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METHOD OF PREPARING A HOMOGENEOUS DYE-SENSITIZED
ELECTROPHOTOGRAPHIC ELEMENT
Filed June 30, 1970

FIG. 1 PRIOR ART

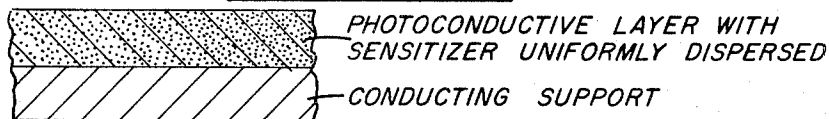
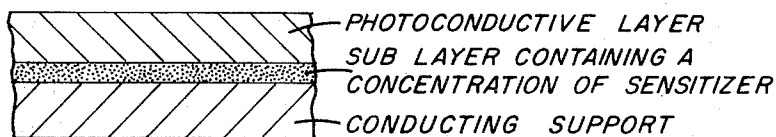


FIG. 2



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3,684,548

METHOD OF PREPARING A HOMOGENEOUS DYE-SENSITIZED ELECTROPHOTOGRAPHIC ELEMENT

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14 Claims

ABSTRACT OF THE DISCLOSURE

A process is described for the dye sensitization of electrophotographic elements. The dye is concentrated in a thin layer by preferential absorption from the photoconductive layer into a subbing layer having a greater affinity for the dye.

This invention relates to electrophotography and more particularly to novel techniques for sensitizing photoconductive recording elements and to the elements thus produced.

Electrophotographic imaging processes and techniques are based on the discovery that certain materials which are normally insulating become conductive during exposure to electromagnetic radiation of certain wavelengths after being electrically charged. Such materials, which may be either organic or inorganic, are termed photoconductors. They are conveniently formed into usable image-forming elements by coating a layer of the photoconductive composition, together with an electrically insulating resinous binder where necessary or desirable, onto a suitable support. Such an element will accept and retain an electrostatic charge in the absence of actinic radiation. In use, the surface of the element is charged in the dark to a uniform potential and exposed to an imagewise pattern of actinic radiation, which selectively reduces the surface potential to produce a charge pattern corresponding to the imagewise radiation pattern. The resultant electrostatic charge pattern can be developed by contacting it with suitably charged marking particles which adhere in accordance with the charge pattern, or it can be transferred to another insulating surface upon which it is developed. The marking particles can then be fixed to the surface by known means such as heat or solvent vapor or they can be transferred to another surface and similarly be fixed to produce a permanent reproduction of the original radiation pattern.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. For example, vapors of selenium and vapors of selenium alloys deposited on a suitable support and particles of photoconductive zinc oxide held in a resinous film-forming binder have found wide application in present-day document copying applications.

Since the introduction of electrophotography, a great many organic compounds have been found to possess some degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Optically clear organic photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements can be exposed through a transparent base, if desired, thereby providing unusual flexibility in equipment design. Such compositions, when coated as a film or layer on a suitable support, also yield an element which is reusable; that is, it can be used to form subsequent images after residual toner from prior images has been removed by transfer and/or cleaning.

Although some of the organic photoconductor materials referred to above are inherently light sensitive, their

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degree of sensitivity is usually low and not always in a desired wavelength portion of the spectrum so that it is common practice to add materials to increase the speed and to shift the spectral sensitivity.

Increasing the speed and shifting the sensitivity of such systems has several advantages in that it reduces exposure time, allows projection printing through various optical systems, etc. By increasing the speed through the use of sensitizers, photoconductors which would otherwise have been unsatisfactory are useful in processes where higher speeds are required.

Sensitizing is generally carried out by dissolving the sensitizer, photoconductor and binder in a common solvent, coating the solution onto a suitable conductive substrate, and removing the solvent by any suitable means. This procedure results in an element having the dye uniformly distributed throughout the thickness of the photoconductive layer. Although such elements are very useful for a number of applications, it is difficult to obtain maximum sensitization. Increasing the dye concentration generally increases the sensitization. However, a point is reached beyond which the addition of dye does not further increase sensitization and may even produce desensitization of the layer. Consequently, there is a limit of the degree of dye sensitization that can be obtained in such photoconductive layers having the dye uniformly distributed therein.

It is, therefore, an object of this invention to provide a novel process for sensitizing organic photoconductive elements.

It is another object of this invention to provide a process for dye sensitizing organic photoconductive elements to high speeds.

It is a further object of this invention to provide efficient dye-sensitized organic photoconductive elements comprising a single photoconductive layer which adheres well to its support.

These and other objects and advantages are accomplished in accordance with this invention by means of a selective dye imbibition technique. It has been discovered that, in the formation of an electrophotographic element comprising in sequence a conductive support, a first polymeric layer and a photoconductive layer, the photoconductive layer containing a homogeneous mixture comprising an organic photoconductor, a sensitizer and a binder therefor, greatly enhanced speeds are obtained when the first polymeric layer comprises a material having a greater affinity for the sensitizing dye than does the photoconductive layer. By homogeneous is meant that the photoconductive composition is substantially clear and free of any particulate matter, as observed under up to about 2500X magnification. During the coating of the photoconductive layer, a substantial portion of the sensitizing dye contained in the coating dope appears to be preferentially absorbed out of the photoconductive layer into the first polymeric layer. The amount of dye that is so concentrated in this manner varies; but generally at low dye concentrations, substantially all of the dye migrates into the first or under layer. The speeds that are obtained in the elements formed in accordance with this invention are markedly higher than those obtained when the dye is uniformly distributed throughout the photoconductive layer.

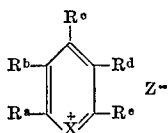
Reference is now made to the drawings, wherein:

FIG. 1 is a schematic cross-section of a sensitized organic photoconductor-containing element according to the prior art.

