 812                                           | 810        | 818          | 120,000            | 289               |

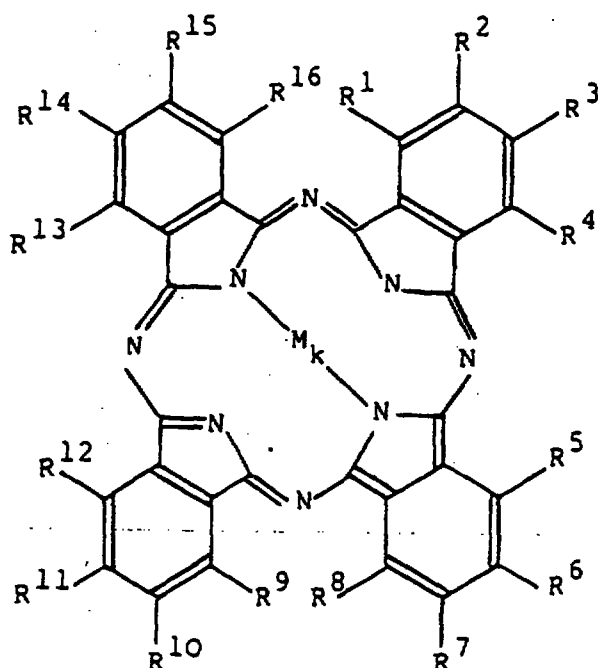
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Table 6 (cont'd)

|          | <u>Example</u> | <u>Absorption Maxima (mμ)</u> |            |              | <u>Extinction</u>  | <u>Melting</u>    |
|----------|----------------|-------------------------------|------------|--------------|--------------------|-------------------|
| <i>s</i> |                | <u>Chlor</u>                  | <u>Tol</u> | <u>Glass</u> | <u>Coefficient</u> | <u>Point (°C)</u> |
|          | 55             | 818                           | 811        |              |                    | <30               |
|          | 56             | 805                           | 801        |              | 133,000            | 260-280           |
| 10       | 57             | 810                           | 809        |              | 84,000             | 100-180           |
|          | 58             | 790                           |            |              |                    |                   |
|          | 59             | 802                           |            |              | 167,000            |                   |
| 15       | 60             | 783                           | 785        | 805          | 170,500            | 260               |
|          | 61             | 784                           | 783        |              | 182,000            | <30               |
|          | 62             | 789                           | 781        | 803          | 163,000            | 286               |
| 20       | 63             | 787                           | 778        |              | 168,000            | 270-280           |
|          | 64             | 797                           | 789        |              | 109,000            | 100-200           |
|          | 65             | 838                           | 830        | 840          | 111,000            | 175-230           |
| 25       | 66             | 835                           |            |              |                    |                   |

## Claims

1. A phthalocyanine compound in which the 16 peripheral carbon atoms carry a substituent, R<sup>1</sup> to R<sup>16</sup>, of the following formula:



wherein at least 5 of the groups represented by R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>16</sup> are independently —X—J or —X—L—X<sup>1</sup>—, wherein

J and L are independently an alkyl, an alkenyl, a homo-alicyclic, a phenyl, a phenylene, a naphthyl, a naphthylene or a mono- or bi-valent, mono- or bi-cyclic, heteroaromatic group;

M is H, a metal atom or an oxymetal group;

k is the inverse of half the valency of M;

X is S, Se, Te or NT;

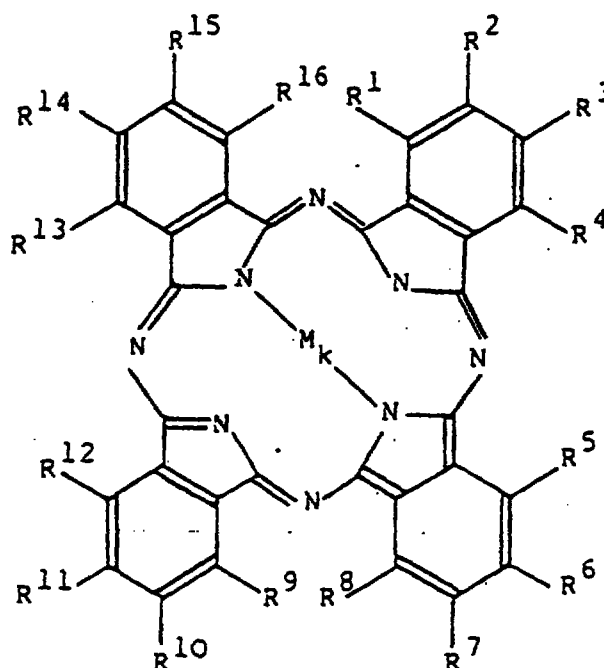


Table 6 (cont'd)

