2136431

SULFONATED ZINC AND ALUMINIUM PHTHALOCYANINE DERIVATIVES AND THEIR PREPARATION

The present invention relates to novel sulfonated zinc and aluminium phthalocyanine derivatives and their preparation.

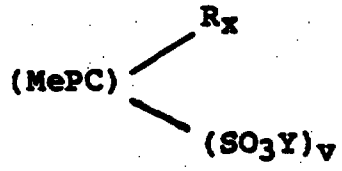
In our copending British Patent Application No. 8126991 (Serial No. 2083815) processes are described and claimed for bleaching textiles or removing stains from textiles and for combating micro-organisms in an organic or inorganic substrate, or for protecting the latter against attack by micro-organisms, employing the new derivatives; as well as bleaching agents, washing agents, soaking agents and agents having an antimicrobial action for carrying out the claimed processes.

Photosensitising compounds, for example, water-soluble, in particular sulfonated phthalocyanine derivatives, for use in processes for bleaching textiles, and the corresponding washing agents are already known c.f. US Patent Specifications 3927967, 4033718 and 4094806, German Offenlegungsschriften 2,222,829 and 2,627,449 and European Patent Applications 3149, 3371 and 3861. Sulfonated aluminium phthalocyanine compounds for use in bleaching textiles and in the corresponding washing agents are known from U.S. Patent Specification 4166718. The compounds disclosed in US 4166718 (= GB 1589652) however are not substituted with neutral groups which do not confer solubility in water. By contrast the compounds claimed in the present Application are sulfonated phthalocyanines containing, in addition to the sulfo groups, neutral groups which do not confer water solubility. The compounds of the present invention have surprisingly superior photoactivator action relative to those of US 4166718.

Water-soluble phthalocyanine compounds, e.g. aluminium and zinc phthalocyanine compounds, especially sulfonated aluminium and zinc phthalocyanines, useful for combating micro-organisms on various substrates, and compositions containing these active ingredients are known from German Offenlegungsschrift 2812261.

We have now found new sulfonated zinc phthalocyanines and aluminium phthalocyanines which are further substituted by neutral groups which do not confer solubility in water and which are more active, more economical and more advantageous in combating micro-organisms on various substrates than those of German Offenlegungsschrift 2812261.

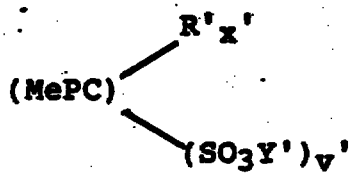
Accordingly, the present invention provides a zinc phthalocyanine or aluminium phthalocyanine compound of the formula:



(1)

in which MePC is the zinc phthalocyanine or aluminium phthalocyanine ring system; Y is hydrogen, an alkali metal ion, an ammonium ion or amine salt ion; v is any number between 0.1 and 4; R is fluorine, chlorine, bromine, iodine or cyano, and x is any number between 0.1 and 8, it being possible for the substituents R present in the molecule to be identical or different.

Preferred compounds of the invention are those having the formula:



(2)

in which MePC has its previous significance; Y' is hydrogen, an alkali metal ion or an ammonium ion; v' is any number between 1.3 and 4; R' is chlorine, bromine or iodine and x' is any number between 0.5 and 8.

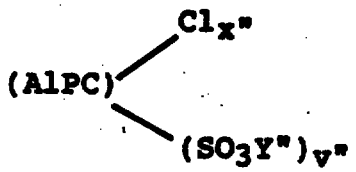
In the formula (2) v' is preferably any number between 2 and 4, in particular between 3 and 4, and x' is preferably any number between 0.8 and 4.

As is customary in phthalocyanine chemistry, the individual products frequently consist of mixtures because pure products are not formed in their preparation (for example by sulfonation, halogenation or the like).

(12)

In the context of the formula (2), possible compounds are, in particular, those in which Y' is hydrogen, sodium or potassium, v' is any number between 2 and 4, in particular between 3 and 4, R' is chlorine or bromine, preferably chlorine, and x' is any number between 0.8 and 2, for example those in which Y' is hydrogen, sodium or potassium, v' is any number between 3 and 4, R' is bromine and x' is any number between 0.5 and 1.5.

