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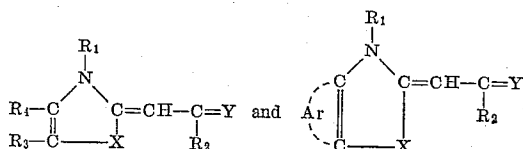
ELECTROPHOTOGRAPHIC PROCESS UTILIZING ORGANIC PHOTOCONDUCTORS

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6 Claims. (Cl. 96—1)

The present invention relates to an electrophotographic material, and more particularly to an electrophotographic material consisting of a support and a photoconductive layer which contains an organic photoconductive substance or which consists of an organic photoconductive substance.

Electrophotographic materials are already known which consist of a support and a photoconductive layer containing as photoconductor an inorganic substance such as selenium or zinc oxide or an organic substance such as anthracene, benzidine or a heterocyclic compound of a determined type.

Now we have found that an electrophotographic material with particularly favorable properties and suitable to be used in the application of the most widely varying electrophotographic reproduction methods is obtained if in the manufacture of the photoconductive layer compounds are used having one of the general formulae



wherein

R_1 represents an alkyl group, an aryl group, an aralkyl group, a substituted alkyl group, a substituted aryl group or a substituted aralkyl group;

R_2 represents a hydrogen atom, an alkyl group, a substituted alkyl group, an alkyl mercapto group, an aryl group, a substituted aryl group, a heterocyclic group or a substituted heterocyclic group;

R_3 and R_4 (equal or different) each represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, a substituted alkyl group, a substituted aryl group or a substituted aralkyl group;

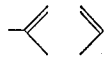
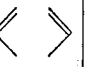
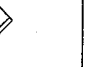
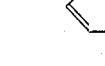
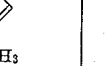
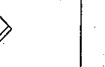
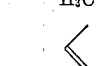
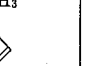
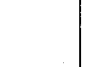
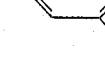
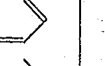
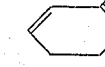
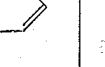
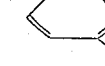
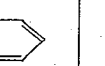
Ar represents the non-metallic atoms necessary to complete an aromatic nucleus selected from the group consisting of a benzene nucleus and a naphthalene nucleus;

X represents an oxygen atom, a sulphur atom, a selenium atom, a vinylene group or a nitrogen atom substituted with an R_1 radical;

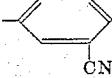
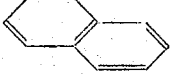
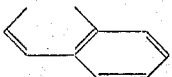
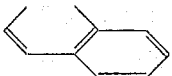
Y represents an oxygen atom, a sulphur atom, a selenium atom, an arylimino group or an alkylsulphonium group.

Some compounds according to the above formula which seemed to be particularly suitable for the manufacture of the electrophotographic material according to the present invention are given hereinafter in the table.

TABLE

Compound	R_3	R_4	R_1	R_2	X	Y
1.....			CH ₃	C ₆ H ₅	S	O
2.....			C ₂ H ₅	C ₆ H ₅	S	O
3.....			CH ₃	C ₂ H ₅	S	O
4.....			CH ₃	C ₆ H ₅	S	O
5.....			CH ₃	C ₆ H ₅	S	O
6.....			CH ₃	CH ₃	S	O
7.....			CH ₃	C ₆ H ₅	S	O
8.....			CH ₃	C ₆ H ₅	S	O
9.....			C ₂ H ₅	CH ₃	Se	O