FIG. 2 is a schematic cross-section of a sensitized organic photoconductor-containing element showing the partitioning of dye which takes place in accordance with this invention.

In accordance with this invention, a homogeneous dye-sensitized photoconductive element is prepared by first coating onto a suitable conductive support a layer of an electrically insulating polymeric subcoating. The subcoating material can be any of those known materials which are mildly attacked by common organic coating solvents, such as halogenated lower alkanes, for example, and which has a greater affinity for the sensitizing dye than has the photoconductive composition to be coated over it. The subcoating is then overcoated with a solution containing an organic photoconductive composition comprising, for example, an organic photoconductor, an electrically insulating film-forming polymeric binder for the photoconductor, a sensitizing amount of a sensitizing dye for the photoconductor and a solvent. As has been mentioned, the solvent is typically one which is capable of mildly attacking the subcoating in order to swell or tackify it, to permit ready penetration of the dye into the layer. It should not be a good solvent for the subcoating. After the photoconductive layer has been coated, the element is dried in the usual manner, by passing air over its surface at a moderate rate of flow, as in a fume hood. Of course, drying can be accelerated, if desired, by coating the photoconductive layer onto the support while the support is held on a heated coating block, as is well known. The finished element is then cured to remove all traces of residual solvent to prepare it for use.

Sensitizing dyes which can be used in producing the highly efficient photoconductive elements of this invention can be selected from a wide range of known sensitizing dyes. One class of sensitizing dyes comprises the pyrylium dyes, including pyrylium and thiapyrylium dye salts such as are disclosed in Van Allan et al. U.S. Pat. 3,250,615, issued May 10, 1966. Such dyes include those which can be represented by the following general formula:



wherein R^a , R^b , R^c , R^d , and R^e can each represent a hydrogen atom; an aliphatic or aromatic group typically having from 1 to 15 carbon atoms, such as alkyl groups, methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl, isoamyl, hexyl, octyl, nonyl, dodecyl, styryl, methoxystyryl, diethoxystyryl, dimethylaminostyryl, 1-butyl-4-p-dimethylaminostyryl, 1,3-butadienyl, β -ethyl-4-dimethylaminostyryl; alkoxy groups like methoxy, ethoxy, propoxy, butoxy, amyloxy, hexoxy, octoxy, and the like; aryl groups like phenyl, 4-diphenyl, alkylphenyls as 4-ethylphenyl, 4-propylphenyl, and the like, alkoxyphenyls as 4-ethoxyphenyl, 4-methoxyphenyl, 4-amyloxyphenyl, 2-hexoxyphenyl, 2-methoxyphenyl, 3,4-dimethoxyphenyl, and the like, β -hydroxyalkoxyphenyls as 2-hydroxyethoxyphenyl, 3-hydroxyethoxyphenyl, and the like, 4-hydroxyphenyl, halophenyls as 2,4-dichlorophenyl, 3,4-dibromophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, and the like, azidophenyl, nitrophenyl, aminophenyls as 4-diethylaminophenyl, 4-dimethylaminophenyl and the like, and naphthyl; vinyl, and the like; and where X is a sulfur, oxygen or selenium atom, and Z is an anionic function, including such anions as perchlorate, fluoroborate, iodide, chloride, bromide, sulfate, sulfonate, periodate, p-toluenesulfonate, hexafluorophosphate, and the like. In addition, the pair R^a and R^b as well as the pair R^c and R^d can together be the necessary atoms to complete an aryl ring fused to the pyrylium nucleus. Preferred dye salts comprise compounds having the above formula in which R^a , R^c and R^e represent groups of the types indicated, R^b and R^d are hydrogen, and Z^- is a perchlorate, fluoroborate or hexafluorophosphate ion. Typical members of such pyrylium dyes are listed in Table 1.

