United States Patent Office 3,287,122 Patented Nov. 22, 1966

3,287,122

PROCESS FOR THE SENSITIZATION OF PHOTOCONDUCTORS

Helmut Hoegl, Geneva, Switzerland, assignor, by mesne assignments, to Azoplate Corporation, Murray Hill, N.J.

No Drawing. Original application July 24, 1961, Ser. No. 125,984. Divided and this application Jan. 18, 1965, Ser. No. 426,372
Claims priority, application Germany, May 29, 1959, K 37,853
32 Claims. (Cl. 96—1.5)

This application is a division of copending application Serial No. 125,984, filed July 24, 1961, now abandoned, which, in turn, is a continuation-in-part of application Serial No. 30,752, filed May 23, 1960, and also now abandoned.

Electrophotographic material normally consists of a support on which there is a photoconductive substance, this coating being provided in the absence of light with an electrostatic charge. Then, the material is exposed to light behind a master, or an episcopic image is projected thereon, so that an electrostatic image is formed which corresponds to the master. This image is developed by being briefly contacted with a resin powder, whereupon a visible image is formed which is fixed by heating or by the action of solvents. In this way, an image of the master which is resistant to abrasion is obtained electrophotographically.

In the electrophotographic process as described an increase in the sensitivity of the photoconductive coatings has already been attempted by the addition of organic dyestuffs, e.g. triphenylmethane, xanthene, phthalein, thiazine and acridine dyestuffs, to the photoconductors.

The absorption maxima of the organic photoconductors are mostly in the ultra-violet region of the spectrum. The addition of these dyestuff sensitizers achieves the result that the photoconductors become sensitive to visible light. Generally, the dyestuff sensitizers cause a displacement of the available sensitivity from the ultraviolet region to the visible region. With increased addition of dyestuff sensitizer, the sensitivity to visible light at first increases rapidly, but further additions give an increase in sensitivity which is much less than would be expected, and still further additions finally give no appreciable increase in sensitivity. The dyestuff sensitizers have the disadvantage that they color the coating considerably. In practice, the maximum achievable increase in sensitivity can seldom be utilized because then the photoconductor coatings have an intensity of color that is undesirable. Colorless or practically colorless photoconductor coatings are desired, since colored material can be employed only in special cases. If additions of dyestuff sensitizers are such as not to adversely affect the coloring of the coating for practical purposes, the sensitizing effect often does not meet the demands of general usage. Further, the dyestuff sensitizers have the disadvantage that they bleach out relatively quickly so that their sensitizing action tends to be lost during the storage of the electrophotographic material.

A process for the sensitization of photoconductor coatings has now been found in which organic substances, containing polarizing residues and being capable of serving as electron-acceptors in a molecule complex, having low molecular weight, i.e. being non-resinous, being colorless or of pale color and having a melting point above room temperature, are added to the photoconductor coatings.

Substances which are primarily of interest as photoconductor coatings in accordance with the present process are those which can serve as electron donors in molecule complexes of the donor/acceptor type (known as "π-complex") and contain at least one aromatic or heterocyclic ring, which may be substituted. Such photoconductors include aromatic hydrocarbons such as naphthalene, anthracene, benzanthrene, chrysene, p-diphenylbenzene, diphenyl anthracene, p-terphenyl, p-quaterphenyl, sexiphenyl; heterocycles such as N-alkyl carbazole, thiodiphenylamine, oxadiazoles, e.g., 2,5-bis-(p-aminophenyl)-1,3,4-oxadiazole and its N-alkyl and N-acyl derivatives; triazoles such as 2,5 - bis-(p-aminophenyl)-1,3,4-triazole and its N-alkyl and N-acyl derivatives; imidazolones and imidazolthiones, e.g., 1,3,4,5-tetraphenyl-imidazolone-2 and 1,3,4,5-tetraphenyl-imidazolthione-2; N-aryl-pyrazolines, e.g. 1,3,5-triphenyl-pyrazoline; hydrated imidazoles, e.g., 1,3-diphenyl-tetrahydroimidazole; oxazole derivates such as 2,5-diphenyloxazole-2-p-dimethylamino-4,5-diphenyloxazole; thiazole derivatives such as 2-p-dialkylaminophenyl-methyl-benzthiazole; as also the following:

Oxazoles and imidazoles described in German patent application K 35,586 IVa/57b, filed Aug. 22, 1958.

Acylhydrazones described in German patent application K 36,517 IVa/57b, filed Dec. 19, 1958.

2,2,4-triazines described in German patent application K 36,651 IVa/57b, filed Jan. 7, 1959.

Metal compounds of mercapto-benzthiazole, mercapto-benzoxazole and mercapto-benzimidazole described in German patent application K 37,508 IVa/57b, filed Apr. 18, 1959.

Imidazoles described in German patent application K 37,435 IVa/57b, filed Apr. 9, 1959.

Triphenylamines described in German patent application K 37,436 IVa/57b, filed Apr. 9, 1959.

Furans, thiophenes and pyrroles described in German patent application K 37,423 IVa/57b, filed Apr. 8, 1959.

Amino compounds with multinuclear heterocyclic and multinuclear aromatic ring system described in German patent application K 37,437 IVa/57b, filed Apr. 9, 1959.

Azomethines described in German patent application K 29,270 IVa/57b, filed July 4, 1956.

Molecule complexes are defined in H. A. Staab's "Einfuhrung in die theoretische organische Chemie" (Introduction to Theoretical Organic Chemistry), Verlag Chemie, 1959, pp. 694–707, and by L. I. Andrews, Chemical Review, vol. 54, 1954, pp. 713–777. In particular, the donor/acceptor complex ("π-complexes") and "charge-transfer" complexes which are formed from an electron-acceptor and an electron-donor are included. In the present case, the photoconductors are the electron-donors and the substances here called activators—to distinguish them from the dyestuff sensitizers—are the electron-acceptors. The electron-donors have a low ionization energy and have a tendency to give up electrons. They are bases in the sense of the definition of acids and bases given by G. N. Lewis (H. A. Staab, as above, p. 600). The electron-donors primarily concerned in the present case are the photoconductors described above. These photoconductors consist of aromatic or heterocyclic systems containing a plurality of fused rings, or, alternatively, single rings having substituents which facilitate further electrophilic substitution of the aromatic ring, so-called electron-repellent substituents, as described by L. F. and M. Fieser, "Lehrbuch der organischen Chemie" (Textbook of Organic Chemistry), Verlag Chemie, 1954, p. 651, Table I. These are, in particular, saturated groups, e.g., alkyl groups such as methyl, ethyl, and propyl; alkoxy groups such as methoxy, ethoxy and propoxy; carbalkoxy groups such as carbmethoxy, carbethoxy and carbpropoxy; hydroxyl groups, amino groups

and dialkylamino groups such as dimethylamino, diethylamino and dipropylamino.