TABLE—Continued

Compound	R ₃	R ₄	R ₁	R ₂	X	Y
10.....			CH ₃	C ₆ H ₅	Se	O
11.....			-(CH ₂) ₂ -OCO- 	C ₆ H ₅	Se	O
12.....			CH ₃	C ₂ H ₅	S	S
13.....			C ₂ H ₅	CH ₃	S	S
14.....			C ₂ H ₅		S	S
15.....			CH ₃	C ₂ H ₅	S	S
16.....			C ₂ H ₅	C ₆ H ₅	S	S
17.....			CH ₃	CH ₃	S	S
18.....			CH ₃	C ₂ H ₅	S	S
19.....			C ₂ H ₅	CH ₃	S	S
20.....			CH ₃	SCH ₃	S	S ⁺ CH ₃ CH ₃ CO ₄ ⁻
21.....			C ₂ H ₅	CH ₃	Se	S
22.....			C ₂ H ₅	C ₂ H ₅	Se	S
23.....			C ₂ H ₅	C ₆ H ₅	Se	S
24.....			C ₂ H ₅	H	O	N-C ₆ H ₅
25.....			C ₂ H ₅	H	O	N-C ₆ H ₅
26.....			C ₂ H ₅	H	O	N-C ₆ H ₅
27.....			C ₂ H ₅	H	O	N-C ₆ H ₅
28.....			C ₂ H ₅	H	O	N-C ₆ H ₅
29.....			C ₂ H ₅	H	S	N-C ₆ H ₅
30.....			C ₂ H ₅	H	Se	N-C ₆ H ₅
31.....			C ₂ H ₅	H	CH=CH	N-C ₆ H ₅

The omega-ketones from this table can be prepared according to the methods described in the U.S. patent specification 2,468,577 and by A. Van Dormael and Th. Ghys in Bull. Soc. Chim. Belg. 57 (1948), 24. The omega-thioketones from the table can be prepared according to the method described in the U.S. patent specification 2,356,569.

For the manufacture of the electrophotographic material according to the present invention, a photoconductive layer containing at least one of the compounds according to the above general formula or mainly consisting of at least one of the compounds according to the above general formulae is applied to a suitable support.

The photoconductive layers according to the present invention can contain besides one or more of the compounds according to the above general formula still one or more other photoconductive compounds with similar or different photoelectric-, mechanical- or other physical properties; moreover, there can be present in the photoconductive layer other compounds which confer the properties desired to the photoconductive layer and/or to the composition wherefrom this layer is formed.

Thus, in the manufacture of the photoconductive layers according to the present invention one or more macromolecular compounds can be added as binding agents to the composition wherefrom the photoconductive layer is formed; preferably, macromolecular compounds with high specific resistivity (i.e. with a specific resistivity higher than 10^9 ohm.(cm.) are used for this purpose; macromolecular compounds particularly suitable as binding agent for the photoconductive layers are e.g. natural resins, such as dammar resin, elemi-resins, gum arabic, manilla gum and sandarac resin; micro-crystalline waxes; modified natural substances such as cellulose diacetate and cellulose triacetate, cellulose acetobutyrate, ethyl cellulose, ethyl cellulose stearate or other cellulose derivatives pentaerythrite polyesters or other modified colophonium resins and ester gums; polymerisates such as polyethylene, polystyrene and copolymers of styrene, polyvinylacetate and copolymers of vinylacetate, polyvinylacetals of formaldehyde, acetaldehyde, butyraldehyde, polyacrylic acid esters and polymethacrylic acid esters and coumarone-indene resins; and polycondensates such as glycerol-phthalate resins or other glyceryl polyesters, alkyd resins, polyethylene glycol esters, diethylene glycol polyesters, formaldehyde resins and silicone resins; particularly good results can be attained by using the polyesters described in U.S. patent application Serial No. 702,252, filed December 12, 1957, and polysulphonates such as described in U.S. patent application Serial No. 797,587, filed March 6, 1959.

In the choice of a suitable binding agent one is not limited to previously polymerized compounds; indeed, also low molecular compounds can be used or mixtures of low and high molecular compounds, or semi polymerisates which are polymerized or condensed in situ or undergo cross-linking according to one of the methods known in polymer chemistry.

If desired, suitable plasticizers such as dibutylphthalate, dimethylphthalate, dimethylglycolphthalate, tricresylphosphate, triphenylphosphate, monocresyldiphenylphosphate, etc., in quantities amounting to 10 to 30% by weight of the amount of binding agent used can be added to the compositions for the formation of the photoconductive layers containing a binding agent.

Further can still be used other additives well known in the coating technique such as for instance pigments, compounds which influence the gloss and/or the resistivity, compounds which counteract the aging and/or the oxidation or which influence the thermal stability of the layers. In the choice of these additives, those are preferred which little or not reduce the dark-resistivity of the photoconductive layer.

The thickness of the layers is not critically established but is determined by the requirement of each separate

case. Good results are attained with electrophotographic layers the thickness of which varies between 1 and 20μ and preferably between 3 and 10μ , for layers which are too thin possess an insufficient insulating power whereas layers which are too thick require long exposure times.