The said aluminium phthalocyanine compounds, in particular those of the formula:

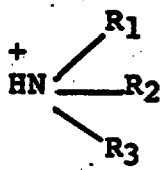


(3)

in which AlPC is the aluminium phthalocyanine ring system, x" is any number between 0.8 and 1.5, v" is any number between 3 and 4 and Y" is hydrogen or sodium, are particularly preferred.

As is known from phthalocyanine chemistry, the third valency of the aluminium in the aluminium phthalocyanine ring system is saturated by an additional ligand, for example an anion. This anion can be identical to the anion of the aluminium compound which was used for the preparation of the complex. It is not significant in terms of the activity of the particular compound. Examples of these anions are halide, sulfate, nitrate, acetate or hydroxyl ions.

The expression "an amine salt ion" Y is to be understood as meaning a substituted ammonium ion, for example one of the formula:



(13)

in which R_1, R_2 and R_3 independently of one another are hydrogen or alkyl (preferably having 1-4 C atoms) which is unsubstituted or substituted by halogen, hydroxyl, phenyl or cyano, at least one substituent R being different from hydrogen. Two radicals R together can also complete a saturated 5-membered or 6-membered nitrogen heterocyclic ring which, if appropriate, additionally contains an oxygen atom or nitrogen atom as a ring member. Examples of these heterocyclic rings are: piperidine, piperazine, morpholine, pyrrolidine, imidazoline and the like.

The index v indicates the degree of sulfonation, which of course does not have to be an integer. Preferred degrees of sulfonation are between 1.3 and 4, in particular between 2 and 4. The number of sulfo groups required in the molecule also depends on the number of substituents R present. In every case, there must be a sufficient number of sulfo groups present to ensure adequate solubility in water. A minimum solubility of only 0.01 g/litre can be sufficient; in general, a solubility of 0.1 to 20 g/litre is advantageous.

The sulfonated zinc phthalocyanine and aluminium phthalocyanine compounds of the invention to the invention can be prepared by processes known per se in phthalocyanine chemistry. For example, the substituents which do not confer solubility in water (for example substituents R in the formulae (1) and (2)) can already be present in the starting materials (for example phthalic anhydride, phthalodinitrile or phthalimide) used for the synthesis of the phthalocyanine ring structure. After the synthesis of the now correspondingly substituted and, if appropriate, already metallised phthalocyanine has been carried out, the sulfonic acid groups can be introduced if they were not

(14)

already present in the starting materials. Some substituents can also be introduced into the already synthesised phthalocyanine ring system, for example by chlorination, bromination or iodination (R = Cl, Br or I). The sulfonic acid groups can be introduced beforehand (cf., for example, U.S. Patent Specification 2,647,126) or, preferably afterwards. If the synthesis of the phthalocyanine ring system is carried out from phthalic anhydride or phthalodinitrile in the presence of chlorides, for example $AlCl_3$ or $Zn\ Cl_2$, already chlorinated phthalocyanines having a chlorine content of, in particular, 0.5-1.5 mols of chlorine per mol of aluminium or zinc phthalocyanine are formed. The sulfonic acid groups can likewise be introduced into such products afterwards. For the preparation of phthalocyanine compounds having mixed substituents, the said methods can be combined in a suitable manner. All the processes are well known in phthalocyanine chemistry and are described in detail therein.

The introduction of the sulfonic acid groups can be carried out, for example, by sulfonation, if appropriate with the aid of oleum. Alternatively, corresponding unsulfonated phthalocyanines can also be reacted with chlorosulfonic acid to give the corresponding phthalocyanine-sulfochlorides, and then hydrolysed to the sulfonic acids. In both cases, the free sulfonic acid groups can be converted to their salts afterwards.

All the rections on the synthesised phthalocyanine ring system can be carried out when the latter is already in the form of the zinc or aluminium complex. However, it is also possible to introduce the substituents into the metal-free phthalocyanine structure and to metallise the latter afterwards, by customary

methods (cf., for example, U.S. Patent Specification 4,166,780), for example by reacting the metal-free phthalocyanine compounds with a zinc or aluminium salt or alcoholate.

