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(19)

(54) NEW BLACK PIGMENTS AND ELECTROPHOTOGRAPHIC PROCESSES USING THEM

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of Basle, Switzerland,

do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrophotographic imaging proceesses.

Among the electrophotographic image reproduction processes there are those which of necessity use electrically photosensitive particles for the image formation. In other processes, the use of electrically photosensitive particles for image reproduction is not necessary, but yet advantageous. In the electrostatic processes, it is necessary to use a recording material provided with an electrically photosensitive layer. The present invention has for its object to provide electrically photosensitive, organic black pigments for all these processes.

The imaging processes in which of necessity electrically photosensitive particles are used for the image formation, are based on the interaction of electromagnetic radiation with suitable electrically photosensitive particles which are dispersed in an insulating medium. If, for example, a suspension of these particles is brought in the form of a thin layer into an electric field, which is produced for example by a plate capacitor, and if the layer is imagewise exposed, then the exposed and unexposed electrically photosensitive particles move in opposite directions, i.e. an imagewise separation of the particles takes place. A positive and negative copy respectively of the original image is formed on the opposite surfaces of the electrodes. This effect forms the basis of image reproduction with electrically photosensitive particles.

Of the large number of patent specifications which describe such processes, a number are discussed below.

A dry process is described in U.S. Patent Specification 2,758,939. In this process, a charge exchange takes place at the exposed areas between the electrically photosensitive particles and an electrode.

In U.S. Patent Specifications 2,940,847, 3,384,565, 3,384,566, 3,384,488 and 3,383,993, the electrically photosensitive particles are suspended in an insulating liquid and a "photoelectrophoretic imaging process" is described. In this process, it is also assumed that a charge exchange takes place at the exposed areas between the electrically photosensitive particles and an electrode ("injection electrode").

German Offenlegungsschrift 2,356,687 discloses a photoelectrophoretic imaging process in which a charge exchange takes place at the exposed areas between the electrically photosensitive particles and the liquid surrounding them.

German Offenlegungsschrift 2,459,078 describes a photoelectrophoretic imaging process in which the charge exchange takes place at the unexposed areas between the electrically photosensitive particles and an electrode which carries a homogeneous layer containing or consisting of a dark charge exchange material. The applicant calls this process a "photoimmobilised electrophoretic recording process".

In addition, there are a large number of photoelectrophoretic imaging processes, of which only a few are discussed here. U.S. Patent Specification 3,870,517 and German Offenlegungsschrift 2,047,099 disclose processes in which the electrically photosensitive particles are suspended in a "white colored opaque" medium or in a coloured medium. By means of photoelectrophoresis, the optical reflectance properties of the suspension layer are changed according to the radiation image. These processes are suitable less for producing a hard copy but much more for produicng a soft copy

or display. German Offenleungsschrift 2,331,833 discloses a photoelectrophoretic process in which the exposure is effected through a partly transparent sheet of paper which lies between the injection electrode and the suspension. In German Offenlegungsschrift 2,028,364, an electrode is replaced by an electrostatic charge.

In the "migration imaging process" described for example in U.S. Patent Specification 3,520,681, the electrically photosensitive particles are finely distributed in a solid, but softenable or soluble matrix. In order to make possible the imagewise migration of the particles, the substance is softened or dissolved by heat, treatment with solvents in fluid or vapour form, by a combination of these means or by other means, before, during or after the exposure. A very good survey of the migration processes is to be found in the periodical "Bild und Ton", *28*, Fasc. 5, page 135 (1975).

A further imaging process, described for example in U.S. Patent 3,707,368 and which also of necessity uses electrically photosensitive particles, is the "manifold imaging process", in which the imaging layer is sandwiched between a donor and a receiving sheet.

A further process to be mentioned is that described for example in German Offenlegungsschrift 1,472,906, wherein an earthed, uncharged "image carrier" is dusted with an electrically photosensitive "colour carrier" powder which is electrostatically charged before or after the dusting. After imagewise exposure the less firmly adhering particles (at the exposed areas) are removed, whilst the more firmly adhering ones are fixed.