Finally, according to the present invention compounds which themselves possess either or not photoconductive properties and which cause an increase of the general sensitivity and/or of the sensitivity to electromagnetic rays from a determined part of the spectrum can also be present in the photoconductive layers.

Thus, for example, the general sensitivity and/or the sensitivity to electromagnetic rays from the visible part of the spectrum can be enhanced by adding to the composition from which the electrophotographic layer is to be formed one or more of the sensitizing compounds listed in the copending U.S. patent application Serial No. 11,129, preferably in a quantity of 0.1 to 5% in respect of the amount of the photoconductive compound according to the above general formulae.

In the manufacture of the electrophotographic material according to the present invention is preferably used as support for the photoconductive layer an electrically conductive plate or sheet, or an insulating plate or sheet provided with an electrically conductive layer. Under electrically conductive plate, sheet or layer is understood a plate, sheet or layer the specific resistivity of which is smaller than that of the photoconductive layer, i.e., in general smaller than 10^9 ohm. cm. Supports the specific resistivity of which is smaller than 10^5 ohm. cm. are preferably used.

Suitable insulating plates are e.g., glass plates; these plates must be coated with a conductive layer, e.g., with a transparent layer of silver, gold or stannous oxide deposited thereon e.g. by vacuum evaporation.

Suitable insulating sheets are for instance films of synthetic macromolecular substances with high specific resistivity such as for instance the polysulphozates described and claimed in U.S. patent application Serial No. 797,587 for "Production of Linear Aromatic Polyesters," filed March 6, 1959, polyesters such as those described and claimed in U.S. patent applications Serial No. 702,252, for "Production of Linear Aromatic Polyesters," filed December 12, 1957, Serial No. 725,498, for "Production of Linear Aromatic Polyesters," filed April 1, 1958, and Ser. No. 731,874, for "Production of Linear Aromatic Polyesters," filed April 30, 1958, polystyrene, polyethylene, cellulose esters, etc., or sheets of paper with high specific resistivity. These insulating sheets must be provided with a conductive layer e.g. a thin metal sheet, with a layer comprising a metal powder dispersed in the smallest possible amount of binding agent, or with a thin hydrophilic layer comprising a hygroscopic and/or antistatic compound and a hydrophilic binding agent. Suitable hygroscopic and/or antistatic compounds are for instance glycerine, glycol, polyethylene glycols, calcium chloride, sodium acetate, condensation products of maleic acid and polyethylene glycols, citric acid amides, hydroxypropyl sucrosemonolaurate, quaternary ammonium compounds such as Antistatin LF (trade name of Badische Anilin- & Soda-Fabrik A.G., Ludwigshafen (Rhine), Arquad 16 and Ethoquad 18/25 (trade names of Armour and Company, Chicago, Ill.) amine salts of lyophilic alkylphosphates such as Zelec NK (trade name of E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Del.), lyophilic dialkylpolyoxyalkylene phosphates such as Victawet 12 (trade name of Victor Chemical Works, Chicago, Ill.) and polyoxyalkyleneamides such as Ethomid HT/60 (trade name of Armour and Company, Chicago, Ill.). Suitable hydrophilic binding agents are for instance gelatin, glue, polyvinyl alcohol, methylcellulose, carboxymethylcellulose, cellulosesulphate, cellulose hydrogen phthalate, cellulose-acetatesulphate, hydroxyethyl cellulose, polyacrylic acid or colloidal silica; for obtaining a good adhesion of the hydrophilic layer and the hydro-

phobic polymeric sheet, the polymeric sheet can be provided with a suitable subbing layer such as for instance one of the subbing layers described in U.S. patent application Serial No. 509,333, for "Manufacture of Photographic Film," filed May 18, 1955 (for polyester films), the British Patent 819,592 and British patent application No. 41732/58, filed December 24, 1958 (for films of polystyrene and substituted polystyrene), U.S. patent application Serial No. 826,129, for "Subbing Method for Polyalkylene Materials," filed July 10, 1959, the Belgian Patent No. 569,129 (for polyalkylene films), U.S. Patent 2,867,542 (for cellulose ester films), and the Belgian Patent No. 573,005 (for hydrophilic layers with polyvinyl alcohol as binding agent).

Suitable conductive plates are for instance plates of metals such as aluminum, zinc, copper, tin, iron or lead.

