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3,139,338
ELECTROPHOTOGRAPHIC MATERIAL AND PROCESS

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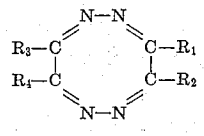
Claims priority, application Germany Mar. 18, 1959
32 Claims. (Cl. 96—1)

Among modern reproduction processes the electrophotographic process, also known as xerography, is becoming of increasing practical importance. This dry reproduction process is becoming of particular interest in certain fields, for example, office duplicating, and it consists of the application to a material, consisting of a support and a photoconductive insulating layer adherent thereto, of an electrostatic charge which imparts to the insulating layer the property of light-sensitivity. Such light-sensitive material can be used for the production of images by electrophotographic means; it is exposed to light beneath a master, so that the electrostatic charge is leaked away in the parts of the layer struck by light. The invisible electrostatic image thereby produced is made visible (developed) by powdering over with finely divided, colored, synthetic resin and then made permanent (fixed) by the application to the support of heat.

Material known for the preparation of the photoconductive insulating layers required for the aforedescribed process include selenium, sulphur, zinc oxide, and also organic substances, such as anthracene or anthraquinone. Consideration has also been given to a method of preparation of the photoconductive insulating layers whereby the photoconductive substances, in association with binders, are dispersed in solvents and the resultant dispersions are applied to electrically conductive supports, primarily metal foils, and dried. However, the photoelectrically sensitizable material thus obtained has not yet satisfied the extensive demands made upon modern duplicating material as regards range of use, reliability, simplicity in handling and, not least in importance, light-sensitivity and storageability qualities.

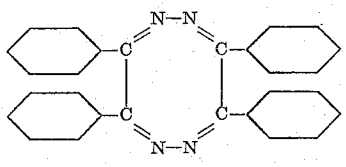
Now it has been found that unexpectedly successful photoelectrically sensitizable layers, with a surprising range of practical applications, are produced if, as photoconductive substances 1,2,5,6-tetraazacyclooctatetraenes-(2,4,6,8) are used which correspond to the following general formula



in which R_1, R_2, R_3, and R_4 are aryl, or substituted aryl radicals, or heterocyclic radicals of aromatic nature.

Exemplary of the compounds which may be employed in accordance with the present invention are:

Formula 1



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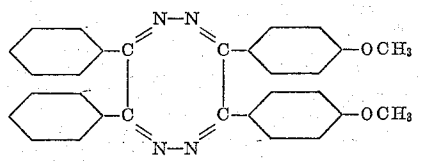

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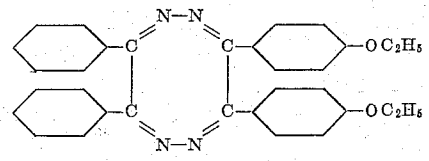

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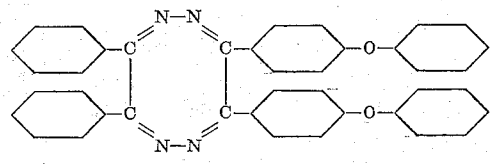

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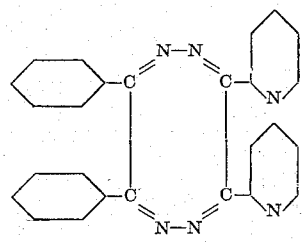

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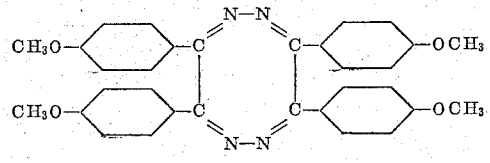

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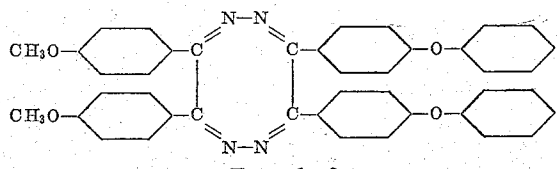