| Example | Absorption Maxima (nm) |     |       | Extinction  | Melting    |
|---------|------------------------|-----|-------|-------------|------------|
|         | Chlor                  | Tol | Glass | Coefficient | Point (°C) |
| 55      | 818                    | 811 |       |             | <30        |
| 56      | 805                    | 801 |       | 133,000     | 260-280    |
| 57      | 810                    | 809 |       | 84,000      | 100-180    |
| 58      | 790                    |     |       |             |            |
| 59      | 802                    |     |       | 167,000     |            |
| 60      | 783                    | 785 | 805   | 170,500     | 260        |
| 61      | 784                    | 783 |       | 182,000     | <30        |
| 62      | 789                    | 781 | 803   | 163,000     | 286        |
| 63      | 787                    | 778 |       | 168,000     | 270-280    |
| 64      | 797                    | 789 |       | 109,000     | 100-200    |
| 65      | 838                    | 830 | 840   | 111,000     | 175-230    |
| 66      | 835                    |     |       |             |            |

## Claims

1. A phthalocyanine compound in which the 16 peripheral carbon atoms carry a substituent, R<sup>1</sup> to R<sup>16</sup>, of the following formula:



wherein at least 5 of the groups represented by R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>16</sup> are independently —X—J or —X—L—X<sup>1</sup>—, wherein

J and L are independently an alkyl, an alkenyl, a homo-alicyclic, a phenyl, a phenylene, a naphthyl, a naphthylene or a mono- or bi-valent, mono- or bi-cyclic, heteroaromatic group;

M is H, a metal atom or an oxymetal group;

k is the inverse of half the valency of M;

X is S, Se, Te or NT;



X<sup>1</sup> is S, Se, Te, O or NT which is directly attached to the adjacent peripheral carbon atom on the same phthalocyanine nucleus or to a peripheral carbon atom on a different phthalocyanine nucleus;

T is H, alkyl or phenyl; or

when X is NT, J and T together form an aliphatic or aromatic ring;

5 and the remaining groups from R<sup>1</sup> to R<sup>16</sup> are H, —O—J, halogen or form part of the group —X—L—X<sup>1</sup>—.

2. A compound according to Claim 1 wherein

J & L are each independently selected from:

(i) phenyl, phenylene, naphthyl, naphthylene, pyridyl, thienyl, furyl, pyrimidyl and benzothiazolyl each of which is unsubstituted or substituted by a group selected from alkyl, alkoxy, alkenyl and alkylthio  
10 containing up to 20 carbon atoms and halo substituted derivatives thereof, phenyl, phenylthio, halogen, nitro, cyano, carboxyl, aralkyl, phenylsulphone, C<sub>1-20</sub>-alkylsulphone, phenylsulphonamide, C<sub>1-20</sub>-alkylsulphonamide, phenylsulphoxide, C<sub>1-20</sub>-alkylsulphoxide, hydroxy, NH<sub>2</sub>, secondary and tertiary amino, methoxycarbonyl and phenylmethoxycarbonyl; or

(ii) C<sub>1-20</sub>-alkyl, C<sub>1-20</sub>-alkenyl and C<sub>4-8</sub>-homoalicyclic each of which is unsubstituted or substituted by a  
15 group selected from C<sub>1-20</sub>-alkoxy, C<sub>1-20</sub>-alkylthio, halo, cyano and mono- or bihomo- or hetero-cyclic aryl;

M is H, a metal atom or an oxymetal group;

k is the inverse of half the valency of M;

X is S, Se, Te or NT

X<sup>1</sup> is S, Se, Te, O or NT which is also directly attached to the adjacent peripheral carbon atom on the  
20 same phthalocyanine nucleus;

T is H, C<sub>1-4</sub>-alkyl or phenyl; or

when X is NT, J & T together form an aliphatic or aromatic ring selected from pyrid-1-yl, pyrimid-1-yl, piperidin-1-yl, morpholin-1-yl, pyrrol-1-yl, and pyrrolidin-1-yl;

25 and the remaining groups from R<sup>1</sup> to R<sup>16</sup> are H, —O—J, halogen or form part of the group —X—L—X<sup>1</sup>—.