Suitable conductive sheets are for instance films made of polymeric substances with low specific resistivity such as for instance polyamide films or paper sheets with low specific resistivity. Good results can be attained by using paper sheets containing hygroscopic and/or antistatic substances as described above. These hygroscopic and antistatic substances are preferably incorporated into the paper sheets during the paper manufacturing process either by adding them to the paper pulp or by an after-treatment, before or after calendering the paper sheets.

These substances can likewise be incorporated into the paper sheets by applying to the raw paper stock a composition containing the hygroscopic and/or the antistatic substances and a hydrophilic binding agent as described above.

It was likewise stated that particularly good results are attained when using paper sheets provided with a coating of a polymeric substance in order to obtain a smooth surface and to prevent the organic liquid wherein the photoconductive substance is dissolved, from penetrating within the paper sheet. This coating, however, must not prevent the carrying-off of the electrons from the exposed image areas during the irradiation. Suitable coatings are for instance coatings with a thickness of 2 to 10 μ and composed of one or more of the macromolecular compounds described above as binding agent for the photoconductive compound.

Besides the usual paper sorts can likewise be used synthetic paper sorts such as those prepared from polyesters, e.g. Dacron and Terlenka-fibers (trade names for polyester fibers from terephthalic acid and glycols manufactured by E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Del., resp. Algemene Kunstzijde Unie N.V., Arnhem, Netherlands), from polyamide fibers such as Enkalon-fibers (trade name of Algemene Kunstzijde Unie N.V., Arnhem, Netherlands) or Nylon-fibers or from polyacrylonitrile fibers such as Orlon-fibers (trade name of E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Del.). Before coating the photoconductive layers on such paper sheets, the latter are preferably impregnated with substances enhancing their conductivity, for instance polycaprolactam, the polyester of 2,5-di(p-hydroxyphenyl)-1,3,4-oxadiazole and 1-chloro-3-aminobenzene-4,6-disulphochloride, a copolyamide of hexamethylenediamine, caprolactam, adipic acid and sebacic acid, N-methylene polyhexamethylene adipamide, or polyamides such as Ultramid 1C (trademark for a polyamide manufactured by Badische Anilin- & Soda-Fabrik A.G., Ludwigshafen (Rhine)).

In practice, the compounds according to the above general formulae either alone or together with other additives such as for instance binding agents, compounds which enhance the sensitivity etc. are preferably first dissolved or dispersed in a suitable organic solvent such as for instance benzene, acetone, methylene chloride, dioxane, dimethylformamide or glycol monomethylether, or in a mixture of two or more of such solvents. The solution or dispersion thus obtained is uniformly spread

on a surface of a suitable support, for instance by centrifuging, spraying, brushing or coating whereafter the layer formed is dried in such a way that a uniform photoconductive layer is formed on the surface of the support.

A particularly interesting method for applying to a support a photoconductive layer containing little or no binding agent is described in U.S. patent application Serial No. 6624, for "Electrophotographic Material," filed February 4, 1960. According to the method as described in said patent application, a solution of the photoconductive substance is applied to the support in such a way that a micro-crystalline layer is formed; for this purpose is preferably used a heated, strongly concentrated solution of the photoconductor in a strong organic solvent and the layer formed is preferably quickly dried for instance in a hot air current or by action of infrared radiation.

Electrophotographic materials according to the present invention can be used in any of the different techniques whatever which are based on the exposure and the discharge of an electrostatic charge provided in or on a photoconductive layer.

The electrostatic charging of the photoconductive layer according to the present invention can be effected according to one of the methods known in electrophotography, for instance by friction with a smooth material, by friction with a material possessing a high electric resistivity such as for instance a cylinder coated with polystyrene, by corona discharge, by contact charge or by discharge of a capacitor. A positive charge applied at the rear side of the printing material gives about the same result as a negative charge at the front side.

The electrophotographic material is thereafter image-wise exposed to a suitable electromagnetic radiation whereby the radiated parts of the layer are image-wise discharged and an electrophotographic latent image is obtained. The electrostatic latent image formed is then converted into a visible image either on the electrophotographic material whereon the latent image was formed, or on a material onto which the electrostatic latent image was transferred for instance by application of the method as described in the Belgian Patent No. 529,234.