The activators in accordance with the invention, which are electron-acceptors, are compounds with a high electron-affinity and have a tendency to take up electrons. They are acids in the sense of Lewis' definition. Such properties are possessed by substances having strongly polarizing residues or groupings such as cyano and nitro groups, halogens such as fluorine, chlorine, bromine and iodine; ketone groups, ester groups, acid anhydride groups, acid groups such as carboxyl groups or the quinone grouping. Strongly polarizing electron-attracting groups of this type are described by L. F. and M. Fieser in the "Lehrbuch der organischen Chemie," Verlag Chemie, 1954, p. 651, Table I. Of these substances with a melting point above room temperature (25° C.) are preferable, i.e. solid substances, because these impart a particularly long shelf life to the photoconductive coatings as a result of their low vapor pressure. Substances which are rather deeply colored such as quinones can be used, but those that are colorless or only weak in color are preferable. Their absorption maximum should preferably be in the ultra-violet region of the spectrum, i.e. below 4,500 A. Further, the activator substances in accordance with the present process should be of lower molecular weight, i.e. between about 50 and 5000, preferably between about 100 and 1000, because with activators of lower molecular weight it is possible for reproducible results to be obtained insofar as sensitivity is concerned. Also, the sensitivity remains constant over rather long periods, since substances of lower molecular weight, unlike those of high molecular weight, undergo hardly any change during storage. The following are examples of such substances:

2-bromo-5-nitro-benzoic acid	o-Chloronitrobenzene.
2-bromobenzoic acid	Chloracetophenone.
2-chloro-toluene-4-sulphonic acid	2-chlorocinnamic acid.
Chloromaleic anhydride	
9-chloroacridine	2-chloro-4-nitro-1-benzoic acid.
3-chloroacridine	2-chloro-5-nitro-1-benzoic acid.
5-chloronitrobenzene-5-sulphochloride.	3-chloro-6-nitro-1-benzoic acid.
4-chloro-3-nitro-1-benzoic acid	Mucochloric acid.
4-chloro-2-hydroxy-benzoic acid	Mucobromic acid.
4-chloro-1-phenol-3-sulphonic acid	Styrenedibromide.
2-chloro-3-nitro-1-toluene-5-sulphonic acid.	Tetrabromo xylene.
4-chloro-3-nitro-benzene-phosphonic acid.	β-Trichlorolactic acid nitrile.
Dibromosuccinic acid	Triphenylchloromethane.
2,4-dichlorobenzoic acid	Tetrachlorophthalic acid.
Dibromomaleic anhydride	Tetrabromophthalic acid.
9,10-dibromoanthracene	Tetraiodophthalic acid.
1,5-dichloronaphthalene	Tetrachlorophthalic anhydride.
1,8-dichloronaphthalene	Tetrabromophthalic anhydride.
2,4-dinitro-1-chloronaphthalene	Tetraiodophthalic anhydride.
3,4-dichloro-nitrobenzene	Tetrachlorophthalic acid monoethylester.
2,4-dichloro-benzisatin	Tetrabromophthalic acid monoethylester.
2,6-dichloro-benzaldehyde	Tetraiodophthalic acid monoethylester.
Hexabromonaphthalic anhydride	Iodoform.
bz-1-cyano-benzanthrone	Fumaric acid dinitrile.
Cyan acetic acid	Tetracyanethylene.
2-cyanocinnamic acid	s-Tricyano-benzene.
1,5-dicyanonaphthalene	
3,5-dinitrobenzoic acid	2,4-dinitro-1-chloronaphthalene.
3,5-dinitrosalicylic acid	1,4-dinitro-naphthalene.
2,4-dinitro-1-benzoic acid	1,5-dinitro-naphthalene.
2,4-dinitro-1-toluene-6-sulfonic acid	1,8-dinitro-naphthalene.
2,6-dinitro-1-phenol-4-sulphonic acid.	2-nitrobenzoic acid.
1,3-dinitro-benzene	3-nitrobenzoic acid.
4,4'-dinitro-biphenyl	4-nitrobenzoic acid.
3-nitro-4-methoxy-benzoic acid	3-nitro-4-ethoxy-benzoic acid.
4-nitro-1-methyl-benzoic acid	3-nitro-2-cresol-5-sulphonic acid.
6-nitro-4-methyl-1-phenol-2-sulphonic acid.	5-nitrobarbituric acid.
2-nitrobenzenesulphinic acid	4-nitro-acenaphthene.
3-nitro-2-hydroxyl-1-benzoic acid	4-nitro-benzaldehyde.
2-nitro-1-phenol-4-sulphonic acid	4-nitro-phenol.
3-nitro-N-butyl-carbazole	Picryl chloride.
4-nitrobiphenyl	2,4,7-trinitro-fluorenone.
Tetranitrofluorenone	s-Trinitro-benzene.
2,4,6-trinitro-anisole	
Anthraquinone	1-chloro-2-methyl-anthraquinone.
Anthraquinone-2-carboxylic acid	Duroquinone.
Anthraquinone-2-aldehyde	2,6-dichloroquinone.
Anthraquinone-2-sulphonic acid anilide.	1,5-diphenoxy-anthraquinone.
Anthraquinone-2,7-disulphonic acid.	2,7-dinitro-anthraquinone.
Anthraquinone-2,7-disulphonic acid bis-anilide.	1,5-dichloro-anthraquinone.
Anthraquinone-2-sulphonic acid dimethylamide.	1,4-dimethyl-anthraquinone.
Acenaphthenequinone	2,5-dichloro-benzoquinone.
Anthraquinone-2-sulphonic acid methylamide.	2,3-dichloro-naphthoquinone-1,4.
Acenaphthenequinonedichloride	1,5-dichloro-anthraquinone.
Benzoquinone-1,4	1-methyl-4-chloro-anthraquinone.
4-nitro-1-phenol-2-sulphonic acid	Picric acid.
1,2-benzanthraquinone	2-methylanthraquinone.
Bromanil	Naphthoquinone-1,2.
1-chloro-4-nitro-anthraquinone	Naphthoquinone-1,4.
Chloranil	Pentacenequinone.
1-chlor-anthraquinone	Tetracene-7,12-quinone.
Chrysenequinone	1,4-toluquinone.
Thymoquinone	2,5,7,10-tetrachloropyrenequinone.