TABLE 1

Compound No.	Name of compound
1	4-(4-bis(2-chloroethyl)aminophenyl)-2,6-diphenylthiapyrylium perchlorate.
2	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate.
3	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate.
4	4-(4-dimethylamino-2-methylphenyl)-2,6-diphenylpyrylium perchlorate.
5	4-(4-bis(2-chloroethyl)aminophenyl)-2-(4-methoxyphenyl)-6-phenylthiapyrylium perchlorate.
6	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium sulfate.
7	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium p-toluenesulfonate.
8	4-(4-dimethylaminophenyl)-2,6-diphenylpyrylium p-toluenesulfonate.
9	2-(2,4-dimethoxyphenyl)-4-(4-dimethylaminophenyl)-benzo(b)pyrylium perchlorate.
10	2,6-bis(4-ethylphenyl)-4-(4-dimethylaminophenyl)-thiapyrylium perchlorate.
11	4-(4-dimethylaminophenyl)-2-(4-methoxyphenyl)-6-phenylthiapyrylium perchlorate.
12	4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenylthiapyrylium perchlorate.
13	4-(4-dimethylaminophenyl)-2-(4-methoxyphenyl)-6-(4-methylphenyl)pyrylium perchlorate.
14	4-(4-diphenylaminophenyl)-2,6-diphenylthiapyrylium perchlorate.
15	2,4,6-triphenylpyrylium perchlorate.
16	4-(4-methoxyphenyl)-2,6-diphenylpyrylium perchlorate.
17	4-(2,4-dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
18	4-(3,4-dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
19	2,6-bis(4-methoxyphenyl)-4-phenylpyrylium perchlorate.
20	6-(4-methoxyphenyl)-2,4-diphenylpyrylium perchlorate.
21	2-(3,4-dichlorophenyl)-4-(4-methoxyphenyl)-6-phenylpyrylium perchlorate.
22	4-(4-amyloxyphenyl)-2,6-bis(4-ethylphenyl)pyrylium perchlorate.
23	4-(4-amyloxyphenyl)-2,6-bis(4-methoxyphenyl)pyrylium perchlorate.
24	2,4,6-triphenylpyrylium fluoroborate.
25	2,6-bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium perchlorate.
26	2,6-bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium fluoroborate.
27	6-(3,4-diethoxystyryl)-2,4-diphenylpyrylium perchlorate.
28	6-(3,4-diethoxy- β -amylstyryl)-2,4-diphenylpyrylium fluoroborate.
29	6-(4-dimethylamino- β -ethylstyryl)-2,4-diphenylpyrylium fluoroborate.
30	6-(1-n-amy-4-p-dimethylaminophenyl)-1,3-butadienyl)-2,4-diphenylpyrylium fluoroborate.
31	6-(4-dimethylaminostyryl)-2,4-diphenylpyrylium fluoroborate.
32	6-[α -ethyl- β , β -bis(dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium fluoroborate.
33	6-(1-butyl-4-p-dimethylaminophenyl)-1,3-butadienyl)-2,4-diphenylpyrylium fluoroborate.
34	6-(4-dimethylaminostyryl)-2,4-diphenylpyrylium perchlorate.
35	6-[β , β -bis(4-dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium perchlorate.
36	2,6-bis(4-dimethylaminostyryl)-4-phenylpyrylium perchlorate.
37	6-(β -methyl-4-dimethylaminostyryl)-2,4-diphenylpyrylium fluoroborate.
38	6-(1-ethyl-4-p-dimethylaminophenyl)-1,3-butadienyl)-2,4-diphenylpyrylium fluoroborate.
39	6-[β , β -bis(4-dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium fluoroborate.
40	6-(1-methyl-4-p-dimethylaminophenyl)-1,3-butadienyl)-2,4-diphenylpyrylium fluoroborate.
41	4-(4-dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate.
42	2,6-bis(4-ethylphenyl)-4-phenylpyrylium perchlorate.
43	2,6-bis(4-ethylphenyl)-4-methoxyphenylthiapyrylium fluoroborate.
44	2,4,6-triphenylthiapyrylium perchlorate.
45	4-(4-methoxyphenyl)-2,6-diphenylthiapyrylium perchlorate.
46	6-(4-methoxyphenyl)-2,4-diphenylthiapyrylium perchlorate.
47	2,6-bis(4-methoxyphenyl)-4-phenylthiapyrylium perchlorate.
48	4-(2,4-dichlorophenyl)-2,6-diphenylthiapyrylium perchlorate.
49	2,4,6-tri(4-methoxyphenyl)thiapyrylium perchlorate.
50	2,6-bis(4-ethylphenyl)-4-phenylthiapyrylium perchlorate.
51	4-(4-amyloxyphenyl)-2,6-bis(4-ethylphenyl)thiapyrylium perchlorate.
52	6-(4-dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
53	2,4,6-triphenylthiapyrylium fluoroborate.
54	2,4,6-triphenylthiapyrylium sulfate.
55	4-(4-methoxyphenyl)-2,6-diphenylthiapyrylium fluoroborate.
56	2,4,6-triphenylthiapyrylium chloride.
57	2-(4-amyloxyphenyl)-4,6-diphenylthiapyrylium fluoroborate.
58	4-(4-amyloxyphenyl)-2,6-bis(4-methoxyphenyl)thiapyrylium perchlorate.

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TABLE 1.—Continued

Compound No.	Name of compound
59.....	2,6-bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
60.....	4-anisyl-2,6-bis(4-n-amylxyphenyl)thiapyrylium chloride.
61.....	2-[β , β -bis(4-dimethylaminophenyl)vinylene]-4,6-diphenylthiapyrylium perchlorate.
62.....	6-(β -ethyl-4-dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
63.....	2-(3,4-diethoxystyryl)-4,6-diphenylthiapyrylium perchlorate.
64.....	2,4,6-trianisylthiapyrylium perchlorate.
65.....	6-ethyl-2,4-diphenylpyrylium fluoroborate.
66.....	2,6-bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium chloride.
67.....	6-[β , β -bis(4-dimethylaminophenyl)vinylene]-2,4-di-(4-ethylphenyl)pyrylium perchlorate.
68.....	2,6-bis(4-amylxyphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
69.....	6-(3,4-diethoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoroborate.
70.....	6-(4-methoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoroborate.
71.....	2-(4-ethylphenyl)-4,6-diphenylthiapyrylium perchlorate.
72.....	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium perchlorate.
73.....	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium fluoroborate.
74.....	2,6-bis(4-ethylphenyl)-4-(4-n-amylxyphenyl)thiapyrylium perchlorate.
75.....	2,6-bis(4-methoxyphenyl)-4-(4-n-amylxyphenyl)thiapyrylium perchlorate.
76.....	2,4,6-tri(4-methoxyphenyl)thiapyrylium fluoroborate.
77.....	2,4-diphenyl-6-(3,4-diethoxystyryl)pyrylium perchlorate.
78.....	4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenylthiapyrylium fluoroborate.
79.....	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium hexafluorophosphate.