To introduce halogen atoms, it is also possible to diazotise zinc phthalocyanine or aluminium phthalocyanine substituted by amino groups, and to replace the diazonium group(s) by halogen (Sandmayr reaction). The introduction of the sulfo groups can likewise be carried out before or after the introduction of the halogen atoms.

The synthesis of the phthalocyanine ring structure from pthalic acid derivatives, with the formation of chlorinated phthalocyanines, is described in Ullmann's Encyclopadie der technischen Chemie (Ullmann's Encyclopedia of Chemical Technology), 4th edition, Volume 18, page 508 et seq., and by F.H. Moser and A.L. Thomas in "Phthalocyanine" ("Phthalocyanines") (1963), page 104 et seq. Halogenated phthalocyanines or phthalocyanines carrying other inert substituents can be obtained by the co-condensation of unsubstituted or correspondingly substituted phthalic acids or phthalic acid derivatives by customary processes known in pthalocyanine chemistry. The following preparation instructions 1a, 2a, 3a and 5a show how such processes can be carried out.

In the Examples, which illustrate the preparation of the active substances and the process according to the invention in greater detail, parts and percentages are always by weight, unless stated otherwise. In all the Examples, AlPC is the aluminium phthalocyanine ring system and ZnPC is the zinc phthalocyanine ring system. Furthermore, some of the phthalocyaninesulfonic acids are obtained in the preparation as

(16)

the sodium salts. As is customary in dye chemistry, the group $-SO_3H$ therefore also includes its sodium salts. The λ_{max} values from the abosrption spectrum, used to characterise the phthalocyanine compounds, were determined in a 1:1 mixture of ethanol/water at pH 7.

Example 1

a) 128 g of phthalic acid dinitrile, 40 g of $AlCl_3$ and 650 g of 1,2-dichlorobenzene are intially introduced into an autoclave. After flushing with nitrogen, the reaction mixture is heated at about 170°C for 26 hours. After it has been cooled and deaerated, the suspension is poured, with stirring, into 400 ml of water containing 100 g of trisodium phosphate. The mixture is then evaporated to dryness on a rotary evaporator, the crude product is stirred with 750 ml of water and treated with 60 g of 50% NaOH and the mixture is heated to 75°C and kept at this temperature for 2 hours. Finally, the crude product is filtered off and stirred in 500 ml of water containing 80 g of 32% HCl (2 hours at 90-95°C), the mixture is filtered hot and the product is washed. This gives aluminium phthalocyanine which contains about 1 mol of bonded chlorine per mol.

b) 60 parts of the monochloro-aluminium phthalocyanine obtained according to a) are introduced into 260 parts by volume of chlorosulfonic acid, with thorough stirring. The temperature is kept at 20 to 25°C by external cooling. The reaction mixture is first stirred for half an hour at room temperature and the temperature is then raised to 110 to 115°C over a period of one hour. After half an hour, the reaction temperature is increased to 130 to 135°C over a period of one hour and maintained for four hours. The reaction mixture is then cooled to 70 to 75°C and

(19)

treated with 125 parts by volume of thionyl chloride over a period of 45 minutes. The reaction mixture is stirred for a further one hour at 85 to 90°C and then left to cool to room temperature, and it is then discharged onto an ice/water mixture. The cold sulfochloride suspension is filtered with suction and the product is washed with ice-water until the washings are free of acid.

The moist sulfochloride paste is suspended in 1,200 parts of water. At 50 to 60°C, the sulfochloride groups are saponified to sulfo groups by adding sodium hydroxide. The saponification can be accelerated by adding catalytic amounts of pyridine.

After the saponification has ended, the weakly alkaline solution is evaporated to dryness. This gives 105 parts of a readily water-soluble, blue powder. According to analysis, the product contains, per mol of aluminium phthalocyanine, 1 mol of organically bonded chlorine and about 3.5 mols of sulfonic acid groups, and thus corresponds to the formula $(AlPC)Cl(SO_3H)_{3-4}$ having a λ_{max} of 674 nm.