3. A compound according to Claim 1 or Claim 2 wherein each of the eight groups R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>16</sup> are —X—J.

4. A compound according to Claim 3 wherein the remaining groups from R<sup>1</sup> to R<sup>16</sup> are H.

5. A compound according to Claim 1 or Claim 2 wherein each of from nine to sixteen of the groups from R<sup>1</sup> to R<sup>16</sup> are —X—J or —X—L—X<sup>1</sup>—.

30 6. A compound according to any one of Claims 1 to 3 and 5 wherein 15 or 16 of the groups from R<sup>1</sup> to R<sup>16</sup> are selected from —X—J, —O—J and —X—L—X<sup>1</sup>—.

7. A compound according to Claim 6 wherein at least one of the groups from R<sup>1</sup> to R<sup>16</sup> is —O—J.

8. A compound according to any one of Claims 1 to 7 having an absorption maximum above 750 mμm.

9. A process for the preparation of a phthalocyanine compound according to Claim 4 in which X is  
35 sulphur which comprises heating an octa-3,6-halophthalocyanine with at least eight equivalents of a thiol, J—SH, in an organic solvent.

10. A process for the preparation of phthalocyanine compound according to Claim 4 in which X is sulphur which comprises heating a 3,6-di(J—S—)phthalonitrile in a solvent in the presence of a base.

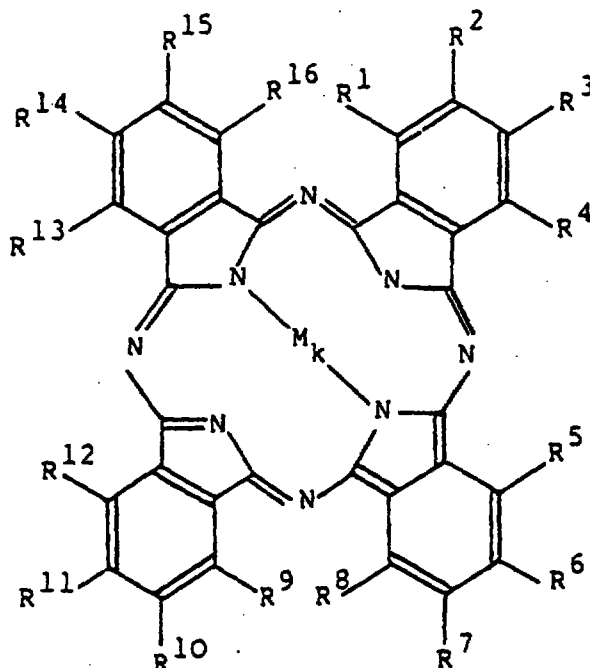
40 11. A process for the preparation of a phthalocyanine compound according to Claim 5 in which X is sulphur which comprises heating a phthalocyanine carrying from nine to sixteen halo groups attached to the peripheral carbon atoms, with from nine to sixteen equivalents of a thiol, J—SH, in an organic solvent.

12. A substrate capable of absorbing infra-red radiation containing or coated with a phthalocyanine compound according to any one of Claims 1 to 8.