Another class of useful dyes comprises cyanine and merocyanine dyes which (1) have a cathodic polarographic halfwave potential more positive than -1.0 volt; (2) have an anodic polarographic and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than -0.10 volt; and (3) desensitize negative silverbromiodide emulsions which contain 99.35 mole percent bromide by more than $0.4 \log E$ to radiation having a wavelength of 365 nm. when incorporated therein at a concentration of 0.2 millimole per mole of silver halide. Typical dyes from this class which are useful in the practice of this invention include the simple cyanines derived from the imidazoquinoxaline nucleus, e.g., 6-chloro-1',3'-diethyl-1,3-diphenyl-imidazo[4,5-b]quinoxalinocyanine perchlorate; 1,3-diallyl-1',3'-diethylimidazo[4,5-b]quinoxalinocyanine perchlorate and 1,3-diethyl - 1',3' - dimethylimidazo[4,5-b]quinoxalinocyanine perchlorate; and dyes derived from the imidazoquinoxaline nuclei containing an aryl or allyl substitution on the N-atoms and a halogen or nitro substitution in the nuclei, e.g., 6,6',7,7'-tetrachloro-1,1',3,3'-tetraphenylimidazo[4,5-b]quinoxalinocarbocyanine p-toluenesulfonate; 1,3-diallyl-2-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-6-nitro-1H-imidazo[4,5-b]quinoxalinium p-toluenesulfonate and 2-[2-(1-methyl-2-phenyl-3-indolyl)-vinyl]-6-nitro-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate. Dyes from these classes are more fully described in Jones and Fox Belgian Pat. 713,875, granted June 14, 1968. Other classes of useful dyes include cyanine dyes having a pyrrolo[2,3-b]quinoxaline nucleus or a pyrrolo[2,3-b]pyrazine nucleus joined at the 3-carbon atom thereof to the methine linkage of the cyanine dye, such as 1,3'-diethyl-6'-nitro-3-pyrrolo[2,3-b]quinoxalinocarbocyanine p-toluenesulfonate and 1,3-diallyl-1'-ethylimidazo[4,5-b]quinoxalino - 3' - pyrrolo[2,3-b]quinoxalinocarbocyanine p-toluenesulfonate, these dyes being more fully disclosed in Mee et al. Belgian Pat. 731,444, granted June 16, 1969; methine dyes containing a 1,3,2-dioxaborinium salt moiety, a 1,3,2-oxazaborinium salt moiety, or a 1,3,2-diazaborinium salt moiety, such as 2,2'-difluoro - 4,4' - (benzo[e]1,3,2-dioxaborino)carbocyanine fluoride or 4-(4-dimethylaminostyryl)-2-fluorobenzo[e]-1,3,2-dioxaborinium fluoride, these dyes being more fully disclosed in Daniel et al. U.S. application Ser. No. 761,860, filed Sept. 23, 1968, entitled Novel Dyes

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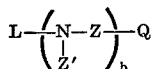
and Electrophotographic Compositions, now U.S. Pat. 3,567,439; quaternized merocyanine dyes containing a 2-isoxazolin-5-one nucleus, a 2-pyrazolin-5-one nucleus, or a complex pyrimidinedione nucleus, such as 11-[(2-methyl-5-oxo-3-phenyl - 3 - isoxazolin-4-yl)-methylene]isoindolo-[1,2-b]benzothiazolium p-toluenesulfonate or 3-[(1,3-diethyl - 2 - (1H)-imidazo[4,5-b]quinoxalinyldene)-ethylidene]-3,4-dihydro-1-methyl - 2,4 - dioxo-2H-pyrido[1,2-a]-pyrimidinium iodide, these dyes being more fully disclosed in Brooker et al. Belgian Pat. 732,049, granted June 30, 1969; polymethine dyes containing an imidazole ring joined at the carbon atom in the 5-position of the imidazole ring to a dimethine linkage, the imidazole ring having fused to the [a] side thereof the nonmetallic atoms required to complete at least one fused ring, and a second desensitizing nucleus joined at a carbon thereof to the dimethine linkage, such as 1,3,3-triethyl-2-[2-[8-methyl - 2 - (4-phenylazophenyl)imidazo[1,2-a]-pyrid-3-yl]vinyl]-5-nitro - 3H - indolium p-toluenesulfonate, 3-ethyl-2-[2-[2-methyl - 6 - (4-nitrophenyl)imidazo[2,1-b]-1,3,4 - triadiazol-5-yl]vinyl]-6-nitrobenzothiazolium p-toluenesulfonate or 2-[2-(4-bromophenyl)-6-methoxyimidazo-[1,2-b]pyridazin - 3 yl]vinyl]-1,3-diethylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, these dyes being more fully disclosed in Carpenter et al. Belgian Pat. 731,443, granted June 13, 1969; merocyanine dyes which contain a complex fused pyrimidinedione nucleus linkage by a double bond or a dimethine linkage to a desensitizing nucleus, such as 3-[1,3-diethyl-2(1H)imidazo-[4,5-b]quinoxalinyldene)ethylidene] - 2H - pyrido[1,2-a]pyrimidine-2,4(3H)-dione or 3-[(6-chloro-1,3-diphenyl-2(1H)-imidazo[4,5-b]-quinoxalinyldene)ethylidene] - 2H - pyrido[1,2-a]pyrimidine-2,4-dione, these dyes being more fully disclosed in Webster et al. Belgian Pat. 731,367, granted June 13, 1969; cyanine dyes containing a carbazole nucleus, such as 1,3-diethyl-2- β -(9-methyl-3-carbazolyl)vinylimidazo[4,5-b]quinoxalinium iodide, 3-methyl-2- β -(9-methyl-3-carbazolyl)vinyl-6-nitrobenzothiazolium p-toluenesulfonate or 5-chloro-3-methyl-2- β -(9-methyl-3-carbazolyl)vinyl-6-nitrobenzothiazolium p-toluenesulfonate, these dyes being more fully disclosed in Mee et al. Belgian Pat. 731,210, granted June 13, 1969; pyrylium dyes containing a 2-arylindole nucleus, a carbazole nucleus or an imidazo[4,5-b]quinoxaline nucleus, such as 4-[2-(1-methyl-2-phenyl - 3 - benz[g]indolyl)-vinyl]-2-phenyl-1-benzopyrylium perchlorate, 2-(4-chlorophenyl)-4-[2-(9-methyl - 3 - carbazolyl)vinyl]-1-benzopyrylium perchlorate or 5,6,7,8-tetrahydro-8-[(9-methyl-3-carbazolyl)methylene]-2,4-diphenylcyclohexa[b]pyrylium perchlorate, these dyes being more fully disclosed in Brooker et al. Belgian Pat. 730,291, granted May 30, 1969; cyanine dyes containing a pyrrole nucleus linked by the 2-carbon atom thereof to the methine chain of the dye, such as 3-ethyl-6-nitro - 2 - [2-(2-pyrrolyl)vinyl]benzothiazolium p-toluenesulfonate, 1,3,3 - trimethyl-5-nitro-2-[2-(2-pyrrolyl)vinyl]-3H-indolium p-toluenesulfonate or 1,3,3-trimethyl-2-[2-(1-methyl - 2 - pyrrolyl)vinyl]-5-nitro-3H-indolium iodide, these dyes being more fully disclosed in Fumia et al. Belgian Pat. 728,463, granted Apr. 15, 1969; and cyanine dyes containing a pyrazole nucleus, such as 1,3-diallyl-2-[[1-(2-benzothiazolyl) - 3,5 - dimethyl-4-pyrazolyl]-vinyl]imidazo[4,5-b]quinoxalinium p-toluenesulfonate, 3-ethyl-6-nitro-2-[(1-phenyl-4-pyrazolyl)vinyl]benzothiazolium p-toluenesulfonate or 1,3-diallyl-2-[(1-phenyl - 4 - pyrazolyl)-vinyl]imidazo-[4,5-b]quinoxalinium p-toluenesulfonate; these dyes being more fully disclosed in Van Lare Belgian Pat. 727,703, granted Mar. 31, 1969. Combinations of two or more of these dyes may, of course, be used, if desired.