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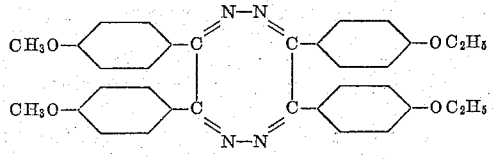

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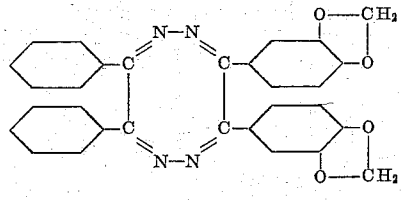

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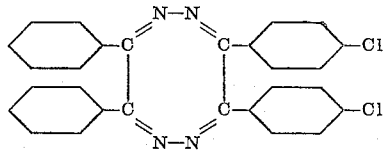

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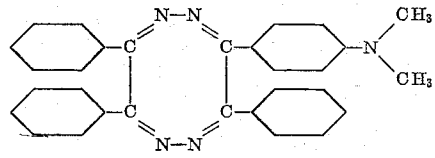

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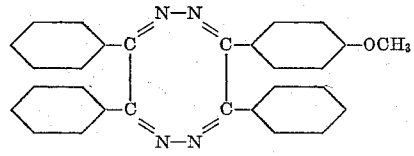
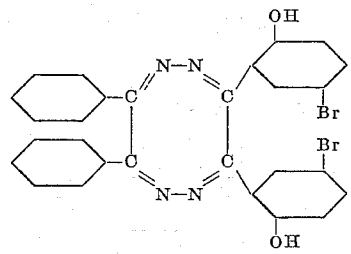


Formula 13



The 1,2,5,6 - tetraaza - cyclooctatetraenes - (2,4,6,8)-according to the present invention can be prepared by condensing dihydrazones of aromatics or heterocyclic 1,2-diketones with equimolecular quantities of such 1,2-diketones, either by fusing the reactants with each other at temperatures ranging above 100° C. using, if desired, higher pressure, or by heating the reactants with each other in a dissolved state.

For example, 3,4-di-(4'-methoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8), corresponding to Formula 2, is prepared by heating 11.9 g. (=0.05 mole) of benzil-dihydrazone with 13.5 g. (=0.05 mole) of 4,4'-dimethoxy-benzil in a sealed tube for 13 hours to a temperature of 160° C. and purifying the crude product thus obtained by recrystallization from benzene. 3,4,7,8-tetra - phenyl - 1,2,5,6 - tetraaza - cyclooctatetraene-(2,4,6,8), corresponding to Formula 1, is prepared, e.g., by heating with reflux 11.9 g. (=0.05 mole) of benzil-dihydrazone with 10.5 g. (=0.05 mole) of benzil for 45 hours in 100 ml. of ethyleneglycol monomethylether, the tetraene precipitating upon cooling and being purified by recrystallization from benzene. All the other 1,2,5,6-tetraaza-cyclooctatetraenes-(2,4,6,8) to be used according to the present invention can be prepared by analogous methods, if need be with slight changes in the conditions employed during reaction.

The following schedule contains details of a number of compounds given here as examples of compounds corresponding to the above general formula which are to be used in accordance with the present invention. In the schedule:

Column 1 states the number under which the constitutional formula corresponding to the 1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) is to be found in the formula list above;

Column 2 states the 1,2-diketone reactant;

Column 3 states the 1,2-diketone-dihydrazone reactant;

Column 4 states the melting point (° C.) of the respective 1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8);

Column 5 states the color of the respective 1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8).

			Degrees	
1	Benzil	Benzil-dihydrazone	285-286	Colorless.
2	4,4'-dimethoxy benzil.	do	228-229	Do.
3	4,4'-diethoxy-benzil.	do	187-188	Do.
4	4,4'-diphenoxy-benzil.	do	233-234	Do.
5	2,2'-pyridil	do	270-271	Do.
6	4,4'-dimethoxy . benzil.	4,4'-dimethoxy-benzil-dihydrazone.	322-323	Do.
7	4,4'-diphenoxy-benzil.	do	235-236	Do.
8	4,4'-diethoxybenzil	do	228-229	Do.
9	bis-3,4-methylene-dihydroxy-benzil (=piperil).	Benzil-dihydrazone	249-250	Do.
10	4,4'-dichlorbenzil	do	238	Do.
11	4-dimethylamino-benzil.	do	251-252	Do.
12	4-methoxy-benzil	do	229-230	Do.
13	2,2'-dihydroxy-5,5'-dibromo-benzil.	do	279-280	Do.