# Patentansprüche

1. Phthalocyaninverbindung, bei welcher die 16 peripherischen Kohlenstoffatome einen Substituenten,  $R^1$  bis  $R^{16}$ , tragen und welche die folgende Formel aufweist:



wobei mindestens 5 der durch  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$  und  $R^{16}$  dargestellten Gruppen für  $-X-J$  oder  $-X-L-X'$  stehen, worin

J und L unabhängig für eine Alkyl-, eine Alkenyl-, eine homoalicyclische, eine Phenyl-, eine Phenylen-, eine Naphthyl-, eine Naphthylen- oder eine ein- oder zweiwertige, mono- oder bicyclische heteroaromatische Gruppe stehen;

M für H, ein Metallatom oder eine Oxymetallgruppe steht;

k für den Kehrwert der Hälfte der Wertigkeit von M steht;

X für S, Se, Te oder NT steht;

$X'$  für S, Se, Te, O oder NT steht, welches auch direkt an das benachbarte peripherische Kohlenstoffatom des gleichen Phthalocyaninkerns oder an ein peripherisches Kohlenstoffatom eines anderen Phthalocyaninkerns gebunden ist;

T für H, alkyl oder Phenyl steht;

oder, wenn X für NT steht, J und T gemeinsam einen aliphatischen oder aromatischen Ring bilden; und die restlichen Gruppen  $R^1$  bis  $R^{16}$  für H,  $-O-J$  oder Halogen stehen oder einen Teil der Gruppe  $-X-L-X'$  bilden.

2. Verbindung nach Anspruch 1, worin

J und L unabhängig ausgewählt sind aus

(i) Phenyl, Phenylen, Naphtyl, Naphthylen, Pyridyl, Thienyl, Furyl, Pyrimidyl und Benzothiazolyl, die jeweils unsubstituiert oder durch eine Gruppe substituiert sind, die ausgewählt ist aus Alkyl, Alkoxy, Alkenyl und Alkylthio mit bis zu 20 Kohlenstoffatomen und halogensubstituierten Derivaten davon, Phenyl, Phenylthio, Halogen, Nitro, Cyano, Carboxyl, Arylalkyl, Phenylsulfon,  $C_{1-20}$ -Alkylsulfon, Phenylsulfonamid,  $C_{1-20}$ -Alkylsulfonamid, Phenylsulfoxid,  $C_{1-20}$ -Alkylsulfoxid, Hydroxy,  $NH_2$ , sekundärem und tertiärem Amino, Methoxycarbonyl und Phenylmethoxycarbonyl; oder

(ii)  $C_{1-20}$ -Alkyl,  $C_{2-20}$ -Alkenyl und  $C_{4-8}$ -Homoalicyclen, die jeweils unsubstituiert oder durch eine Gruppe substituiert sind, die ausgewählt ist aus  $C_{1-20}$ -Alkoxy,  $C_{1-20}$ -Alkylthio, Halogen, Cyano und mono- oder bicyclischem, homo- oder heterocyclischem Aryl;

M für H, ein Metallatom oder eine Oxymetallgruppe steht;

k für den Kehrwert der Hälfte der Wertigkeit von M steht;

X für S, Se, Te oder NT steht;

$X'$  für S, Se, Te, O oder NT steht, welches auch direkt an das benachbarte peripherische Kohlenstoffatom des gleichen Phthalocyaninkerns gebunden ist;

T für H,  $C_{1-4}$  Alkyl oder Phenyl steht;

oder, wenn X für NT steht, J und T gemeinsam einen aliphatischen oder aromatischen Ring bilden, der ausgewählt ist aus Pyrid-1-yl, Pyrimid-1-yl, Piperidin-1-yl, Morpholin-1-yl, Pyrrol-1-yl und Pyrrolidin-1-yl;



und die restlichen Gruppen  $R^1$  bis  $R^{16}$  für H,  $-O-J$  oder Halogen stehen oder einen Teil der Gruppe  $-X-L-X^1-$  bilden.

3. Verbindung nach Anspruch 1 oder 2, worin jede der acht Gruppen  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{16}$  für  $-X-J$  steht.

5 4. Verbindung nach Anspruch 3, worin die restlichen Gruppen  $R^1$  bis  $R^{16}$  für H stehen.

5. Verbindung nach Anspruch 1 oder 2, worin 9 bis 16 der Gruppen  $R^1$  bis  $R^{16}$  für  $-X-J$  oder  $-X-L-X^1-$  stehen.

6. Verbindung nach einem der Ansprüche 1 bis 3 und 5, worin 15 oder 16 der Gruppen  $R^1$  bis  $R^{16}$  aus  $-X-J$ ,  $-O-J$  und  $-X-L-X^1-$  ausgewählt sind.