The quantity of the solid, non-resinous, substantially colorless electron-acceptors (activators) which is best incorporated in the photoconductive coating to be sensitized is easily established by simple experiments. The photoconductive coating containing at least one photoconductor and at least one solid, non-resinous, substantially colorless, electron-acceptor, should contain the photoconductor and electron-acceptor in proportions ranging from substantially less than equal amounts to a substantial excess of the photoconductor with respect to the electron-acceptor. The optimum of the proportions varies somewhat according to the substance used. Generally, minor amounts are used, i.e. from about 0.1 to about 300 moles, preferably from about 1 to about 50 moles of electron-acceptor per 1000 moles of photoconductor. Alternatively, it has also been found that in the photoconductive coatings containing at least one photoconductor and at least one solid, non-resinous, substantially colorless electron-acceptor, it is also very useful to have present the photoconductor and the electron-acceptor in proportions ranging from substantially less than equal amounts to a substantial excess of the electron-acceptor with respect to the photoconductor. These proportions in which minor amounts of the photoconductor are added to the activator vary according to the substance used; however, in general, amounts from about 0.1 to about 300 moles, preferably from about 1 to about 50 moles photoconductor per 1000 moles activator are used. In some cases, it is also possible to use more than 300 moles photoconductor or activator per 1000 moles activator or photoconductor, respectively, but by exceeding the above range the dark decay of the mixture usually increases, and in such cases coatings made therefrom are inferior.

Mixtures of several photoconductors and activator substances may also be used. Moreover, in addition to these substances, sensitizing dyestuffs may be added.

By means of the present process, photoconductor coatings can be prepared which have a high degree of light-sensitivity, particularly in the ultra-violet region, and which are practically colorless. There is the further possibility of the photoconductor coatings being thereby strongly activated in the ultra-violet region and afterwards being invested with a high degree of sensitivity to visible light by a very small addition of dyestuff sensitizer without it being necessary for so much dyestuff to be added that the coating takes on a deep color. Also, it is possible, by means of activators, for photoconductors such as naphthalene, whose initial sensitivity is very slight, to be given adequate sensitivity for the production of satisfactory images by electrophotographic processes.

Furthermore, by addition of minor amounts of photoconductors to activators, photoconductive mixtures are obtained which have photoconductivity much higher than could be expected from the amount of the photoconductor added to the activator. A further increase in the photoconductivity may be obtained by the addition of dyestuff sensitizers in the same amounts as in the photoconductor-activator mixtures in which the photoconductor is present in a major amount.

The coatings are treated in other respects in accordance with the known processes of electrophotography, i.e. the photoconductor substances are used in the form of thin, coherent homogeneous coatings on a supporting material. The materials used as supports are primarily metals, such as aluminum, zinc, and copper; cellulose products, such as paper and cellulose hydrate; plastics, such as polyvinyl alcohol, polyamides, and polyurethanes. Other plastics, such as cellulose acetate and cellulose butyrate, especially in a partially saponified form, polyesters, polycarbonates, and polyolefins, if they are covered with an electroconductive layer or if they are converted into materials which have the above-mentioned specific conductivity, e.g. by chemical treatment or by introduction of materials which render them electrically conductive, can also be used, as well as glass plates. In general, materials are suitable the specific resistance of which is less than 10^{12} ohm-cm., preferably less than 10^{10} ohm-cm.

If paper is used as the supporting material, it is preferably pretreated against the penetration of coating solutions, e.g., it can be treated with a solution of methyl cellulose or polyvinyl alcohol in water or with a solution of an interpolymer of acrylic acid methyl ester and acrylonitrile in a mixture of acetone and methylethyl ketone, or with solutions of polyamides in aqueous alcohols or with dispersions of such substances.

For the preparation of the electrophotographic material, the photoconductive compounds are preferably dissolved in organic solvents such as benzene, acetone, methylene chloride or ethyleneglycol monomethylether or other organic solvents or in mixtures of such solvents, and resins and the activators—and possibly also the dyestuff sensitizers—are advantageously added thereto. These solutions are coated upon the supporting material in the normal manner, e.g., by immersion processes, painting or roller application or by spraying. The material is then heated so that the solvent will be removed.

A number of the compounds in question can be applied together to the supporting material or the compounds can be applied in association with other photoconductive substances.

Further, it is often advantageous for the photoconductor substances to be applied to the supporting material in association with one or more binders, e.g., resins. Resins primarily of interest as additions to the photoconductor coatings include natural resins such as balsam resins, colophony and shellac, synthetic resins such as coumarone resins and indene resins, processed natural substances such as cellulose ethers; polymers such as vinyl polymers, e.g. polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl alcohol, polyvinyl ethers, polyacrylic and polymethacrylic acid esters, isobutylene and chlorinated rubber.

If the photoconductive compounds in accordance with the invention are used in association with the resins described above, the proportion of resin to photoconductor substance can vary very greatly. Mixtures of from two parts of resin and one part of photoconductor substance to two parts of photoconductor substance and one part of resin are to be preferred. Mixtures of the two substances in equal parts by weight are particularly favorable.

For the displacement of sensitivity from the ultra-violet to the visible range of the spectrum, dyestuff sensitizers can be used in addition to the activators. Even very small additions of sensitizer, e.g., less than 0.01 percent, give good results. In general, however, 0.01 to 5 percent, and preferably 0.1 to 3 percent of dyestuff sensitizer is added to the photoconductor coatings. The addition of larger quantities is possible but in general is not accompanied by any considerable increase in sensitivity.

Some examples are given below of dyestuff sensitizers which may be used with good results, and some with very good results. They are taken from Schultz' "Farbstofftabellen" (7th edition, 1931, 1st vol.):

Triarylmethane dyestuffs such as Brilliant 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); cyanine dyestuffs, e.g., Cyanine (No. 921, p. 394) and chlorophyll.

For the production of copies with the electrocopying material, the photoconductive coating is charged by means of, for example, a corona discharge with a charging apparatus maintained at 6000–7000 volts. The electro-copying material is then exposed to light in contact with a master. Alternatively, an episcopic or diascopic image is projected thereon. An electrostatic image corresponding to the master is thus produced on the material. This invisible image is developed by contact with a developer consisting of carrier and toner. The carriers used may be, for example, tiny glass balls, iron powder or tiny plastic balls. The toner consists of a resin-carbon black mixture or a pigmented resin. The toner is used in a grain size of 1 to 100μ. The developer may also consist of a resin or pigment suspended in a non-conductive liquid in which resins may be dissolved. The image that is made visible by development is then fixed, e.g., by heating with an infra-red radiator to 100–170° C., preferably 120–150° C. or by treatment with solvents such as trichloroethylene, carbon tetrachloride or ethyl alcohol, or steam. Images corresponding to the master characterized by good contrast effect are obtained.

If transparent supporting material is used, the electrophotographic images can also be used as masters for the production of further copies on any type of light-sensitive sheets.

If translucent supports are used for photoconductive layers such as are provided by the invention, reflex images can be produced also.

The application of the activators in accordance with the present process is not restricted to electrophotographic coatings, but can extend to other devices containing photoconductors, e.g., photoelectric cells, photoresistances, sensing heads or camera tubes and electroluminescent apparatus.