The compounds to be used in accordance with the invention have very good light-sensitivity and are particularly suitable for the production of homogeneous layers with unlimited shelf life.

For the preparation of the photoconductive insulating layers, it is advantageous to use solutions or suspensions of the 1,2,5,6-tetraaza-cyclooctatetraenes-(2,4,6,8) of the present invention. As solvents, there may be used organic solvents such as chloroform, benzene, acetone, methylene chloride, ethyleneglycol monomethylether, and others, or mixtures of such solvents. The compounds to be used according to the present invention can also be used in admixture with each other or with other organic photoconductive substances.

As has further been discovered, it may be an advantage in the production of the photoconductive layers for organic water-insoluble resins to be used in association with the compounds in accordance with the invention and corresponding to the general formula given above. The following may appropriately be mentioned: water-insoluble natural and synthetic resins, e.g., balsam resins, phenol resins modified with colophony, and other resins of which colophony constitutes the major part, coumarone resins and indene resins and the substances covered by the collective term "synthetic lacquer resins," which according to the Kunststofftaschenbuch (Plastics Pocket Book) published by Saechtling-Zebrowski (11th edition, 1955, page 212 at seq.) include processed natural substances such as cellulose ether; polymers such as polyvinyl chlorides, polyvinyl acetate, polyvinyl acetals, polyvinyl ethers, polyacrylic and polymethacrylic esters, as also polystyrene and isobutylene; polycondensates, e.g., polyesters, such as phthalate resins, alkyd resins, maleic acid resins, maleic acid/colophony/mixed esters of higher alcohols, phenol-formaldehyde resins, particularly colophony-modified phenol - formaldehyde condensates, urea - formaldehyde resins, melamine-formaldehyde condensates, aldehyde resins, ketone resins of which particular mention is to be made of AW 2 resins of the Badische Anilin- und Soda-fabrik, xylene formaldehyde resins and polyamides; and polyadducts, such as polyurethanes.

If the tetraaza-cyclooctatetraene compounds to be used in accordance with the invention are used in association with organic water-insoluble resins, the proportion of resin to photoconductive substance can vary very greatly. The use of mixtures of approximately equal parts of resin and 1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) compound has been found advantageous. If such mixtures of approximately equal parts of resin and tetraene compound are used, their solution in most cases gives, on drying, transparent layers which are regarded as solid solutions.

The base materials used as electroconductive supports may be any that satisfy the requirements of xerography,

e.g., metal or glass plates, paper or plates or films made of resins or plastics. If paper is to be used as the support for the photoconductive layer, pretreatment of the paper against penetration of the coating solution is advisable, e.g., with methyl cellulose in aqueous solution or polyvinyl alcohol in aqueous solution or with a solution in acetone and methylethylketone of a copolymer of acrylic acid methyl ester and acrylonitrile or with solutions of polyamides in aqueous alcohols. Aqueous dispersions of substances suitable for the pretreatment of the paper surface may also be used.

The solutions of the compounds to be used in accordance with the invention, with or without the resins, are applied to the supports in the usual manner, for example by spraying, by direct application, by means of rollers and the like, and are then dried in order to produce a homogeneous photoconductive layer on the electroconductive support.

After the layers have been positively or negatively charged, by means of, for example, a corona discharge, they are light-sensitive and can be used advantageously with long-wave U.V. light of 3600–4200 A. for electrophotographic image production. Very short exposure under a master to a high pressure mercury lamp will give good images.