10 7. Verbindung nach Anspruch 6, worin mindestens eine der Gruppen  $R^1$  bis  $R^{16}$  für  $-O-J$  steht.

8. Verbindung nach einem der Ansprüche 1 bis 7, welche ein Absorptionsmaximum oberhalb 750 nm aufweist.

9. Verfahren zur Herstellung einer Phthalocyaninverbindung nach Anspruch 4, worin X für Schwefel steht, bei welchem ein Octa-3,6-halogenophthalocyanin mit mindestens acht Äquivalenten eines Thiols,  $J-SH$ , in einem organischen Lösungsmittel erhitzt wird.

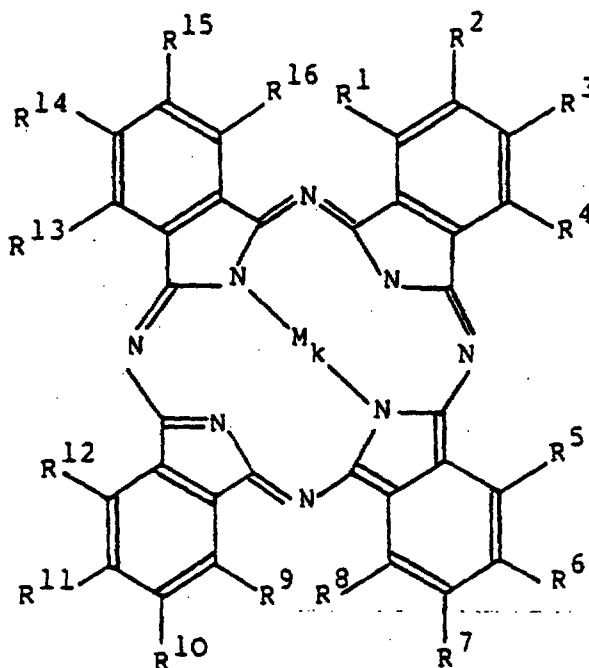
15 10. Verfahren zur Herstellung einer Phthalocyaninverbindung nach Anspruch 4, worin X für Schwefel steht, bei welchem ein 3,6-Di( $J-S$ )phthalonitril in einem Lösungsmittel in Gegenwart einer Base erhitzt wird.

20 11. Verfahren zur Herstellung einer Phthalocyaninverbindung nach Anspruch 5, worin X für Schwefel steht, bei welchem ein Phthalocyanin, das 9-16 an periphere Kohlenstoffatome gebundene Halogenogruppen trägt, mit 9 bis 16 Äquivalenten eines Thiols  $J-SH$ , in einem organischen Lösungsmittel erhitzt wird.

12. Substrat, welches Infrarotstrahlung absorbieren kann und welches eine Phthalocyaninverbindung nach einem der Ansprüche 1 bis 8 enthält oder damit beschichtet ist.

## Revendications

1. Phthalocyanine dont les 16 atomes de carbone périphériques portent un substituant  $R^1$  à  $R^{16}$ , de la formule suivante:



55 où au moins 5 des radicaux représentés par  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$  et  $R^{16}$  sont indépendamment  $-X-J$  ou  $-X-L-X^1-$ ,

où J et L sont indépendamment un alcoyle, un alcényle, un homo-alicyclique, un phényle, un phénylène, un naphyle, un naphtylène ou un radical hétéroaromatique mono- ou bicyclique mono- ou bivalent;

60 M est H, un atome métallique ou un radical oxymétal;

k est l'inverse de la moitié de la valence de M;

x est S, Se, Te ou NT;

$X^1$  est S, Se, Te, O ou NT, qui est directement uni à l'atome de carbone périphérique adjacent sur le même noyau de phthalocyanine ou à un atome de carbone périphérique sur un noyau de phthalocyanine différent;



T est H, alcoyle ou phényle;

ou bien, lorsque X est NT,

J et T forment ensemble un cycle aliphatique ou aromatique;

et les radicaux restants parmi  $R^1$  à  $R^{16}$  sont H, —O—J, halogène ou font partie du radical —X—L—X'—.