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

EXAMPLE 1

A solution containing 26 parts by weight of polyvinyl acetate (e.g., "Mowilith 50"), 25.6 parts by weight of naphthalene, 0.0415 part by weight of 2,3,7-trinitrofluorenone and 800 parts by volume of toluene is applied by means of a coating device to an aluminum foil. After the coating has dried, direct images are produced thereon by the electrophotographic process in the following manner: the coated foil is given a negative electric charge by corona discharge, exposed behind a master to the light of a high-pressure mercury vapor lamp (125 watts, at a distance of 30 cm.) for about 10 seconds and then dusted over with a developer.

The developer consists of tiny glass balls and a mixture of resin and carbon black which has been melted together and then finely divided. A developer of this sort consists of, e.g., 100 parts by weight of tiny glass balls (grain size: 100–400μ approx.) and a toner (grain size: 20–50μ

approx.). The toner is prepared by melting together 30 parts by weight of Polystyrol LG, 30 parts by weight of modified maleic acid resin ("Beckacite" K 105) and 3 parts by weight of "Peerless Black" Russ 552. The melt is then ground and screened. The finely divided resin adheres to the parts of the coating not struck by light during the exposure and a positive image of the master becomes visible. It is slightly heated and thereby fixed.

If 2,4,7-trinitrofluorenone is not added to the coatings described above, even an exposure of two minutes will not produce an electrophotographic image.

EXAMPLE 2

26 parts by weight of polyvinyl acetate, 16.6 parts by weight of fluorene and 0.3602 part by weight of tetranitrofluorenone are dissolved in 800 parts by volume of toluene. This solution is applied to an aluminum foil and further procedure is as described in Example 1. Exposure time, if a 125-watt high-pressure mercury vapor lamp is used, is 10 seconds.

Without the tetranitrofluorenone addition, the images obtained even after an exposure of two minutes are not free of background, i.e., the exposed parts are not fully discharged and therefore retain a certain amount of developer.

EXAMPLE 3

A solution of 26 parts by weight of polyvinyl acetate, 17.8 parts by weight of anthracene and 0.3357 part by weight of hexabromonaphthalic anhydride in 800 parts by volume of toluene is applied to aluminum and further procedure is as described in Example 1. With a 125-watt high-pressure mercury vapor lamp, the exposure time is 4 seconds.

Without the hexabromonaphthalic anhydride addition, an exposure of as much as 30 seconds gives an image which contains background.

EXAMPLE 4

A solution containing 18 parts by weight of polyvinyl acetate, 18.2 parts by weight of 2,4-bis-(4'-diethylaminophenyl)-1,3,4-triazole and 0.130 part by weight of tetrachlorophthalic anhydride to 500 parts by volume of toluene is applied to an aluminum foil and further procedure is as described in Example 1. The exposure time with a 100-watt incandescent lamp is 2 seconds.

Without the tetrachlorophthalic anhydride addition, the image obtained after an exposure of 1 minute is not free of background.

EXAMPLE 5

A solution of 26 parts by weight of polyvinyl acetate, 21.6 parts by weight of 1,5-diethoxynaphthalene and 0.258 part by weight of 1,2-benzanthraquinone in 800 parts by volume of toluene is applied to paper and the material is further processed as described in Example 1. The exposure time (125-watt high-pressure mercury vapor lamp) is 20 seconds.

Without the 1,2-benzanthraquinone addition, the copy still has considerable background after an exposure of 80 seconds.

EXAMPLE 6

26 parts by weight of polyvinyl acetate, 17.8 parts by weight of phenanthrene and 0.245 part by weight of chloranil are dissolved together in 800 parts by volume of toluene. The solution is applied to a superficially roughened aluminum foil and then the material is further processed as described in Example 1. If the material is exposed to a 125-watt high-pressure mercury vapor lamp, an exposure of 10 seconds gives an image free of background and rich in contrast, whereas without the chloranil addition there is heavy background even after an exposure of one minute.

EXAMPLE 7

A solution containing 26 parts by weight of polyvinyl acetate, 24.4 parts by weight of o-dianisidine and 0.0256 part by weight of dibromomaleic anhydride in 800 parts by volume of toluene is applied to an aluminum foil and the material is further processed as described in Example 1. The exposure time (125-watt high-pressure mercury vapor lamp) is 2 seconds. Without the dibromomaleic anhydride addition, it is 10 seconds.

TABLE A

No.	A	B	C	D	E
1	Polyvinylacetate, 10 parts (1)	8			120 sec. (b) (ca.).
2	do	8	Anthraquinone, 0.08		30 sec. (b).
3	do	8	Anthraquinone, 0.17		20 sec. (b).
4	do	8	Anthraquinone, 0.25		20 sec. (b).
5	do	8		0.001	60 sec. (b).
6	do	8		0.005	60 sec. (b).
7	do	8		0.010	60 sec. (b).
8	do	8		0.030	90 sec. (b).
9	do	8		0.050	90 sec. (b).
10	do	8	Anthraquinone, 0.17	0.001	20 sec. (b).
11	do	8	do	0.010	20 sec. (b).
12	do	8	do	0.50	20 sec. (b).
13	do	8			240 sec. (a).
14	do	8	Anthraquinone, 0.25		180 sec. (a).
15	Cyclized rubber, 10 parts (2)	8			240 sec. (a).
16	do	8	Anthraquinone, 0.25		30 sec. (a).
17	Afterchlorinated polyvinylchloride, 7 parts (3)	8			10 sec. (a).
18	Polyvinylchloride, afterchlorinated, 7 parts (3)	8	Anthraquinone, 0.25 part		3 sec. (a).
19	Maleic acid resin, 10 parts (4)	8			240 sec. (a).
20	do	8	Anthraquinone, 0.25 part		60 sec. (a).
21	Chlorinated rubber, 10 parts (5)	8			20 sec. (a).
22	do	8	Anthraquinone, 0.25 part		10 sec. (a).
23	Chlorinated rubber, 10 parts (6)	8			20 sec. (a).
24	do	8	Anthraquinone, 0.25		10 sec. (a).
25	do	8	1,2-benzanthraquinone, 0.31 part		1–1.5 sec. (a).
26	do	8	Hexabromonaphthalic anhydride, 0.80 part		1–1.5 sec. (a).
27	do	8	2,4,5,7-tetranitrofluorenone, 0.43 part		1.5 sec. (a).
28	do	8	Dibromomaleic anhydride, 0.30 part		4–6 sec. (a).
29	do	8	Nitro-terephthalic acid-dimethylester, 0.28 part.		6–8 sec. (a).
30	do	8	Tetracyano ethylene, 0.15 part		4–6 sec. (a).
31	do	8	1,3,5-trinitrobenzene, 0.25 part		1.5–2 sec. (a).