All these processes, which of necessity use electrically photosensitive particles for the image reproduction, are suitable for producing both monochrome and polychromatic line and continuous tone images. In the case of monochrome images, it will be appreciated that black and white images are of especial interest. This means, however, that black, electrically photosensitive particles must be available. To the skilled person it is obvious that, in this connection, it is most advantageous to use pigments—i.e. single component particles—which are both chromophoric and electrically photosensitive. As against this, composite particles, i.e. multicomponent particles, have distinct disadvantages. However, the search for organic pigments which are both black and sufficiently electrically photosensitive for image reproduction has up to now been unsuccessful. In a number of patent specifications, the problem of producing black and white images by those processes which, of necessity, use electrically photosensitive particles, has been solved by using composite particles or by another roundabout route: In German Offenlegungsscrhift 2,048,380, for example, composite particles are used which consist of a polymer matrix into which at least two differently coloured and electrically photosensitive pigments are incorporated. In German Offenlegungsschrift 2,256,329, very similar particles are used in which at least one of the pigments or the polymer matrix is electrically photosensitive. By using suitably chosen pigments, for example cyan, magenta and yellow, an attempt is made to obtain a black toner. However, it is obvious to the skilled person that no deep black can thereby be attained. Composite particles are also used especially for the photoelectrophoretic process in German Offenlegungsschrift 2,050,068. These particles are suitably coloured resin particles to which very finely divided electrically photosensitive pigment particles adhere. For black, there are used resin particles pigmented with carbon black to which phthalocyanine particles as electrically photosensitive component adhere. Yet another means of producing black and white images by the photoelectrophoretic imaging process is employed in German Offenlegungsschrift 2,400,185. In this process, zinc oxide particles, which are electrically photosensitive but not coloured, migrate to an image-receiving sheet which carries a layer of a vinylidene/acrylonitrile copolymer. Since this copolymer is colourless, a white-in-white image is initially formed. On heating the image-receiving sheet, the image then becomes brown or black as a consequence of the decomposition and carbonisation of the copolymer in contact with the zinc oxide. It is perfectly obvious to the skilled person what the drawbacks of the processes just referred to for producing black and white images are: for example the complicated and uneconomic production of such composite particles, poor photosensitivity, inadequate colour strength and poor image quality.

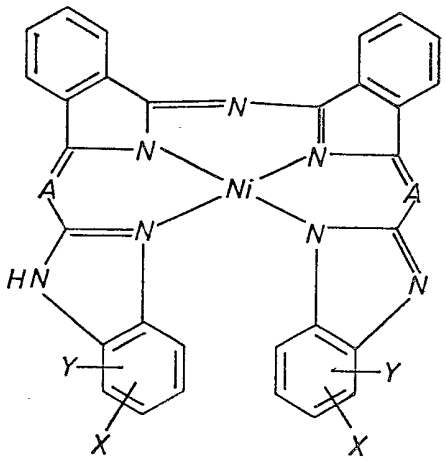
There are in addition a substantial number of electrophotographic imaging processes, viz. the highly successful electrostatic processes employed for many years in the office copying sector (for example the Xerox, electrofax, TESI process, both with dry and wet development of the electrostatic image) and which use—even if not of necessity, yet with advantage—electrically photosensitive particles as toner particles for the image development. For example, in German Offenlegungsschrift 2,256,329, attention

is drawn on page 38 to the advantages possessed by electrically photosensitive toners in such processes. Owing to the elecrtical photosensitivity, the charging rate and charge disintegration of the toners can be regulated. Moreover, the image developed with an electrically photosensitive toner can be exposed, whereby its conductivity and thus its charge can be regulated in order to improve the image transfer, if necessary. In addition, exposure can be effected after the transfer in order to reduce the charges on the residual toner particles, thereby increasing the cleansing effect.

The use of black, electrically photosensitive pigments is also advantageous for the production of polychromatic images, namely where the contrast effect of polychromatic photocopies is to be increased with black. In the production of a polychromatic image, a number of colour selection copies are superimposed, for example in the order black, yellow, magenta, cyan. Because of the necessity to recharge the photoconductor used as electrophotographic recording material repeatedly, namely after the deposit of each partial image, and to expose it imagewise, the use of electrically photosensitive toners for developing the partial images is advantageous. In German Auslegeschrift 2,006,003, the proposal has been made to use photoconductor particles coloured with pigments or dyes, i.e. multicomponent particles, as toner particles. Attention has already been drawn to the disadvantages of such multicomponent particles.