Photoconductors useful in the practice of this invention are described below.

(A) Arylamine photoconductors including substituted and unsubstituted arylamines, diarylamines, nonpolymeric triarylamines and polymeric triarylamines such as those described in U.S. Pats. 3,240,597 and 3,180,730.

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(B) Photoconductors represented by the formula



wherein Z represents a mononuclear or polynuclear divalent aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, binaphthyl, etc.), or a substituted divalent aromatic radical of these types wherein said substituent can comprise a member such as an acyl group having from 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from 1 to about 6 carbon atoms (e.g., methoxy, ethoxy, propoxy, pentoxy, etc.), or a nitro group; Z' represents a mononuclear or polynuclear monovalent or polynuclear monovalent aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.); or a substituted monovalent aromatic radical wherein said substituent can comprise a member, such as an acyl group having from 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from 1 to about 6 carbon atoms (e.g., methoxy, propoxy, pentoxy, etc.), or a nitro group; Q can represent a hydrogen atom or an aromatic amino group, such as Z'NH—; b represents an integer from 1 to about 12, and L represents a hydrogen atom, a mononuclear or polynuclear aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.), a substituted aromatic radical wherein said substituent comprises an alkyl group, an alkoxy group, an acyl group, or a nitro group, or a poly(4'-vinylphenyl) group which is bonded to the nitrogen atom by a carbon atom of the phenyl group, these materials being more fully described in U.S. Pat. 3,265,496.

(C) Polyaryllalkane photoconductors including leuco bases of diaryl or triarylmethane dye salts, 1,1,1-triaryllalkanes wherein the alkane moiety has at least two carbon atoms and tetraarylmethanes having an amino group substituted in at least one of the aryl nuclei attached to the alkane and methane moieties of the latter two classes of photoconductors which are non-leuco base materials; and also other polyaryllalkanes included by the formula:



wherein each of D, E and G is an aryl group and J is a hydrogen atom, an alkyl group, or an aryl group, at least one of D, E and G containing an amino substituent, the aryl groups attached to the central carbon atom being preferably phenyl groups, although naphthyl groups can also be used including substituted aryl groups containing substituents such as alkyl and alkoxy typically having 1 to 8 carbon atoms, hydroxy, halogen, etc., in the ortho, meta or para positions, ortho-substituted phenyl being preferred; the aryl groups can also be joined together or cyclized to form a fluorene moiety, for example; the amino substituent can be represented by the formula:

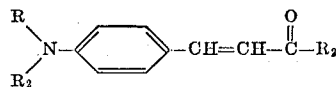


wherein each R can be an alkyl group typically having 1 to 8 carbon atoms, a hydrogen atom, an aryl group, or together the necessary atoms to form a heterocyclic amino group typically having 5 to 6 atoms in the ring such as morpholino, piperidino, tetrahydropyrrolo, etc.; at least one of D, E and G preferably being a p-dialkylaminophenyl group, when J is an alkyl group, such an alkyl group more generally has 1 to 7 carbon atoms, these ma-

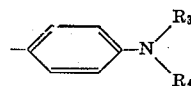
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terials being more fully described in U.S. Pat. 3,274,000, French Pat. 1,383,461 and in U.S. Ser. No. 627,857, filed Apr. 3, 1967 by Seus and Goldman, now U.S. Pat. 3,542,544.