Explanations on Table A

Column A: Quantity and kind of binder used. In all cases, the quantities stated were dissolved in 200 parts by volume of toluene.

Column B: Quantity of the photoconductor. In all examples, the same amount of pyrene was used.

Column C: Quantity of the activator used.

Column D: Quantity of dyestuff sensitizer used (Rhodamine B extra).

Column E: Time of exposure, using:

(a) a 250 watt photographic lamp (Philips "Photocrescenta").

(b) a customary 100 watt incandescent lamp.

The tests were carried through under the same experimental conditions, with the exception of the variations stated in the table.

(1) The polyvinyl acetate used was the product commercially available under the registered trademark "Mowilith 5C."

(2) The cyclized rubber used was the product commercially available under the registered trademark "Pliolite S–5D."

(3) The afterchlorinated polyvinylchloride used was the product commercially available under the registered trademark "Rhenoflex."

(4) The maleic acid resin used was the product commercially available under the designation "Alrosat."

(5) The chlorinated rubber used in Table A, col. A, under No. 21 (5) was the product commercially available under the registered trademark "Parlon S–5 cps."

(6) The chlorinated rubber used in Table A, col. A, under No. 23 (6) was a product commercially available under the registered trademark "Pergut S–40."

The following Table B shows further examples of various photoconductors which were activated, and the reduction in exposure time caused by the activators:

TABLE B

A	B	C	D
13.6 hydroquinonedimethylether.*	26	Chloranil	½
		Hexabromonaphthalic anhydride.	½
		2,4,5,7-tetranitrofluorenone	¼
25.6 naphthalene*	26	Hexabromonaphthalic anhydride.	⅓
		2,4,5,7-tetranitrofluorenone	⅙
21.6 1,5-diethoxynaphthalene.	26	1,5-dinitronaphthalene	⅛
		1,4-benzoquinone	¼
		Chloranil	1/20
		3,5-dinitrosalicylic acid	¼
		Dibromomaleic anhydride	¼
		Tetrachlorophthalic anhydride	1/16
		Hexabromonaphthalic anhydride	1/16
		Picrylchloride	1/16
		2,4,5,7-tetranitrofluorenone	1/80
15.4 acenaphthene*	26	Chloranil	½
		1,2-benzanthraquinone	½
		Dibromomaleic anhydride	½
		Hexabromonaphthalic anhydride	¼
		Picrylchloride	½
		2,4,5,7-tetranitrofluorenone	¼
15.2 acenaphthylene*	26	Chloranil	½
		Hexabromonaphthalic anhydride	½
		2,4,5,7-tetranitrofluorenone	¼
15.4 diphenyl*	18	Chloranil	¼
		1,2-benzanthraquinone	¼
		Tetrachlorophthalic anhydride	¼
		Picrylchloride	¼
		2,4,5,7-tetranitrofluorenone	1/10
24.4 o-dianisidine	26	Chloranil	¼
		1,2-benzanthraquinone	⅛
		Tetrachlorophthalic anhydride	½
		Hexabromonaphthalic anhydride	¼
		Picrylchloride	⅛
16.6 fluorene	26	Chloranil	⅛
		1,2-benzanthraquinone	½
		Hexabromonaphthalic anhydride	¼
		Picrylchloride	½
17.8 anthracene	26	3,5-dinitrosalicylic acid	½
		1,2-benzanthraquinone	⅓
		Dibromomaleic anhydride	½
		Tetrachlorophthalic anhydride	¼
		2,4,5,7-tetranitrofluorenone	1/10
22.8 chrysene	52	Benzoquinone	½
		Chloranil	¼
		3,5-dinitrosalicylic acid	¼
		1,2-benzanthraquinone	½
		Tetrachlorophthalic anhydride	¼
		Hexabromonaphthalic anhydride	1/10
		Picrylchloride	⅛
		2,4,5,7-tetranitrofluorenone	1/10
16.9 diphenylamine*	26	Benzoquinone	½
		Chloranil	¼
		2,4,5,7-tetranitrofluorenone	⅛
26.9 2,2'-dinaphthylamine.	26	1,4-benzoquinone	⅛
		Chloranil	⅛
		3,5-dinitrosalicylic acid	⅛
		1,2-benzanthraquinone	⅛
		Dibromomaleic acid anhydride	⅛
		Tetrachlorophthalic anhydride	⅛
		Hexabromonaphthalic anhydride	⅛
		Picrylchloride	⅛
		2,4,5,7-tetranitrofluorenone	⅛
17.8 phenanthrene	26	1,2-benzanthraquinone	¼
		Dibromomaleic anhydride	½
		Tetrachlorophthalic anhydride	½
		Hexabromonaphthalic anhydride	⅛
		Picrylchloride	⅛
		2,4,5,7-tetranitrofluorenone	1/40
19.3 2-phenyl-indole	26	Chloranil	¼
		1,2-benzanthraquinone	¼
		Dibromomaleic anhydride	¼
		Tetrachlorophthalic anhydride	¼
		Hexabromonaphthalic anhydride	¼
		Picrylchloride	½
		2,4,5,7-tetranitrofluorenone	⅛
16.7 carbazole	26	Chloranil	1/10
		1,2-benzanthraquinone	1/10
		3,5-dinitrosalicylic acid	⅛
		Dibromomaleic anhydride	1/10
		Tetrachlorophthalic anhydride	⅛
		Hexabromonaphthalic anhydride	1/10
		Picrylchloride	¼
		2,4,5,7-tetranitrofluorenone	1/10
19.9 thiodiphenylamine	26	1,2-benzanthraquinone	⅛
25.48 2,4-bis-(4'-diethylaminophenyl)-1,3,4-oxadiazole.	26	2,4,5,7-tetranitrofluorenone	1/30
		1,2-benzanthraquinone	1/10
		2,4-dichlorobenzoic acid	1/10
		Tetrachlorophthalic acid	1/20
18.2 2,4-bis-(4'-diethylaminophenyl)-1,3,4-triazole.	18	3,5-dinitrosalicylic acid	1/10
		1,2-benzanthraquinone	⅛
		Dibromomaleic anhydride	⅛
		Hexabromonaphthalic anhydride	1/60
		Picrylchloride	1/10
		2,4,5,7-tetranitrofluorenone	1/30

Explanations on Table B

The table describes a series of experiments carried through for improving the photoconductivity of organic substances by adding activators.

In Column A the quantity and nature of the substance used is stated. The substances marked with a "*" yielded no electrophotographic images even after an exposure time of several minutes.

In Column B the quantity of the binder used is stated. In all of the cases, polyvinyl acetate having a K-value of 50 was used. Binder, photoconductive substance, and activator were dissolved in toluene, coated onto an aluminum foil, and dried.