The further discovery has been made that the light sensitivity to the visible range of the spectrum of the photoconductive layer can be highly improved by means of sensitizers. As sensitizers, dyestuffs in particular are suitable, for the readier identification of which the number is given under which they are listed in Schultz' "Farbstofftabellen" (7th edition, 1st vol., 1931). The following are examples of particularly effective sensitizers: triarylmethane dyestuffs such as Brillant Green (No. 760, p. 314), Victoria Blue B (No. 822, p. 347), Methyl Violet (No. 783, p. 327), Crystal Violet (No. 785, p. 329), Acid Violet 6B (No. 831, p. 351), xanthene dyestuffs, namely rhodamines, such as Rhodamine B (No. 864, p. 365), Rhodamine 6G (No. 866, p. 366), Rhodamine G Extra (No. 865, p. 366), Sulphorhodamine B (No. 863, p. 364) and Fast Acid Eosin G (No. 870, p. 368), as also phthaleins such as Eosin S (No. 883, p. 375), Eosin A (No. 881, p. 374), Erythrosin (No. 886, p. 376), Phloxin (No. 890, p. 378), Bengal Rose (No. 889, p. 378), and Fluorescein (No. 880, p. 373), thiazine dyestuffs such as Methylene Blue (No. 1038, p. 449), acridine dyestuffs such as Acridine Yellow (No. 901, p. 383), Acridine Orange (No. 908, p. 387) and Trypaflavine (No. 906, p. 386), quinoline dyestuffs such as Pinacyanol (No. 924, p. 396) and Cryptocyanine (No. 927, p. 397), quinone dyestuffs and ketone dyestuffs such as Alizarin (No. 1141, p. 499), Alizarin Red S (No. 1145, p. 502) and Quinizarine (No. 1148, p. 504), cyanine dyestuffs, e.g. Cyanine (No. 921, p. 394) and chlorophyll.

The production of images by electrophotographic means is performed as follows: when the photoconductive layer has been charged by means of, for example, a corona discharge with a charging apparatus maintained at 6000–7000 volts, the support, e.g., paper or aluminum foil or plastic film, with the sensitized coating, is exposed to light under a master or by episcopic or diascopic projection and is then dusted over in known manner with a resin powder colored with carbon black. The image that now becomes visible can be easily wiped off. It therefore must be fixed; it can, for example, be briefly heated to about 120° C. or, according to the fusion temperature of the developer used, it can be exposed to infrared radiation. The temperature required is less if the heat treatment is effected in the presence of vapors of solvents such as trichloroethylene, carbon tetrachloride or ethyl alcohol. The fixing of the powder image can also be accomplished by steam treatment. From positive masters, positive images, characterized by good contrast, are produced.

If transparent supports are used, the electro-photographic images can also be used as masters for the production of additional copies on any type of light-sensitive sheet. In this respect the photoconductive compounds to be used as provided by the invention are superior to the substances used hitherto, such as selenium or zinc oxide, inasmuch as the latter produce only cloudy layers not readily capable of further reproduction, because solid solutions can not be produced with these materials, and only suspensions are possible.

If translucent supports are used for photoconductive layers such as are provided by the invention, images can also be produced by the reflex process. The production of a reflex copy also constitutes an advance over the known art.

Moreover the photoconductive layers prepared in accordance with the invention have a further important advantage in that they can be charged positively as well as negatively. With positive charging the images are particularly good and evolution of ozone, which with negative charging is very copious and, because it is injurious to health calls for the adoption of special measures, such as the installation of fans, is scarcely to be detected.

The invention will be further illustrated by reference to the following specific examples:

Example 1

0.5 g. of 3,4-di-(4'-phenoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) corresponding to Formula 4, and 0.5 g. of a ketone resin, e.g., the product commercially available under the designation "Kunstharz EM," are dissolved in 15 ml. of chloroform and the solution is coated onto paper, the surface of which had been pretreated to prevent the penetration of organic solvents, and dried. By means of the thus coated paper, a direct image is produced in an electrophotographic process. With a corona discharge produced by means of a charging apparatus maintained at about 6000 volts, the coated dried layer is provided with a negative electric charge, then exposed under a positive original using a high pressure mercury lamp, and then dusted over in known manner with a developer powder.