Example 2

a) In a flask fitted with a stirrer, 118 parts of urea, 20 parts of 4-chlorophthalic acid, 44.4 parts of phthalic anhydride, 27 parts of xylenesulfonic acid (mixture of isomers), 1 part of ammonium molybdate, 15 parts of aluminium chloride and 200 parts by volume of trichlorobenzene (mixture of isomers) are stirred thoroughly, warmed to 195 to 205°C over a period of 3 hours and stirred at this temperature for 16 hours. After cooling, 500 parts by volume of isopropanol are added, the mixture is stirred for a short time and the suspension is then filtered with suction. The residue is washed with 500 parts by volume of

isopropanol. The residue is taken up in 800 parts by volume of dilute sodium hydroxide solution, the mixture is stirred at 80 to 90°C for 2 hours and the product is then filtered off with suction and washed with warm water. The same process is then carried out in dilute hydrochloric acid and the pigment obtained is washed with warm water until the washings are free of acid, and dried. About 50 parts of monochloro-aluminium phthalocyanine (201) are obtained in the form of a blue powder.

If the 4-chlorophthalic acid is replaced in the above instructions by corresponding amounts of dichlorophthalic acid or anhydride, tetrachlorophthalic acid or anhydride, 4-bromophthalic acid or anhydride, tetrabromophthalic acid or anhydride, 4-iodophthalic acid or anhydride or diiodophthalic acid or anhydride, and the procedure is otherwise as indicated above, the following halogenated phthalocyanines (pigments) are obtained:

(202) dichloro-aluminium phthalocyanine

(203) tetrachloro-aluminium phthalocyanine

(204) monobromo-aluminium phthalocyanine

(205) tetrabromo-aluminium phthalocyanine

(206) monoiodo-aliminium phthalocyanine

(207) diiodo-aluminium phthalocyanine

b) The halogenated phthalocyanine pigments (201) to (207) prepared according to a) are converted to the corresponding compounds containing sulfo groups, by the method indicated in Example 1b). This gives the following compounds:

(211) (AlPC)Cl$(SO_3H)_{3-4}$ λ_{max} = 674 nm

(212) (AlPC)$Cl_2(SO_3H)_{3-4}$

(213) (AlPC)$Cl_4(SO_3H)_{3-4}$

(214) (AlPC)Br$(SO_3H)_{3-4}$ λ_{max} = 675 nm

(215) (AlPC)$Br_4(SO_3H)_{3-4}$ λ_{max} = 677 nm

(216) (AlPC)I$(SO_3H)_{3-4}$ λ_{max} = 678 nm

(217) (AlPC)$I_2(SO_3H)_{3-4}$

Example 3

a) In a sulfonating flask, 44.4 parts of phthalic anhydride, 22.7 parts of 4-bromophthalic anhydride, 74 parts of urea and 17 parts of aluminium chloride are warmed to 215 to 220°C and stirred at this temperature for 2 hours. After cooling, the solid mass is comminuted. Purification is carried out by extraction with hot dilute sodium hydroxide solution, hot water, hot dilute hydrochloric acid and again hot water. After drying, 16.5 parts of monobromo-aluminium phthalocyanine are obtained as a blue powder.

b) The monobromo-aluminium phthalocyanine obtained according to a) is reacted with chlorosulfonic acid analogously to Example 1b), and the monobromo-aluminium phthalocyanine-sulfochloride obtained is converted to the corresponding sulfonic acid by alkaline saponification. This gives a product which, according to analysis, contains, per mol of aluminium phthalocyanine, 1 mol of organically bonded bromine and about 3.5 mols of sulfonic acid groups, and therefore corresponds to the formula (AlPC)Br$(SO_3H)_{3-4}$ (λ_{max} = 675 nm).

If corresponding amounts of monofluoro-, monoiodo- or monocyano-aluminium phthalocyanine are used in Example 1b) or 3b) instead of the monochloro-aluminium phthalocyanine or monobromo-

aluminium phthalocyanine, and the procedure is otherwise the same as indicated under 1b) or 3b), products of analogous composition, i.e. (AlPC)F$(SO_3H)_{3-4}$, (AlPC)I$(SO_3H)_{3-4}$ (λ_{max} - 678 nm) and (AlPC)CN$(SO_3H)_{3-4}$, are obtained. The fluoro-, iodo- or cyano-substituted aluminium phthalocyanines can be prepared analogously to Example 3a), in a known manner, by conjoint synthesis from the corresponding substituted phthalic acid compounds and unsubstituted phthalic acid compounds.