(D) Photoconductors comprising 4-diarylamino substituted chalcones having the formula:



wherein R₁ and R₂ are each phenyl radicals including substituted phenyl radicals, R₂ preferably having the formula:

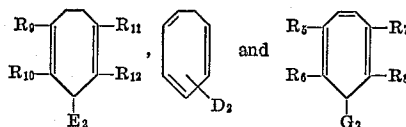


wherein R₃ and R₄ are each aryl radicals, aliphatic residues of 1 to 12 carbon atoms such as alkyl radicals preferably having 1 to 4 carbon atoms, or hydrogen; particularly advantageous results being obtained when R₁ is a phenyl radical including a substituted phenyl radical and where R₂ is diphenylaminophenyl, dimethylaminophenyl or phenyl, these materials being more fully described in Fox application U.S. Ser. No. 613,846, now U.S. Pat. 3,526,501.

(E) Non-ionic cycloheptenyl compounds which may be substituted with substituents such as:

- (1) an aryl radical including substituted as well as unsubstituted aryl radicals,
- (2) a hydroxy radical,
- (3) an azido radical,
- (4) a heterocyclic radical having 5 to 6 atoms in the heterocyclic nucleus and at least one hetero nitrogen atom, and including substituted and unsubstituted heterocyclic radicals, and
- (5) an oxygen linked cycloheptenyl moiety.

The substitution on the cycloheptenyl nucleus occurs at an unsaturated carbon atom when the cycloheptenyl moiety is a conjugated triene with no aromatic structure fused thereto. However, if there is at least one aromatic structure fused to the cycloheptenyl moiety, then the substituents are attached to a saturated carbon atom. Additional photoconductors within this class are included in one of the following formulae:



where

E₂ and G₂ can be either:

- (1) a phenyl radical,
- (2) a naphthyl radical,
- (3) a heterocyclic radical having 5 to 6 atoms in the heterocyclic nucleus and at least one hetero nitrogen atom,
- (4) a hydroxyl radical, or
- (5) an oxygen containing radical having a structure such that the resultant cycloheptenyl compound is a symmetrical ether;

D₂ can be any of the substituents defined for E₂ and G₂ above and is attached to a carbon atom in the cycloheptenyl nucleus having a double bond; (R₉ and R₁₀), (R₁₁ and R₁₂), (R₅ and R₆), and (R₇ and R₈) are together the necessary atoms to complete a benzene ring fused to the cycloheptenyl nucleus; these compounds being more fully described in U.S. Ser. No. 654,091, filed July 18, 1967, now U.S. Pat. 3,533,786.

(F) Compounds containing an

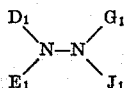


nucleus including:

(1) unsubstituted and substituted N,N-bicarbazyls containing substituents in either or both carbazoyl nuclei such as:

- (a) an alkyl radical including a substituted alkyl radical such as a haloalkyl or an alkoxyalkyl radical,
- (b) a phenyl radical including a substituted phenyl radical such as a naphthyl, an aminophenyl or a hydroxyphenyl radical,
- (c) a halogen atom,
- (d) an amino radical including substituted as well as unsubstituted amino radicals such as an alkyl-amino or a phenylalkylamino radical,
- (e) an alkoxy radical,
- (f) a hydroxyl radical,
- (g) a cyano radical,
- (h) a heterocyclic radical such as a pyrazolyl, carbazoyl or a pyridyl radical; or

(2) tetra-substituted hydrazines containing substituents which are substituted or substituted phenyl radicals, or heterocyclic radicals having 5 to 6 atoms in the hetero nucleus, suitable results being obtained when all four substituents are not unsubstituted phenyl radicals, i.e., if at least one substituent is a substituted phenyl radical or a heterocyclic radical having 5 to 6 atoms in the hetero nucleus. Other tetra-substituted hydrazines include those having the following formula:

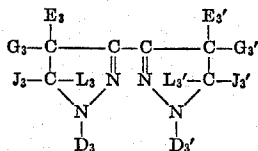


wherein D_1 , E_1 , G_1 and J_1 are each either:

- (a) a substituted phenyl radical such as a naphthyl radical, an alkyl phenyl radical, a halophenyl radical, a hydroxyphenyl radical, a haloalkylphenyl radical or a hydroxy-alkylphenyl radical, or
- (b) a heterocyclic radical such as an imidazolyl radical, a furyl radical, or a pyrazolyl radical. In addition, J_1 and E_1 can also be
- (c) an unsubstituted phenyl radical.

Especially preferred are those tetra-substituted hydrazines wherein both D_1 and G_1 are either substituted phenyl radical or heterocyclic radicals. These compounds are more fully described in U.S. Ser. No. 673,962, filed Oct. 9, 1967, now U.S. Pat. 3,542,546.

(G) Organic compounds having a 3,3'-bis-aryl-2-pyrazoline nucleus which is substituted in either by five-member ring with the same or different substituents. The 1 and 5 positions on both pyrazoline rings can be substituted by an aryl moiety including unsubstituted as well as substituted aryl substituents such as alkoxyaryl, alkaryl, alk-aminoaryl, carboxyaryl, hydroxyaryl and haloaryl. The 4 position can contain hydrogen or unsubstituted as well as substituted alkyl and aryl radicals such as alkoxyaryl, alkaryl, alkaminoaryl, haloaryl, hydroxyaryl, alkoxyalkyl, aminoalkyl, carboxyaryl, hydroxyalkyl and haloalkyl. Other photoconductors in this class are represented by the following structure:



wherein:

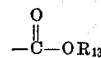
D_3 , D_3' , J_3 and J_3' can be either a phenyl radical including a substituted phenyl radical such as a tolyl radical

or a naphthyl radical including a substituted naphthyl radical,

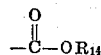
E_3 , E_3' , G_3 , G_3' , L_3 and L_3' can be any of the substituents set forth above and in addition can be either a hydrogen atom or an alkyl radical containing 1 to 8 carbon atoms. These organic photoconductors are more fully described in U.S. Ser. No. 664,642, filed Aug. 31, 1967, now U.S. Pat. 3,527,602.