5 2. Composé suivant la revendication 1, dans lequel

J et L sont chacun choisis indépendamment parmi:

10 (i) phényle, phénylène, naphthyle, naphtylène, pyridyle, thiénylène, furylène, pyrimidyle ou benzothiazolyle dont chacun est non substitué ou substitué par un radical choisi parmi alcoyle, alcoxy, alcényle et alcoylthio comptant jusqu'à 20 atomes de carbone et leurs dérivés halo-substitués, phényle, phénylthio, halogène, nitro, cyano, carboxyle, aralcoyle, phénylsulfone,  $C_{1-20}$ -alcoylsulfone, phénylsulfonamide,  $C_{1-20}$ -alcoylsulfonamide, phénylsulfoxyde,  $C_{1-20}$ -alcoylsulfoxyde, hydroxyle,  $NH_2$ , amino secondaire et tertiaire, méthoxycarbonyl et phénylméthoxycarbonyl; ou

15 (ii)  $C_{1-20}$ -alcoyle,  $C_{2-20}$ -alcényle et  $C_{4-8}$ -homoalicyclique dont chacun est non substitué ou substitué par un radical choisi parmi  $C_{1-20}$ -alcoxy,  $C_{1-20}$ -alcoylthio, halo, cyano et aryle mono- ou bi-homo- ou hétérocyclique;

M est H, un atome métallique ou un radical oxymétal;

k est l'inverse de la moitié de la valence de M;

X est S, Se, Te ou NT;

20 X' est S, Se, Te, O ou NT qui est aussi directement attaché à l'atome de carbone périphérique adjacent sur le même noyau de phtalocyanine;

T est H,  $C_{1-4}$ -alcoyle ou phényle;

ou bien, lorsque X est Nt,

J et T forment ensemble un cycle aliphatique ou aromatique choisi parmi pyrid-1-yle, pyrimid-1-yle, pipéridin-1-yle, morpholin-1-yle, pyrrol-1-yle et pyrrolidin-1-yle;

25 et les radicaux restants parmi  $R^1$  à  $R^{16}$  sont H, —O—J, halogène ou font partie du radical —X—L—X'—.

3. Composé suivant la revendication 1 ou 2, dans lequel chacun des huit radicaux  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^8$ ,  $R^9$ ,  $R^{12}$ ,  $R^{13}$  et  $R^{16}$  est —X—J.

4. Composé suivant la revendication 3, dans lequel les radicaux restants parmi  $R^1$  à  $R^{16}$  sont H.

5. Composé suivant la revendication 1 ou 2, dans lequel chacun de neuf à seize des radicaux  $R^1$  à  $R^{16}$  est —X—J ou —X—L—X'—.

6. Composé suivant l'une quelconque des revendications 1 à 3 et 5, dans lequel quinze ou seize des radicaux  $R^1$  à  $R^{16}$  sont choisis parmi —X—J, —O—J et —X—L—X'—.

7. Composé suivant la revendication 6, dans lequel au moins l'un des radicaux  $R^1$  à  $R^{16}$  est —O—J.

8. Composé suivant l'une quelconque des revendications 1 à 7, ayant un maximum d'absorption au-dessus de 750 nm.

9. Procédé de préparation d'une phtalocyanine suivant la revendication 4 dans laquelle X est le soufre, qui comprend le chauffage d'une octa-3,6-halophtalocyanine avec au moins huit équivalents d'un thiol, J—SH, dans un solvant organique.

40 10. Procédé de préparation d'une phtalocyanine suivant la revendication 4, dans laquelle X est le soufre, qui comprend le chauffage d'un 3,6-di(J—S—)-phtalonitrile dans un solvant en présence d'une base.

11. Procédé de préparation d'une phtalocyanine suivant la revendication 5, dans laquelle X est le soufre, qui comprend le chauffage d'une phtalocyanine portant neuf à seize radicaux halo unis aux atomes de carbone périphériques avec neuf à seize équivalents d'un thiol, J—SH dans un solvant organique.

45 12. Substrat capable d'absorber le rayonnement infrarouge, qui contient ou est revêtu d'une phtalocyanine suivant l'une quelconque des revendications 1 à 8.