In Column C the substance used as activator is stated. In all of the cases 1 mol of the activator stated under C was used per 100 moles of the substance stated under A.

In Column D the reduced time of exposure is stated which is required to produce images equal in quality to those produced without the addition of an activator. In those cases where a prolonged exposure of the photoconductor yielded not even a weak image (marked with a "*"), the calculation of the reduced time of exposure was based on the longest exposure used for the unactivated photoconductor substance.

Alternatively, the increase in sensibility obtained by the addition of activating substances may be taken from a comparison of the degrees of blackening obtained with the activated photoconductive layer and with the unactivated photoconductive layer, under the same customary step wedge (e.g. Kodak No. 2 density strip with color patches).

EXAMPLE 8

A solution containing 20 parts by weight of afterchlorinated polyvinyl chloride with a content of chlorine from 61.7 to 62.3 percent and K-value from 59 to 62, 18.01 parts by weight of 2,4,5,7-tetranitrofluorenone and 0.216 part by weight of 1,5-diethoxynaphthalene dissolved in a mixture of 450 parts by volume toluene and 150 parts by volume butanone is applied to an aluminum foil. The subsequent procedure is that described in Example 1. The exposure time, with a 100 watt incandescent lamp at a distance of 30 centimeters is 2 seconds.

Without the addition of 1,5-diethoxynaphthalene the exposure time is about 40 seconds.

In the following table, the exposure times are given, which were obtained when using other photoconductors instead of the 1,5-diethoxynaphthalene.

Photoconductors (parts by weight):	Exposure time (seconds)
Acenaphthene (0.154)	15
N-ethylcarbazole (0.195)	15
2,2'-dinaphthylamine (0.270)	15
Diphenylamine (0.170)	15
Diphenyleneoxide (0.170)	20
Indole (0.120)	10
Pyrene (0.200)	12
Stilbene (0.110)	5
2,5-bis-(4'-diethylaminophenyl)-1,3,4 - oxdiazole (0.365)	1
Poly-N-vinylcarbazole (0.193)	6
Phenoxathine (0.200)	6

EXAMPLE 9

A solution of 12 parts by weight of chlorinated rubber ("Pergut S–40"), 5.04 parts by weight of 1,3-dinitrobenzene and 0.106 part by weight of anthracene in 150 parts by volume of toluene is applied to a paper foil and the material is further processed as described in Example 1. The exposure time (125 watt high pressure mercury vapor lamp) is 20 seconds. Without the anthracene addition, even after an exposure time of 80 seconds, only traces of an image were obtained. This means that the exposed parts of the coating were not discharged and therefore still attracted developer.

In the following table the exposure times are given, which were obtained, when using other photoconductors instead of the 1,3-dinitrobenzene.

Photoconductors (parts by weight):	Exposure time (seconds)
2,2'-dinaphthylamine (0.180)	20
2,5-bis-(4'-diethylaminophenyl)-1,3,4 - oxdiazole (0.220)	30

EXAMPLE 10

A solution containing 20 parts by weight of the afterchlorinated polyvinyl chloride mentioned in Example 8, 21.02 parts by weight of benzile and 0.370 part by weight of benzidine in a mixture of 450 parts by volume of toluene and 150 parts by volume of butanone is applied to an aluminum foil and the material is further processed as described in Example 1. The exposure time (125 watt high pressure mercury vapor lamp at a distance of 30 centimeters) is 10 seconds. Without the addition of the benzidine activator, even after an exposure time of 4 minutes, no electrophotographic image could be obtained.

In the following table, the exposure times are given which were obtained when using photoconductors other than benzidine.

Photoconductors (parts by weight):	Exposure time (seconds)
2,2'-dinaphthylamine (0.540)	20
2,5-bis-(4'-diethylamino-phenyl) - 1,3,4 - oxdiazole (0.730)	5
Poly-N-vinylcarbazole (0.390)	30

EXAMPLE 11

A solution containing 6.2 parts by weight of afterchlorinated polyvinyl chloride, 3.94 parts by weight of 1,5-dichloronaphthalene and 0.145 part by weight of 2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxdiazole in a mixture of 135 parts by volume of toluene and 45 parts by volume of butanone is applied to a paper base and is further processed as described in Example 1. The exposure time (125 watt high pressure mercury vapor lamp at a distance of 30 centimeters) is 10 seconds. Without the addition of the oxdiazole compound, even after an exposure time of 40 seconds, no image could be obtained. When the oxdiazole compound is replaced by 0.120 part by weight of 2,2'-dinaphthylamine, the exposure time is about 10 seconds.

EXAMPLE 12

To a solution containing 28.6 parts by weight of tetrachlorophthalic acid anhydride and 20 parts by weight of afterchlorinated polyvinyl chloride in a mixture of 150 parts by volume of butanone and 450 parts by volume of toluene, X parts by weight of photoconductor and Y parts by weight of dyestuff sensitizer are added. In the following table, the amounts of the photoconductor and sensitizer are given together with the corresponding exposure times. It is advantageous to dissolve the dyestuff sensitizer in a small amount of ethyleneglycol monomethyl ether before adding it to the solution. The latter is applied to a paper base material and further processed as described in Example 1. The light source used throughout was a 125-watt high pressure mercury vapor lamp and the distance between this lamp and the material exposed was about 30 centimeters.

Photoconductor X parts by weight	Dyestuff Sensitizer Y Parts by weight	Exposure Time (Seconds)
None	None	ca. 200
0.39 N-ethylcarbazole	do	9
Do	0.30 Rhodamine B extra	2–3
0.54 2,2'-dinaphthylamine	None	4–5
Do	0.30 Rhodamine B extra	2
0.73 2,5-bis-(4'-diethylamino-phenyl)-1,3,4-oxdiazole.	None	4
Do	0.30 Rhodamine B extra	1–2
Do	0.025 Basischreinblau 3 G	2
Do	0.015 Brillantgreen extra	3
Do	0.015 Kristallviolet	2
Do	0.015 Methylenblue	0.5
0.39 poly-N-vinylcarbazole	0.30 Rhodamine B extra	9
Do	None	20

EXAMPLE 13

A solution is prepared, containing 57.2 parts by weight of tetrachlorophthalic acid anhydride and 65 parts by weight of afterchlorinated polyvinyl chloride in 700 parts by volume toluene and sufficient butanone is added to make up 1000 parts by volume. To 50 parts by volume of the resulting stock solution, one of the photoconductors listed below is added, and the solution is applied to an aluminum foil and further processed as described in Example 1. In the following table, the added photoconductors are indicated, and the corresponding exposure times are given. As the light source, a 125-watt high pressure mercury vapor lamp in a distance of about 30 centimeters from the exposed material was used in all instances.