The developer used consists of small glass balls and a very finely divided resin-carbon black mixture. The black colored resin adheres to those parts of the layer which were not struck by light during exposure and, thus, a positive image of the original becomes visible, which is fixed by heating.

The developer used consists of 100 g. of glass balls of a particle size from 300 to 400μ and 2.5 g. of a toner having a particle size from 20 to 50μ. The toner is produced by melting together, grinding and sifting:

30 g. polystyrene,
30 g. of resin-modified maleic acid resin, e.g., the product commercially available under the registered trademark "Beckacite" K105, and
3 g. of carbon black, e.g., the product commercially available under the designation "Peerless" Black Russ 552.

Example 2

Paper is coated as described in Example 1 and the layer thus produced is positively charged by means of a corona discharge. After exposure under an original, the latent electrostatic image thus produced on the coated paper is developed by dusting over with a developer powder, as described in Example 1. The developer used contains, as the carrier substance, glass balls coated with a resin, e.g., a coumarone resin. (Advantageously the product commercially available under the designation "Cumaronharz 601/90" is used for coating the glass balls.) By this method a positive image of the original is obtained which is also very good and rich in contrast.

Example 3

In 15 ml. of chloroform there is dissolved a mixture consisting of:

0.2 g. 3,4,7,8-tetraphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8) corresponding to Formula 1,

0.2 g. 3,4-di-(4'-phenoxy-phenyl)-7,8-di-(4''-methoxy-phenyl)-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) corresponding to Formula 7, and

0.2 g. 3,4-di-(4'-ethoxy-phenyl)7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) corresponding to Formula 3.

The solution thus obtained is coated onto an aluminum foil and dried to form a layer which adheres firmly to the support. An electrophotographic image is produced on this material in known manner.

Example 4

1 g. of after-chlorinated polyvinyl chloride, e.g., of the product commercially available under the registered trademark "Rhenoflex" is dissolved in a mixture made up of 10 ml. of methylethylketone and 5 ml. of toluene. To this solution there is added 1 g. of 3,4,7,8-tetramethoxy-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) corresponding to Formula 6. The suspension thus obtained is very finely distributed. A base paper, which has been pretreated to prevent the penetration of organic solvents, is coated with this suspension and dried. In accordance with the method described in Example 1, electrophotographic images are produced on the paper thus coated.

Example 5

The process described in Example 1 is followed with the modification that for coating the base paper a solution is used containing 0.5 g. of 3,4-di-(4'-methoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8) corresponding to Formula 2, and 0.5 g. of zinc resin, e.g., of the product commercially available under the designation "Erkazit Zinkharz 165," in 15 ml. of chloroform.

Example 6

0.5 g. of 3,4-di-pyridyl-(2')-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8), corresponding to Formula 5, and 0.5 g. of a ketone-aldehyde condensation resin, e.g., the product commercially available under the designation "Kunstharz AP" are dissolved in 30 ml. of chloroform and the solution is coated onto a superficially roughened aluminum surface. After evaporation of the solvent, a layer remains which adheres firmly to the surface of the aluminum foil. The thus coated foil is treated as described in Example 1 whereby after fixing the powder image, a positive image is produced on the aluminum surface.

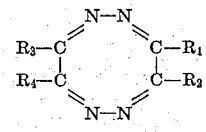
Example 7

0.5 g. of 3,4,7,8-tetraphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8), corresponding to Formula 1, and 0.5 g. of polyvinylacetate, e.g., the product commercially available under the registered trademark "Mowilith" 50, and 0.5 mg. of Rhodamine B extra (Schultz, "Farbstofftabellen," 7th edition, vol. 1, No. 864), dissolved in 0.1 ml. of methanol, are dissolved in 7 ml. of chloroform and an aluminum foil is coated with this solution. After drying, an electrophotographic image is produced as described in Example 1, but instead of a high pressure mercury lamp, a 100 watt incandescent lamp is used for exposure.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula

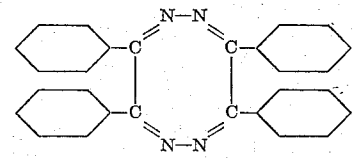


in which R_1, R_2, R_3 and R_4 are selected from the group consisting of aryl groups and heterocyclic groups of aromatic nature.