The conversion of the original or transferred latent image into a visible image can occur according to one of the techniques known in electrophotography wherein use is made of the electrostatic attraction or repulsion of finely divided colored substances which for instance are present in a powder or powder mixture, in an electric insulating liquid (for instance in the form of suspension) or in a gas (for instance in the form of aerosol), or of finely divided colored liquid drops which are for instance present in an electrically insulating liquid (for instance in the form of dispersion) or gas (e.g. in the form of aerosol).

By suitable choice of the sign of the charge of the developing powder or developing liquid a negative or positive print can be obtained at will from any original. If both the printing material and developing powder or developing liquid bear the same charge sign, the powder will only adhere to the discharged areas and a print (positive/positive) is obtained with the same image value as the original. If the sign of the material and of the developing powder or developing liquid is different, the image values become reversed (negative/positive).

Besides development according to the methods generally known in the electrophotography, also other techniques can successfully be used for instance by applying the method according to the U.S. patent application Serial No. 856,357, for "Development of Electrostatic Latent Images," filed December 1, 1959, and U.S. patent application Serial No. 741,017, for "Electrophotographic Process," filed June 10, 1958.

If a colored powder was used for making visible the latent image, the visible image obtained can, if necessary, be fixed according to one of the methods known in electrophotography, e.g. by heating, or it can be transferred onto another support, for instance according to the meth-

od described in the British Patent 658,699 (Can. Patent 518,430) and fixed thereon.

Evidently, the present invention is by no means limited to one or the other particular embodiment as regards the use of the new electrophotographic materials, and the exposure technique, the charging method, the transfer (if any), the developing method, and the fixing method as well as the materials used in these methods can be adapted to the necessities.

Electrophotographic materials according to the present invention can be applied in reproducing techniques wherein different kind of radiations, electromagnetic radiations as well as nuclear radiations are used. For this reason, it should be pointed out that although the invention is mainly intended for being applied in connection with methods comprising an exposure, the term "electrophotography" wherever appearing in the description and the claims, must be broadly understood and comprises both xerography and xeroradiography.

The following examples illustrate the present invention without limiting, however, the scope thereof.

Example 1

A 90 g./sq. m. paper covered with an aluminum sheet of a thickness of 8μ is coated with a layer from a solution consisting of equal parts of a 5% solution in methylene chloride of Hostalit (trademark for a terpolymer of vinylchloride, vinylacetate and maleic anhydride manufactured by Farbwerke Hoechst A.G., Frankfurt am Main) and of a 10% solution in methylene chloride of the compound 19 of the table. After drying this layer for 15 h. at 50°C ., the treated material is negatively charged with a corona apparatus. The electrophotographic material obtained is then exposed through a diapositive for 10 seconds with a 100 watt-lamp at a distance of 10 cm. The latent image formed is developed with a developing powder prepared as follows: 70 g. of gilsonite and 30 g. of carbon black are homogeneously mixed whilst heating and after cooling pulverized; 6 parts of this powder obtained are then mixed with 100 parts of iron filling.

Example 2

A aluminum plate is coated with a layer from a solution consisting of:

Polyester of 2,2'-di(p-hydroxyphenyl)-propane and fumaric acid prepared according to the method described in the Belgian patent specification 563,173 (U.S. patent application Serial No. 702,252, filed December 12, 1957) -----g-- 5
Methylene chloride -----cm.³--- 100
Compound 23 of the table -----g-- 5

After drying and storing this layer for 2 days, this material is negatively charged with a corona apparatus. The electrophotographic material obtained is then exposed for 6 seconds through a diapositive with a 100 watt lamp at a distance of 10 cm. Next, the latent image formed is developed with a powder consisting of 100 parts of iron powder and 5 parts of Toner P 648, manufactured by General Photo Products Co., Chatham, N.J.

Example 3

A cellulose-acetate sheet coated with a thin silver layer of 1μ deposited thereon by vacuum evaporation is covered with a thin layer from a mixture consisting of equal parts of a 10% solution in methylene chloride of Hostalit (registered trademark) and of a 10% solution in methylene chloride of compound 18 of the table. After drying this layer for 15 h. at 50°C ., the material treated is negatively charged with a corona apparatus. The electrophotographic material obtained is then exposed for 0.5 second through a transparent original with a 100 watt lamp at a distance of 10 cm. The latent image formed is then developed as in Example 1.