Photoconductor (parts by weight):	Exposure time (seconds)
None	[1]>180
Naphthalene (0.064)	30
Hydroquinonedimethyl ether (0.070)	30
Anthracene (0.090)	30
Carbazole (0.081)	30
Chrysene (0.114)	30
Pyrene (0.10)	30
o-Dianisidine (0.122)	30
1,5-diethoxynaphthalene (0.101)	30
2,6-dimethylnaphthalene (0.078)	30
Hexamethylbenzene (0.081)	120
Diphenylamine (0.085)	10
Diphenyleneoxide (0.084)	30
Indole (0.059)	20
Fluorene (0.083)	60
Benzodiphenyleneoxide (0.109)	30
2-methoxy-naphthalene (0.079)	60

[1] Image with heavy background.

Photoconductor (parts by weight)—Continued	Exposure time (seconds)
Phenanthrene (0.089)	60
Phenoxathin (0.100)	10
Stilbene (0.090)	30
2,3,5-triphenylpyrrole (0.153)	10
1,1'-dinaphthylamine (0.134)	30
1,2'-dinaphthylamine (0.134)	30
4'-tolyl-1-naphthylamine (0.116)	60
2-phenylindole (0.096)	60
Acenaphthene (0.077)	60
Diphenyl (0.077)	120
N-methyldiphenylamine (0.091)	30
4-hydroxy-diphenylamine (0.092)	30
Phlorglucinediethyl ether (0.091)	120

EXAMPLE 14

57.2 parts by weight of tetrachlorophthalic acid anhydride and 65 parts by weight of polyvinyl acetate are dissolved in sufficient toluene to make up 1000 parts by volume. To 50 parts by volume of this stock solution, one of the photoconductors listed below is added and the coating solution is applied to an aluminum foil and further processed as described in Example 1. The light source and the distance of the light source from the exposed material were the same as in the foregoing example.

Photoconductor (parts by weight):	Exposure time (seconds)
None	>60
Naphthalene (0.064)	10
Hydroquinonedimethyl ether (0.069)	2
N-ethylcarbazole (0.097)	2
Anthracene (0.089)	2
Carbazole (0.081)	3
Chrysene (0.114)	4
Pyrene (0.101)	10
o-Dianisidine (0.122)	3
1,5-diethoxynaphthalene (0.101)	4
2,6-dimethyl-naphthalene (0.078)	10
Hexamethylbenzene (0.081)	10
2,2'-dinaphthylamine (0.134)	4
Diphenylamine (0.084)	2
Diphenyleneoxide (0.084)	10
Indole (0.058)	4
Fluorene (0.083)	4
Stilbene (0.090)	4

EXAMPLE 15

29.62 parts by weight of phthalic acid anhydride and 33 parts by weight of afterchlorinated polyvinyl chloride are dissolved in 670 parts by volume of toluene and 330 parts by volume of butanone. To 50 parts by volume of the resulting stock solution, one of the photoconductors listed in the following table is added; these coating solutions are applied to an aluminum foil, and further processed as described in Example 1. The light source and the distance of the light source were the same as in Example 13.

Photoconductor (parts by weight):	Exposure time (seconds)
None	[1] 60
N-ethylcarbazole (0.10)	5
Anthracene (0.09)	10
Chrysene (0.114)	15
Pyrene (0.10)	10
2,2'-dinaphthylamine (0.134)	10
2,3,5-triphenylpyrrole (0.153)	10

[1] No image obtained.

EXAMPLE 16

49.2 parts by weight of chloranil and 56 parts by weight of afterchlorinated polyvinyl chloride are dissolved in a mixture of 1170 parts by volume of toluene and 100 parts by volume of butanone. The resulting solution is filled up to 2000 parts by volume with chlorobenzene. To 100 parts by volume of this stock solution, one of the photoconductors listed in the following table is added; the coating solution is applied to an aluminum foil and further processed as described in Example 1. The light source and the distance of the light source were the same as in Example 13.

Photoconductor (parts by weight):	Exposure time (seconds)
None	>180
Naphthalene (0.064)	ca. 120
Hydroquinonedimethyl ether (0.070)	30
N-ethylcarbazole (0.097)	10
Anthracene (0.090)	5
Chrysene (0.114)	15
Pyrene (0.10)	10
o-Dianisidine (0.122)	5
2,6-dimethyl-naphthalene (0.078)	30
Hexamethylbenzene (0.081)	120
2,2'-dinaphthylamine (0.134)	1–2
2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxdiazole (0.182)	1
2,3,5-triphenylpyrrole (0.153)	4

EXAMPLE 17

10.6 parts by weight of 2-acetyl fluorene and 12 parts by weight of afterchlorinated polyvinyl chloride are dissolved in 180 parts of toluene and sufficient butanol to make up 250 parts by volume of solution. To 50 parts by volume of this stock solution, one of the photoconductors of the following table is added. The solution is applied to an aluminum foil and further processed as described in Example 1. The light source and the distance of the light source were the same as in Example 13.

Photoconductor (parts by weight):	Exposure time (seconds)
None	[1] >180
o-Dianisidine (0.120)	30
2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxdiazole (0.180)	5

[1] No image obtained.

EXAMPLE 18

44 parts by weight of 9 acetyl-anthracene and 48 parts by weight of afterchlorinated polyvinyl chloride are dissolved in 700 parts by volume of solution. To 50 parts by volume of the resulting stock solution, one of the photoconductors of the following table is added. This solution is applied to an aluminum foil and further processed as described in Example 1. The light source and the distance thereof was the same as in Example 13.

Photoconductor (parts by weight):	Exposure time (seconds)
None	[1] >180
Hydroquinonedimethyl ether (0.069)	30
N-ethyl carbazole (0.097)	60
Anthracene (0.089)	60
Hexamethylbenzene (0.081)	30

[1] Image with heavy background.

EXAMPLE 19

46.2 parts by weight of pyrene-3-aldehyde and 50 parts by weight of afterchlorinated polyvinyl chloride are dissolved in 670 parts by volume of toluene and sufficient butanol to make up 1000 parts by volume of solution. To 50 parts by volume of the resulting stock solution one of the photoconductors of the following table is added. The solution is applied to an aluminum foil and further processed as described in Example 1. The light source

and the distance of the light source were the same as in Example 13.

Photoconductor (parts by weight):	Exposure time (seconds)
None	30
Naphthalene (0.064)	20
Hydroquinonedimethyl ether (0.070)	20
N-ethylcarbazole (0.10)	10
Anthracene (0.090)	20
Chrysene (0.114)	20
Pyrene (0.10)	20
Hexamethylbenzene (0.080)	20
2,2'-dinaphthylamine (0.135)	15
2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxdiazole (0.180)	5
2,3,5-triphenylpyrrole (0.150)	20

EXAMPLE 20

13.1 parts by weight of 1,4,5-trinitronaphthalene and 15 parts by weight of afterchlorinated polyvinyl chloride were dissolved in 180 parts by volume of toluene and sufficient butanone to make up 250 parts by volume. To 50 parts of the resulting stock solution, one of the photoconductors of the following table is added in the amount indicated. This solution is applied to an aluminum foil and further processed as described in Example 1. The light source and the distance thereof were the same as in Example 13.