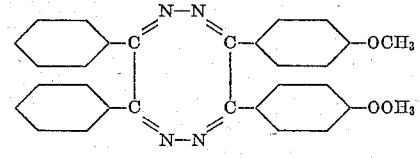
2. An electrophotographic material according to claim 1 in which the photoconductive layer contains an organic water-insoluble resin.

3. An electrophotographic material according to claim 1 in which the photoconductive layer contains an optical sensitizer.

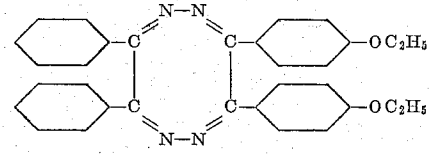
4. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



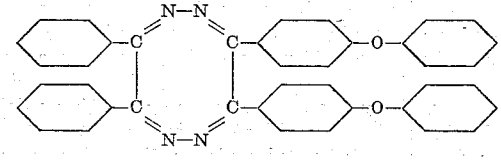
5. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



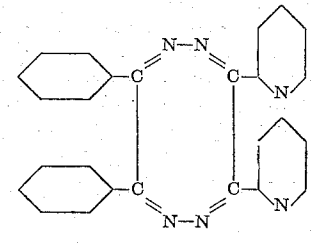
6. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



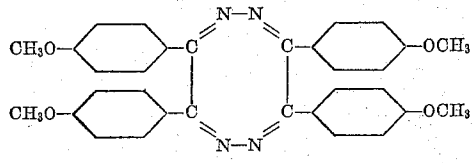
7. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



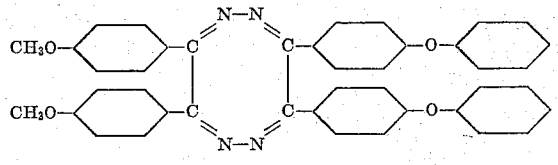
8. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



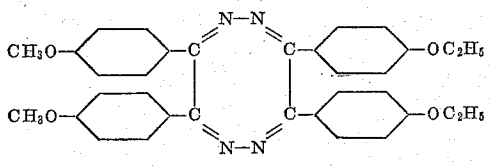
9. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



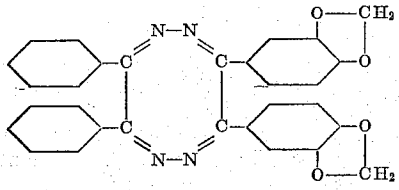
10. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



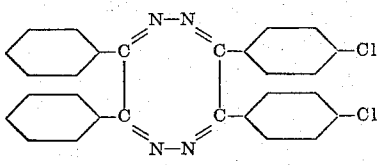
11. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



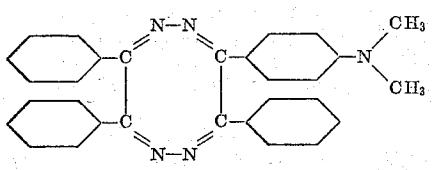
12. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



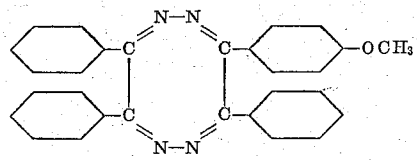
13. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



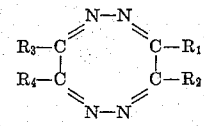
14. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



15. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



16. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula

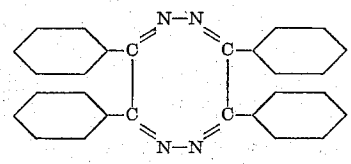


in which R_1, R_2, R_3 and R_4 are selected from the group consisting of aryl groups and heterocyclic groups of aromatic nature.