(H) Triarylamines in which at least one of the aryl radicals is substituted by either a vinyl radical or a vinylene radical having at least one active hydrogen-containing group. The phrase "vinylene radical" includes substituted as well as unsubstituted vinylene radicals and also includes those radicals having at least one and as many as three repeating units of vinylene groups such as $(\text{CH}=\text{CH})_n$ wherein n is an integer of from 1 to 3. Groups which contain active hydrogen are well known in the art, the definition of this term being set forth in several textbooks such as "Advanced Organic Chemistry," R. C. Fuson, pp. 154-157, John Wiley & Sons, 1950. The term "active hydrogen-containing group" as used herein includes those compounds encompassed by the discussion in the textbook cited above and in addition includes those compounds which contain groups which are hydrolyzable to active hydrogen-containing groups. Typical active-hydrogen-containing groups substituted on the vinylene radical of the triarylamine include:

- (1) carboxy radicals,
- (2) hydroxy radicals,
- (3) ethynyl radicals,
- (4) ester radicals (e.g.,



wherein R_{13} is alkyl or aryl) including cyclic ester radicals (e.g.,



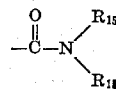
wherein R_{14} is a cyclic alkylene radical connected to a vinylene combination such as is found in coumarin derivatives),

- (5) carboxylic acid anhydride radicals,
- (6) semicarbazono radicals,
- (7) cyano radicals,
- (8) acyl halide radicals (e.g.,



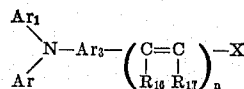
etc.), and

- (9) amido radicals (e.g.,



wherein R_{15} is a hydrogen atom, an alkyl group or an aryl group).

Other active hydrogen-containing groups include substituted alkylidyne oximido radicals. Photoconductors included in this class can be represented by the following structure:



wherein:

- (1) Ar_1 and Ar_2 are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an aminophenyl radical,
- (2) Ar_3 is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical,

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(3) R_{16} and R_{17} are each hydrogen, a phenyl radical including a substituted phenyl radical or a lower alkyl radical preferably having 1 to 8 carbon atoms,

(4) X is either:

(a) an active hydrogen-containing group such as a carboxy radical, an acyl halide radical, an amido radical, a carboxylic acid anhydride radical, an ester radical, a cyano radical, a hydroxy radical, a semicarbazono radical, an ethynyl radical, or a methylidyne oximido radical, or

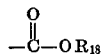
(b) hydrogen, provided that when X is hydrogen, R_{16} and R_{17} are also hydrogen, and

(5) n is an integer of 1 to 3.

The arylene nucleus can be substituted in any position by the vinyl or vinylenic moiety. However, when Ar_3 is phenylene, particularly good results are obtained if the substitution occurs in the para position. These materials are more fully described in U.S. Ser. No. 706,800, filed Feb. 20, 1968, now U.S. Pat. 3,567,450.

(I) Triarylamines in which at least one of the aryl radicals is substituted by an active hydrogen-containing group. The term "active hydrogen-containing group" has the same meaning as set forth above and again includes those compounds encompassed by the discussion in the textbook and additionally includes those compounds which contain groups which are hydrolyzable to active hydrogen-containing groups. Typical active hydrogen-containing groups which are substituted on an aryl radical of the triarylamines include:

- (1) carboxy radicals,
- (2) hydroxy radicals,
- (3) ethynyl radicals,
- (4) ester radicals (e.g.,



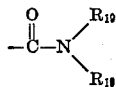
wherein R_{18} is an alkyl or an aryl group),

- (5) lower alkylene hydroxy radicals (e.g., having 1 to 8 carbon atoms),
- (6) carboxylic acid anhydride radicals,
- (7) lower alkylene carboxy radicals (e.g., having 2 to 8 carbon atoms),
- (8) cyano radicals,
- (9) acyl halide radicals (e.g.,



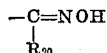
etc.),

- (10) amido radicals (e.g.,



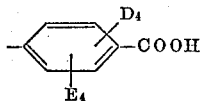
wherein R_{19} is a hydrogen atom, an alkyl group or an aryl group),

- (11) lower alkylidyne oximido radicals having 1 to 8 carbon atoms including substituted alkylidyne oximido radicals (e.g.,



wherein R_{20} is hydrogen or a lower alkyl radical),

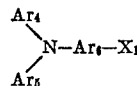
- (12) semicarbazono radicals, and
- (13) arylene carboxy radicals including substituted arylene carboxy radicals (e.g.,



wherein D_4 and E_4 are phenyl or lower alkyl radicals). 75

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Photoconductors included in this class can be represented by the following structure:



wherein:

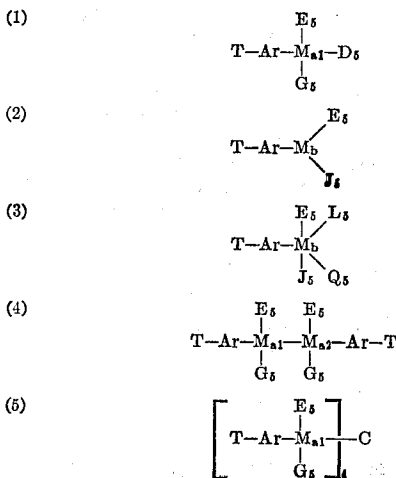
- (1) Ar_4 and Ar_5 are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an amino phenyl radical,
- (2) Ar_6 is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical, and
- (3) X_1 is an active hydrogen-containing group such as a carboxy radical, an acyl halide radical, an amido radical, a carboxylic acid anhydride radical, an ester radical, a cyano radical, a semicarbazono radical, a hydroxy radical, an ethynyl radical, a methylidyne oximido radical or a phenylene carboxy radical.