As is commonly known, a recording material having an electrically photosensitive layer is used in the electrostatic processes. For the production of this recording material an electrically photosensitive substance is required. The electrically photosensitive substances hitherto known and used for this purpose, for example selenium, zinc oxide, cadmium sulphide, phthalocyanine pigments etc., have various disadvantages. An important drawback of these materials is that they are not panchromatic. Consequently, a spectral sensitisation is necessary for practical purposes. However, every skilled person knows what difficulties such a procedure entails. In contradistinction thereto, the black pigments of the present invention possess panchromatic properties, so that a spectral sensitisation is unnecessary. The black pigments of the present invention can be used in different weight ratios with any binders, i.e. both with "active" and with "insulating", or with photoconductive or non-photoconductive, binders. The resulting recording materials can be charged both negatively and positively, which is also advantageous. Furthermore, the ratio of pigment to binder can be kept relatively low, so that the mechanical properties of the recording material are determined largely by the properties of the binder. Since, as already mentioned, the binders can be very freely chosen, there are many ways in which the recording materials can be obtained.

It has been found that in both the above mentioned electrophotographic processes which of necessity, and those which advantageusly, use electrically photosensitive particles, and that in producing an electrophotographic recording material, surprisingly excellent results are obtained by using, as electrically photosensitive material, a black pigment selected from the metal complexes of the formula



(I)

wherein

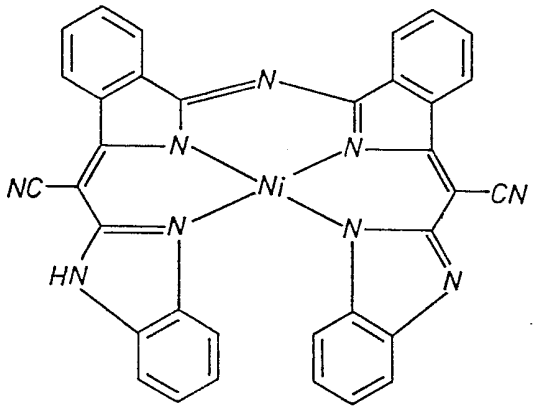
A represents a nitrogen atom or the

group,

X represents a hydrogen or halogen atom or an alkyl group of 1 to 6 carbon atoms,

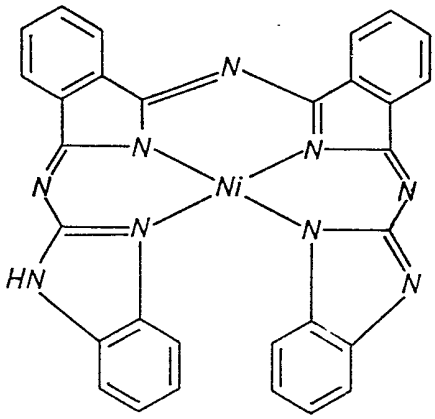
Y represents a hydrogen or halogen atom, an alkyl, alkoxy or alkylsulphonyl group of 1 to 6 carbon atoms, a nitro or carbamoyl group, an alkylcarbamoyl or alkoxycarbonyl group of 2 to 6 carbon atoms or an arylcarbamoyl or aryloxycarbonyl group of 7 to 11 carbon atoms.

Examples of metal complexes are those of the formula



(II)

and



(III)

These are new compounds, the manufacture of which is described in Examples 1 and 2 of this specification.

The pigments are advantageously in finely divided form. It will be understood that, instead of the individual pigments, it is also possible to use mixtures of these pigments with one another or with other pigments, or to use them in the form of suitable liquid or solid preparations, for example in combination with polymeric carriers.

The use of the pigments of the present invention in imaging processes in which electrically photosensitive particles are necessary, is described below in more detail with reference to the enclosed drawing, which shows an example of such a process.

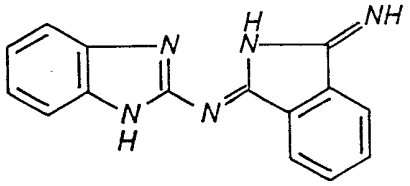
The figure shows a transparent electrode 1, which in this case consists of optically transparent glass 2 coated with a thin, optically transparent layer 3 of tin oxide. This material is available under the registered trademark "NESA Glass". The surface of this electrode 1 is coated with a thin layer 4 of fine-grained, electrically photosensitive particles, dispersed in an insulating medium (e.g. carrier liquid). This layer is designated hereinafter as electrically photosensitive layer. The electrically photosensitive layer 4 can contain in addition a sensitising agent and/or a binder for the pigment particles. Contiguous to the electrically photosensitive layer is a second electrode 5. This electrode is connected to one side of the voltage source 6. The opposite side of the voltage source 6 is connected via a switching means 7 to the electrode 1, so that if the switching means 7 is closed, an electric field is applied