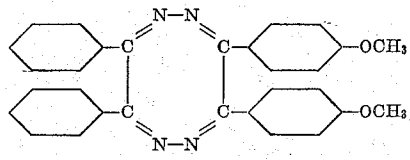
17. A process according to claim 16 in which the photoconductive layer contains an organic water-insoluble resin.

18. A process according to claim 16 in which the photoconductive layer contains an optical sensitizer.

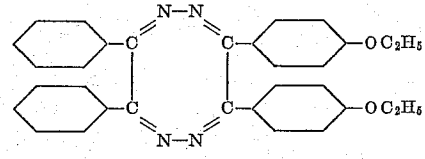
19. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



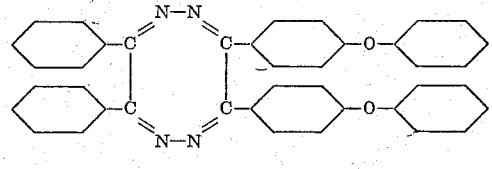
20. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



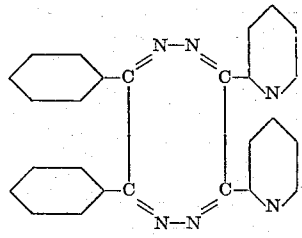
21. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



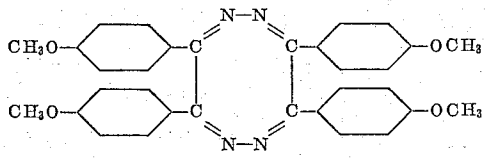
22. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



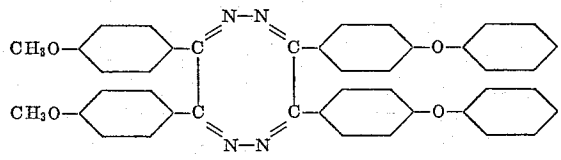
23. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



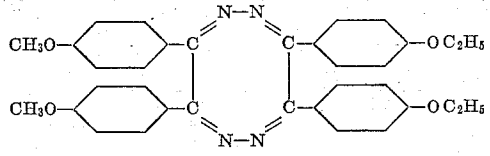
24. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



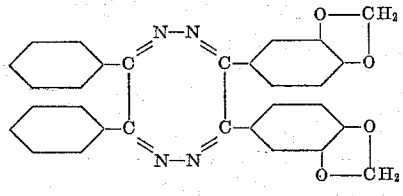
25. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



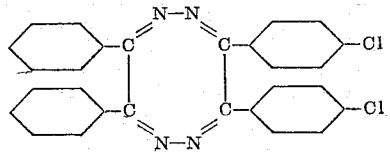
26. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



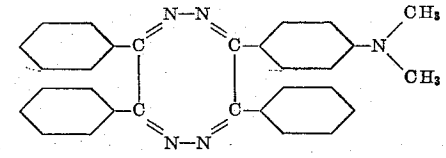
27. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



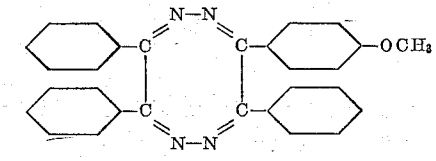
28. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



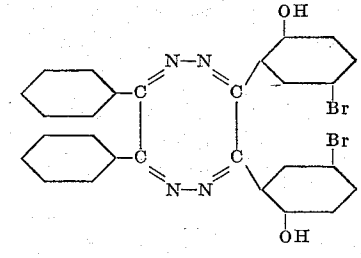
29. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



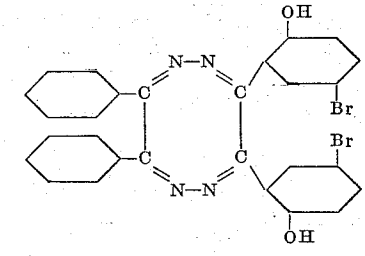
30. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



31. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a compound having the formula



32. A photographic reproduction process which comprises electrically charging a supported photoconductive insulating layer, exposing it to light under a master, and developing the resulting image, the photoconductive layer comprising a compound having the formula



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