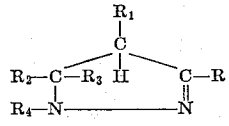
Photoconductor (parts by weight):	Exposure time (seconds)
None	[1] 180
N-ethylcarbazole (0.10)	30
Anthracene (0.09)	30
o-Dianisidine (0.12)	10
2,5-bis-(4'-diethylaminophenyl)-1,3,4-oxdiazole (0.18)	5

[1] Image with heavy background.

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:

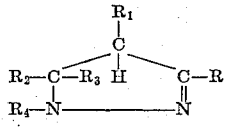
1. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group.

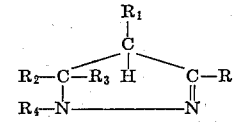
2. A sensitized photoconductive layer according to claim 1 in which the photoconductor is 1,3,5-triphenylpyrazoline.

3. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



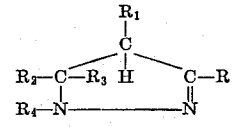
in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; the layer containing the photoconductor and the electron-acceptor in proportions ranging from substantially less than equal amounts to a substantial excess of the photoconductor with respect to the electron-acceptor and from substantially less than equal amounts to a substantial excess of the electron-acceptor with respect to the photoconductor.

4. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



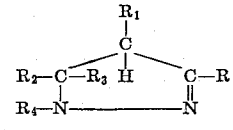
in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 0.1 to about 300 moles of the electron-acceptor per 1000 moles of photoconductor.

5. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



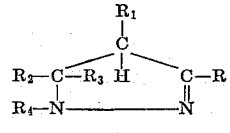
in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 0.1 to about 300 moles of the photoconductor per 1000 moles of the electron-acceptor.

6. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 1 to about 50 moles of the electron-acceptor per 1000 moles of the photoconductor.

7. A sensitized photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 1 to about 50 moles of the photoconductor per 1000 moles of the electron-acceptor.

8. A layer according to claim **1** in which the electron-acceptor is 2,4,7-trinitrofluorenone.

9. A layer according to claim **1** in which the electron-acceptor is tetranitrofluorenone.

10. A layer according to claim **1** in which the electron-acceptor is hexabromonaphthalic anhydride.

11. A layer according to claim **1** in which the electron-acceptor is tetrachlorophthalic anhydride.

12. A layer according to claim **1** in which the electron-acceptor is 1,2-benzanthraquinone.

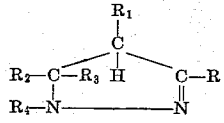
13. A layer according to claim **1** in which the electron-acceptor is chloranil.

14. A layer according to claim **1** in which the electron-acceptor is dibromomaleic anhydride.

15. A layer according to claim **1** including a resin.

16. A layer according to claim **1** including a dyestuff sensitizer.

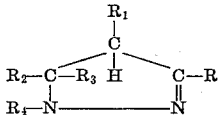
17. A photographic reproduction process which comprises exposing an electrostatically charged, supported, photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group.

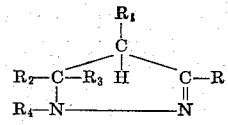
18. A process according to claim **17** in which the photoconductor is 1,3,5-triphenyl-pyrazoline.

19. A photographic reproduction process which comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



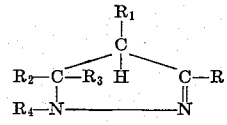
in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; the layer containing the photoconductor and the electron-acceptor in proportions ranging from substantially less than equal amounts to a substantial excess of the photoconductor with respect to the electron-acceptor and from substantially less than equal amounts to a substantial excess of the electron-acceptor with respect to the photoconductor.

20. A photographic reproduction process which comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



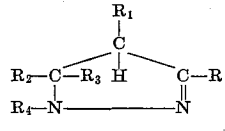
in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 0.1 to about 300 moles of the electron-acceptor per 1000 moles of photoconductor.

21. A photographic reproduction process which comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 0.1 to about 300 moles of the photoconductor per 1000 moles of the electron-acceptor.

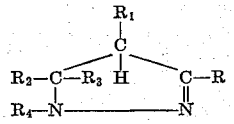
22. A photographic reproduction process which comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 1 to about 50 moles of the electron-acceptor per 1000 moles of the photoconductor.

23. A photographic reproduction process which comprises exposing an electrostatically charged, supported photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer comprising at least

one solid, non-resinous, substantially colorless electron-acceptor, and a compound having the formula



in which R is selected from the group consisting of hydrogen, alkyl, aryl and aralkenyl groups, R_1 is selected from the group consisting of hydrogen, alkyl and aryl groups, R_2 is selected from the group consisting of hydrogen, aryl and heterocyclic groups, R_3 is selected from the group consisting of hydrogen and aryl groups, and R_4 is an aryl group, at least one of R, R_1, R_2, and R_3 being an aryl group; in proportions ranging from about 1 to about 50 moles of the photoconductor per 1000 moles of the electron-acceptor.

24. A process according to claim **19** in which the electron-acceptor is 2,4,7-trinitrofluorenone.

25. A process according to claim **19** in which the electron-acceptor is tetranitrofluorenone.

26. A process according to claim **19** in which the electron-acceptor is hexabromonaphthalic anhydride.

27. A process according to claim **19** in which the electron-acceptor is tetrachlorophthalic anhydride.

28. A process according to claim **19** in which the electron-acceptor is 1,2-benzanthraquinone.

29. A process according to claim **19** in which the electron-acceptor is chloranil.

30. A process according to claim **19** in which the electron-acceptor is dibromomaleic anhydride.

31. A process according to claim **19** in which the layer includes a resin.

32. A process according to claim **19** in which the layer includes a dyestuff sensitizer.

References Cited by the Examiner

UNITED STATES PATENTS

3,037,861	6/1962	Hoegl et al.	96—1
3,113,022	12/1963	Cassiers et al.	96—1
3,155,503	11/1964	Cassiers et al.	96—1
3,180,729	4/1965	Klupfel et al.	96—1

OTHER REFERENCES

Andrews, Chemical Reviews, 54: 713–777, October 1954.

Czekalla et al.: Chemical Abstracts, 52: 4317*h* (1957).

Schneider and Compton et al.: Journal of Chemical Physics, vol. 25: 358, 1075–1076 (1956).

NORMAN G. TORCHIN, *Primary Examiner.*

C. E. VAN HORN, *Assistant Examiner.*