between the electrodes 1 and 5 across the layer 4. A projector consisting of a light source 8, a slide 9 and a lense 10 irradiates the layer 4 with an image of the slide 9 to be reproduced. The layer 4 is thus irradiated with the image to be reproduced, whilst a voltage is applied between the electrodes 1 and 5 by closing the switching means 7. The irradiation causes for example the exposed pigment particles to be activated, so that a pigment image which is a duplicate of the slide 9 is formed on the surface of one of the electrodes. In the case of photoelectrophoresis (liquid medium), the relatively volatile carrier liquid evaporates after the irradiation, and the pigment image remains. This pigment image can subsequently be fixed, for example by applying a coating layer to the surface of the image or with a dissolved binder in the carrier liquid, for example paraffin wax. Approximately 3 to 6% by weight of the paraffin binder in the carrier gives good results. The carrier liquid itself can be a liquid paraffin wax or another suitable binder. According to another embodiment, the pigment image remaining on the electrode 1 or 5 can be transferred to another surface and fixed thereon. Any suitable insulating medium can be used as carrier for the pigment particles in the system. Typical media are decane, dodecane, n-tetradecane, paraffin, beeswax or other thermoplastic materials, Sohio Odorless Solvent 3440 (a kerosene fraction available from the Standard Oil Company) and Isopar G (a branched-chain, saturated aliphatic hydrocarbon available from Esso Standard, 'Isopar' is a registered Trade Mark). Good quality images are obtained at voltages between 200 and 5000 volts which are applied using the device illustrated in the figure. The amount of pigment in the carrier liquid is advantageously 0.5 to 10%. The addition of smaller amounts, for example 0.5 to 5 mole percent of selected electron donors or acceptors to the surface either of the pigment or one of the electrodes or in the suspension, can result in a marked improvement for example of the light sensitivity of the system.

The Examples illustrate the invention with respect to the photoelectrophoretic imaging process, the migration process, and the electrophotographic recording material, but imply no restriction thereto. The parts are by weight.

Example 1.

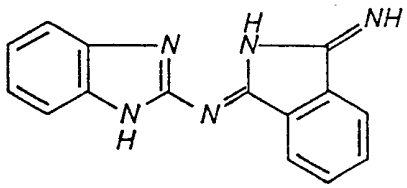
With stirring, 28.5 parts of the condensation product of 2-cyanomethylbenzimidazole and 1-amino-3-imino-isoindolenine of the formula



are kept for 15 hours at 140°—145°C in 700 parts of diethylene glycol monoethyl ether with 9.7 parts of anhydrous nickel acetate. The temperature is then allowed to fall to 130°C and the black precipitate is collected by filtration, washed thoroughly with methanol and hot water and dried in vacuo at 100°C, affording 22.2 parts of a black crystalline powder of the probable formula (II).

Example 2.

35 parts of the condensation product of 2-amino-benzimidazole and 1-amino-3-imino-isoindolenine of the formula



are stirred for 15 hours at 115°—120°C in 500 parts of diethylene glycol monoethyl ether with 13 parts of nickel acetate (anhydrous). The precipitate is filtered off hot, washed with methanol and hot water and dried at 100°C in vacuo, affording 25.8 parts of a black powder of the probable formula (III).

Examples 3 and 4 relate to the photoelectrophoretic process and are carried out in a device corresponding to the type illustrated in the accompanying figure. The imaging suspension 4 is applied between the two electrodes 1 and 5. The irradiation is effected through the transparent electrode 1. The NESA glass surface is connected in series with a switching means 7, a voltage source 6 and the conductive part 11 of a counterelectrode 5 which can be provided with a surface coating 12 of, for example, barytes paper. The plates used have a size of about 10 cm^2. The light intensity is between 1000 and 8000 lux, measured on the non-coated NESA glass surface. The amount of the voltage is between 200 and 1000 volts. The irradiation is carried out with a 3200° K-lamp through a black and white image. A space of 0.1 mm is chosen between the electrodes 1 and 5.

Example 3.