Example 4

60 parts of monochloro-zinc phthalocyanine are introduced into 260 parts by volume of chlorosulfonic acid, with thorough stirring. In this process, the temperature is kept at 20 to 25°C by external cooling. The reaction mixture is first stirred for half an hour at room temperature and the temperature is then raised to 110 to 115°C over a period of one hour After half an hour, the reaction temperature is increased to 130 to 135°C over a period of one hour, and maintained for 4 hours. The reaction mixture is then cooled to 70 to 75°C and treated with 125 parts by volume of thionyl chloride over a period of 45 minutes. The reaction mixture is stirred for a further one hour at 85 to 90°C and then left to cool to room temperature, and it is then discharged onto an ice/water mixture. The cold sulfochloride suspension is filtered with suction and the product is washed with ice-water until the washings are free of acid.

The moist sulfochloride paste is suspended in 1,200 parts of water and saponified to the sodium salt of monochloro-zinc phthalocyaninesulfonic acid, at 50 to 60°C, by adding sodium hydroxide. The weakly alkaline solution is evaporated to

dryness. This gives a readily water-soluble, blue powder. This product corresponds to the formula $(ZnPC)Cl(SO_3H)_{3-4}$ (λ_{max} - 670 nm).

The monochloro-zinc phthalocyanine used as the starting material is prepared (analogously to Example 3a)), by the known urea process, by conjoint synthesis from one equivalent of 4-chlorophthalic anhydride and 3 equivalents of phthalic anhydride, anhydrous $ZnCl_2$ being added.

The zinc phthalocyaninesulfonic acids of the formulae $(ZnPC)F(SO_3H)_{3-4}$, $(ZnPC)Br(SO_3H)_{3-4}$, $(ZnPC)I(SO_3H)_{3-4}$ and $(ZnPC)CN(SO_3H)_{3-4}$ are obtained analogously.

Example 5

a) In a flask fitted with a stirrer, an intimate mixture of 150 parts of urea, 20 parts of 4-chlorophthalic acid, 44.4 parts of phthalic anhydride, 27 parts of xylene-sulfonic acid (mixture of isomers), 1 part of ammonium molybdate and 20 parts of zinc chloride is warmed slowly to 150°C. After 2 hours, the temperature is increased to 180 to 190°C and the mixture is stirred for a further 12 hours. The cooled mass is finely comminuted, stirred with 200 parts by volume of isopropanol and filtered off with suction and the residue is washed with 200 parts by volume of acetone. The residue is stirred in 800 parts by volume of dilute sodium hydroxide solution at 80 to 90°C for 2 hours, filtered off with suction and washed with warm water. The residue is then stirred in dilute hydrochloric acid at 80 to 90°C for 2 hours, filtered off with suction, washed with water until the washings are free of acid, and dried. This gives 34 parts of monochloro-zinc phthalocyanine (501) in the form of a blue powder.

(22)

If the 4-chlorophthalic acid is replaced in the above instructions by corresponding amounts of tetrachloro-, 4-bromo-, tetrabromo-, 4-iodo- or diiodo-phthalic acid, and the procedure is otherwise as indicated above, the following halogenated phthalocyanines (pigments) are obtained:

(502) tetrachloro-zinc phthalocyanine

(503) monobromo-zinc phthalocyanine

(504) tetrabromo-zinc phthalocyanine

(505) monoiodo-zinc phthalocyanine

(506) diiodo-zinc phthalocyanine

b) The halogenated phthalocyanine pigments (501) to (506) prepared according to a) are converted to the corresponding compounds containing sulfo groups, by the method indicated in Example 4. This gives the following compounds:

(511) (ZnPC)Cl$(SO_3H)_{3-4}$ λ_{max} = 670 nm

(512) (ZnPC)$Cl_4(SO_3H)_{3-4}$ λ_{max} = 672 nm

(513) (ZnPC)Br$(SO_3H)_{3-4}$ λ_{max} - 669 nm

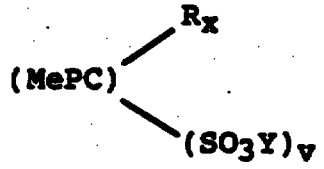
(514) (ZnPC)$Br_4(SO_3H)_{3-4}$

(515) (ZnPC)I$(SO_3H)_{3-4}$

(516) (ZnPC)$I_2(SO_3H)_{3-4}$

claims

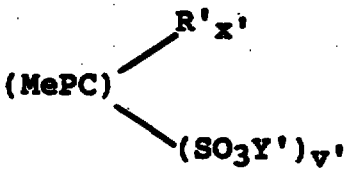
1. A zinc phthalocyanine or aluminium phthalocyanine compound of the formula:



(1)

in which MePC is the zinc phthalocyanine or aluminium phthalocyanine ring system; Y is hydrogen, an alkali metal ion, an ammonium ion or amine salt ion; v is any number between 0.1 and 4; R is fluorine, chlorine, bromine, iodine or cyano and x is any number between 0.1 and 8, it being possible for the substituents R present in the molecule to be identical or different.

2. A phthalocyanine compound according to claim 1, of the formula:



(2)

in which MePC is the zinc phthalocyanine or aluminium phthalocyanine ring system; Y' is hydrogen, an alkali metal ion or an ammonium ion; v' is any number between 1.3 and 4; R' is chlorine, bromine or iodine and x' is any number between 0.5 and 8.

3. A phthalocyanine compound according to claim 2 wherein v is any number between 3 and 4 and x' is any number between 0.8 and 4.

* C L M S *

(24)

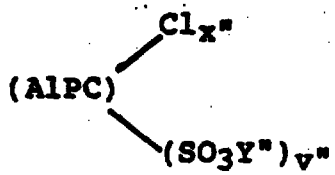
4. A phthalocyanine compound according to claim 2 or 3, of the formula (2), in which Y' is hydrogen, sodium or potassium, v' is a number between 2 and 4, R' is chlorine or bromine and x' is any number between 0.8 and 2.

5. A phthalocyanine compound according to claim 4 wherein v' is a number between 3 and 4 and R' is chlorine.

6. A phthalocyanine compound according to claim 2, of the formula (2), in which Y' is hydrogen, sodium or potassium, v' is a number between 3 and 4, R' is bromine and x' is any number between 0.5 and 1.5.

7. A phthalocyanine compound according to any one of claims 1 to 6, of the formula (1) or (2), in which MePC is the aluminium phthalocyanine ring system.

8. A phthalocyanine compound according to claim 7, of the formula:



in which AlPC is the is the aluminium phthalocyanine ring system, x" is any number between 0.8 and 1.5, v" is any number between 3 and 4 and Y" is hydrogen or sodium.

9. A phthalocyanine compound according to claim 1 substantially as described with reference to any of Examples 1 to 5.

10. A process for the preparation of a phthalocyanine compound of the formula (1) as defined in claim 1 which comprises sulfonating a phthalocyanine of the formula:

$$(MePC)-R_{x'}$$

and, if appropriate, converting the sulfonic acid obtained into a salt.

* C L M S *

11. A process according to claim 10 wherein the sulphonation is effected with oleum.

12. A process according to claim 10 or 11, for the preparation of a phthalocyanine compound of the formula (1), which comprises reacting a phthalocyanine of the formula:

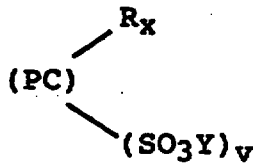
$$(MePC)-R_x$$

with chlorosulfonic acid and hydrolysing the sulfochloride obtained.

13. A process for the preparation of a phthalocyanine compound of the formula (1) as defined in claim 1 in which MePC, Y, v and x are as defined in claim 1 and R is chlorine, bromine or iodine, which comprises chlorinating, brominating or iodinating a sulfonated phthalocyanine of the formula:

$$(MePC)-(SO_3Y)_v$$

14. A process for the preparation of a phthalocyanine compound of the formula (1) as defined in claim 1 which comprises reacting a phthalocyanine of the formula:



in which PC is the metal-free phthalocyanine ring system and R, x, Y and v are defined as in claim 1, with a zinc or aluminium salt or alcoholate.

15. A process for the preparation of a phthalocyanine compound according to claim 10 substantially as described with reference to any of Examples 1 to 5.

16. A phthalocyanine compound when produced by a process claimed in any of claims 10 to 15.

* C L M S *