Example 4

A paper support covered with a thin aluminum layer is coated with a thin layer from the following solution:

5 Butvar (registered trade name for a polyvinylbutyral manufactured by Shawinigan Resins Corporation, Springfield, Mass.) -----g-- 2.5
Methylene chloride -----cm.³--- 100
Compound 13 of the table -----g-- 5

10 After storing this material for 7 days it is charged with a corona apparatus. The electrophotographic material obtained is then exposed for 0.5 second through a transparent original with a 100 watt lamp at a distance of 10 cm. The latent image formed is then developed with a powder consisting of 100 parts of iron powder and 5 parts of Toner P 648.

Example 5

A paper support covered with a thin aluminum layer is coated with a thin layer from a 5% solution of Hostalit (registered trademark) in methylene chloride and next with a thin layer of a 10% solution in methylene chloride of compound 29 of the table. After drying this material for 15 h. at 50°C ., it is negatively charged with a corona apparatus. The electrophotographic material obtained is then exposed for 1.5 sec. through a diapositive with a 100 watt lamp at a distance of 10 cm. The latent image formed is developed with a tribo-electric powder such as in Example 1.

Example 6

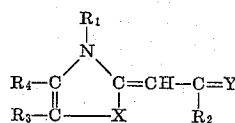
A sheet manufactured from Mylar (registered trade name for sheets manufactured from polyethylene glycol terephthalate by E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Del.) and coated with a thin aluminum sheet of a thickness of 3μ deposited thereon by vacuum evaporation is covered with a thin layer from the following solution:

40 Butvar (trade name) -----g-- 5
Compound 30 of the table -----g-- 5
Methylene chloride -----cm.³--- 100

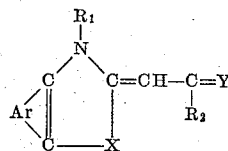
After storing this layer for some days, the material obtained is negatively charged with a corona apparatus at 400 volts. The electrophotographic material obtained is then exposed for 1.5 sec. through a diapositive with a 100 watt lamp at a distance of 10 cm. The latent image formed is developed as in Example 2 to a strong and contrasty image.

We claim:

1. An electrophotographic copying process which comprises exposing an electrostatically charged photoconductive insulating layer comprising an organic compound having a formula selected from the group consisting of



and



wherein:

R_1 , R_2 , R_3 and R_4 each is a member selected from the group consisting of a hydrogen atom, a lower alkyl group and a phenyl group;

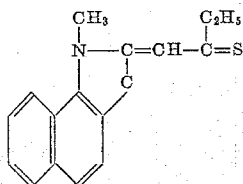
Ar represents the non-metallic atoms necessary to complete an aromatic nucleus selected from the group consisting of a benzene nucleus and a naphthalene nucleus;

11

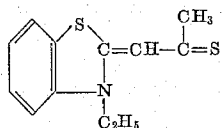
X is a member selected from the group consisting of an oxygen atom, a sulphur atom, a selenium atom, a vinylene group and a lower alkyl-substituted nitrogen atom, and

Y is a member selected from the group consisting of an oxygen, sulphur, selenium, arylimino group and a lower alkyl-sulphonium group, said organic compound being present in sufficient quantity to provide photoconductivity to said layer, to a light image whereby the light struck area is discharged, and developing said image of electrostatic charges with an electroscopic material.

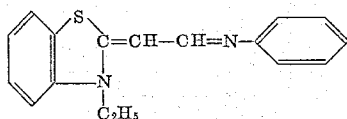
2. The electrophotographic copying process of claim 1 wherein the organic compound has the formula



3. The electrophotographic copying process of claim 1 wherein the organic compound has the formula

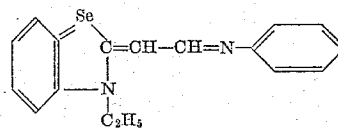


4. The electrophotographic copying process of claim 1 wherein the organic compound has the formula

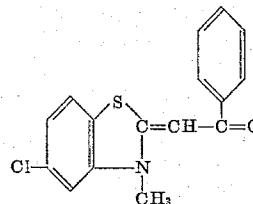


12

5. The electrophotographic copying process of claim 1 wherein the organic compound has the formula



6. The electrophotographic copying process of claim 1 wherein the organic compound has the formula



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