6 parts of the pigment of the formula (II) are ground in a laboratory sand mill in 94 parts of Isopar G until a fine state of division is attained. The resulting suspension, diluted in the ratio 1 to 5 with further Isopar G, is applied as electrically photosensitive layer between the two electrodes. An image is produced by proceeding as described hereinbefore. Good copies of the original are obtained at an illumination intensity of about 3000 lux, measured on the tin oxide/glass surface without pigment suspension and a voltage of −700 volts. A positive copy of the original forms on the tin oxide/glass electrode and a negative copy on the counterelectrode.

Example 4.

Example 3 was repeated using the compound of formula (III). Good copies of the original were obtained at an illumination intensity of about 1200 lux, measured on the tin oxide/glass surface without pigment suspension and a voltage of −700 volts. A positive copy of the original formed on the tin oxide/glass electrode and a negative copy on the counter-electrode.

Examples 5 and 6 relate to the migration process.

Example 5.

1 part of the pigment of the formula (II) is ground in a solution of 9 parts of Piccotex 100 (a copolymer based chiefly on vinyl toluene, available from Hercules) in 10 parts of toluene in a laboratory sand mill until a fine state of division is attained. The resulting suspension is coated on an aluminium sheet using a film drawing rod (wet film thickness 24 micrometres). After evaporation of the solvent, the layer is brought with a corona charging unit to a negative potential of about 240 volts and then exposed imagewise with white light and an illumination intensity of 450 lux. For development, i.e. softening of the layer, the exposed layer is immersed for a few seconds in cyclohexane. A good quality duplicate of the original remains on the aluminium sheet. The resolution is good and the optical density high.

Example 6.

The procedure of Example 5 is prepared with the sole difference that the pigment of formula (III) is used instead of the pigment of the formula (II). A good quality duplicate of the original remains on the aluminium sheet. The resolution is good and the optical density high.

Using another nlm drawing rod, a wet film thickness of 12 micrometres can also be obtained with similarly good results but with the difference that, as is to be expected, the optical density is less high.

Examples 7 to 18 relate to use of the pigments of the present invention for obtaining electrophotographic recording materials.

Examples 7 to 10.

A suspension consisting of 1 part of the pigment listed in Table 1 in a solution of 15 parts of polyvinyl carbazole (available from BASF under the registered trademark "Luvican M 170") in 184 parts of chlorobenzene is ground in a laboratory sand mill until a fine state of division is attained. An aluminium sheet is coated with the resulting suspension using a film drawing rod (wet film thickness of about 60 micrometres). After the coating has dried, a layer is obtained which is tested as recording material with the "Dyntest-90" measuring device (available from ECE, Giessen, West Germany) which is very suitable for electrostatic sensitometry. The characteristic values measured are: V_s = surface potential in volts directly before the exposure,

ΔV_D = drop of potential in the dark in volts per second, and ΔV_{Ph} = initial drop in potential on exposure in volts per second. As is generally known, the sensitivity E in volts per lux second is calculated from Δ_{Ph}. The exposure is effected with white light and an illumination intensity of 35 lux.

The procedure is carried out twice with the recording material negatively charged and then positively charged.

The results are given in Table 1.

TABLE 1

Example	Black Pigment	V_S (V)	V_D (V/s)	V_{Ph} (V/s)	E (V/1x s)
7	of the formula (II)	–335	3.0	169	4.8
8	,, ,,	+363	4.2	227	6.5
9	of the formula (III)	+325	2.8	143	4.1
10	,, ,,	+340	4.0	104	3.0

Examples 11 to 14.

A suspension consisting of 1 part of the pigment listed in Table 2 in a solution of 6 parts of Vinylite VYNS (a copolymer of vinyl chloride and vinyl acetate, available from Union Carbide) in 43 parts of methyl isobutyl ketone is ground in a laboratory sand mill until a fine state of division is attained. An aluminium sheet is coated with the resulting suspension using a film drawing rod (wet film thickness about 30 micrometres).

The measurement of the characteristic values is made as described in Examples 7 to 10.

The results are given in Table 2.

TABLE 2

Example	Black pigment of the formula	Wet film thickness (micrometres)	V_S (V)	ΔV_D (V/s)	ΔV_{Ph} (V/s)	E (V/1x s)
11	(II)	60	–520	3.8	352	10.1
12	,,	,,	+600	5.5	214	6.1
13	(III)	30	–310	3.8	58	1.7
14	,,	,,	+310	4.0	37	1.0

Examples 15 and 16.

Examples 9 and 11 are repeated, but with the difference that the exposure is carried out through different filters of the "Dyntest-90" measuring device instead of with white light. The results are reported in Table 3.

TABLE 3

Filter	Values of V_{Ph} (V/s)	
	Example 15 (as Example 9)	Example 16 (as Example 11)
Yellow	92	460
Red	77	598
Green	46	77
Cyan	46	92

Examples 17 and 18.

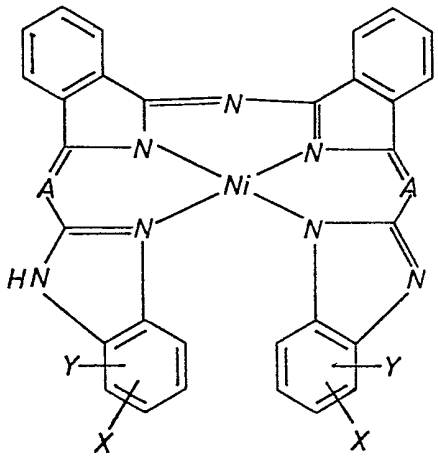
The layers as prepared in Examples 5 and 6 are tested with the "Dyntest-90" measuring device as in Examples 7 to 14. These layers are also suitable for use as electrophotographic recording materials as the results of Table 4 show.

TABLE 4

Example	Black Pigment	V_S (V)	V_D (V/s)	V_{Ph} (V/s)	E (V/1x s)
17	of the formula (II)	−210	4	92	2.6
18	of the formula (III)	−210	2	138	3.9

WHAT WE CLAIM IS:—

1. An electrophotographic imaging process, wherein electrically photosensitive particles for the image reproduction consist of a black pigment selected from the metal complexes of the formula



wherein

A represents a nitrogen atom or the

group, 

X represents a hydrogen or halogen aotm or an alkyl group of 1 to 6 carbon atoms,

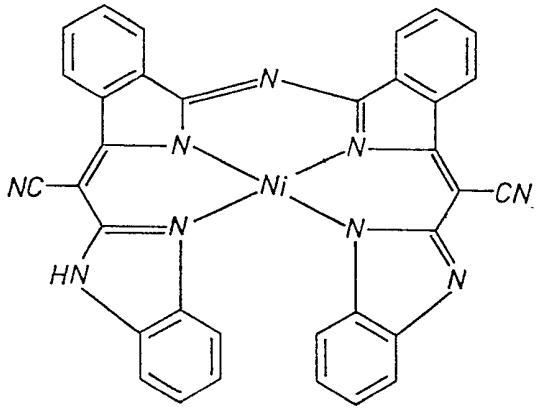
Y represents a hydrogen or halogen atom, an alkyl, alkoxy or alkylsulphonyl group of 1 to 6 carbon atoms, a nitro or carbamoyl group, an alkylcarbamoyl or alkoxycarbonyl group of 2 to 6 carbon atoms or an arylcarbamoyl or aryloxycarbonyl group of 7 to 11 carbon atoms.

2. An electrophotographic imaging process as claimed in claim 1, which is a photoelectrophoretic process.

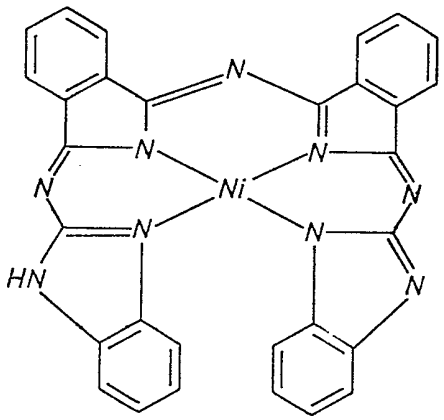
3. An electrophotographic imaging process as claimed in claim 1 which is a migration process.

4. An electrophotographic imaging process as claimed in claim 1 which is a manifold imaging process.

5. A process as claimed in any of claims 1 to 4 wherein the metal complex is a nickel complex of the formula



6. A process as claimed in any of claims 1 to 4 wherein the metal complex is a nickel complex of the formula



7. An electrophotographic recording material which contains as electrically photosensitive component a black pigment according to any of claims 1, 5 or 6.

8. An electrophotographic imaging process substantially as hereinbefore described with reference to any one of Examples 3 to 18.

9. An electrophotographic recording material substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.

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Agent for the Applicants.

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