These materials are more fully described in U.S. Ser. No. 706,780, filed Feb. 20, 1968.

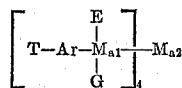
(J) Organo-metallic compounds having at least one amino aryl substituent attached to a Group IVa or Group Va metal atom. The metallic substituents of this class of organic photoconductors are Group IVa or Group Va metals in accordance with the Periodic Table of the Elements (Handbook of Chemistry and Physics, 38th edition, pp. 394-95) and include silicon, germanium, tin and lead from Group IVa and phosphorus, arsenic, antimony and bismuth from Group Va. These materials can be substituted in the metallo nucleus with a wide variety of substituents but at least one of the substituents must be an amino-aryl radical. The amino radical can be positioned anywhere on the aromatic nucleus, but best results are obtained if the aryl moiety is a phenyl radical having the amino group in the 4 or para position. Typical substituents attached to the metal nucleus include the following:

- (1) a hydrogen, sulfur or oxygen atom,
- (2) an alkyl radical,
- (3) an aryl radical including unsubstituted as well as substituted aryl radicals such as amino-aryl, alkylaryl and haloaryl,
- (4) an oxygen-containing radical such as an alkoxy or aryloxy radical,
- (5) an amino radical including unsubstituted and substituted amino radicals such as mono- and diarylamino and mono- and dialkylamino radicals,
- (6) a heterocyclic radical, and
- (7) a Group IVa or Va organo metallic radical

Photoconductors included in this class can be represented by the following structures:



(6)



where

E₅, G₅, L₅ and Q₅ can be:

- (a) a hydrogen atom,
- (b) an aryl radical including unsubstituted as well as substituted aryl radicals such as a phenyl radical, a naphthyl radical, a dialkylaminophenyl radical, or a diarylaminophenyl radical,
- (c) an alkyl radical having 1 to 8 carbon atoms,
- (d) an alkoxy radical having 1 to 8 carbon atoms,
- (e) an aryloxy radical such as a phenoxy radical,
- (f) an amino radical having the formula



wherein R₂₁ and R₂₂ can be hydrogen atoms or alkyl radicals having 1 to 8 carbon atoms, or (g) a heterocyclic radical having 5 to 6 atoms in the hetero nucleus including at least one nitrogen atom such as a triazolyl, a pyridyl radical, etc.,

T is an amino radical such as an alkylamino radical having 1 to 8 carbon atoms or an arylamino radical such as a phenylamino radical;

Ar is an aromatic radical such as phenyl or naphthyl; M_{a1} and M_{a2} are the same or different Group IVa metals;

M_b is a Group Va metal;

D₅ can be any of the substituents set forth above for E₅, G₅, L₅ and Q₅ and in addition, can be a Group IVa organo-metallic radical or, when taken with E, an oxygen atom or a sulfur atom;

J₅ can be any of the substituents set forth above for E₅, G₅, L₅ and Q₅ and in addition, can be, when taken with E, an oxygen atom or a sulfur atom. These materials are described in U.S. Ser. No. 650,664, filed July 3, 1967.

(K) Any other organic compound which exhibits photoconductive properties such as those set forth in Australian Pat. 248,402.

Representative organic photoconductors useful in this invention include the compounds listed below:

TABLE II

diphenylamine
dinaphthylamine
N,N'-diphenylbenzidine
N-phenyl-1-naphthylamine
N-phenyl-2-naphthylamine
N,N'-diphenyl-p-phenylenediamine
2-carboxy-5-chloro-4'-methoxydiphenylamine
p-anilinophenol
N,N'-di-2-naphthyl-p-phenylenediamine
4,4'-benzylidene-bis-(N,N-dimethyl-m-toluidine)
triphenylamine
N,N,N',N'-tetraphenyl-m-phenylenediamine
4-acetyltriphenylamine
4-hexanoyltriphenylamine
4-lauroyltriphenylamine
4-hexyltriphenylamine
4-dodecyltriphenylamine
4,4'-bis(diphenylamino) benzil
4,4'-bis(diphenylamino) benzophenone
poly[N,4'-(N,N',N'-triphenylbenzidine)]
polyadipyltriphenylamine
polysebacyltriphenylamine
polydecamethylenetriphenylamine
poly-N-(4-vinylphenyl) diphenylamine
poly-N-(vinylphenyl)-α,α'-dinaphthylamine
4,4'-benzylidene-bis(N,N-diethyl-m-toluidine)

- 4',4''-diamino-4-dimethylamino-2',2''-dimethyltriphenylmethane
- 4',4''-bis(diethylamino)-2,6-dichloro-2',2''-dimethyltriphenylmethane
- 5 4',4''-bis(diethylamino)-2',2''-dimethyldiphenyl-naphthylmethane
- 2',2''-dimethyl-4,4',4''-tris(dimethylamino) triphenylmethane
- 4',4''-bis(diethylamino)-4-dimethylamino-2',2''-dimethyltriphenylmethane
- 10 4',4''-bis(diethylamino)-2-chloro-2',2''-dimethyl-4-dimethylaminotriphenylmethane
- 4',4''-bis(diethylamino)-4-dimethylamino-2,2',2''-trimethyltriphenylmethane
- 15 4',4''-bis(dimethylamino)-2-chloro-2',2''-dimethyltriphenylmethane
- 4',4''-bis(dimethylamino)-2',2''-dimethyl-4-methoxytriphenylmethane
- bis(4-diethylamino)-1,1,1-triphenylethane
- 20 bis(4-diethylamino) tetraphenylmethane
- 4',4''-bis(benzylethylamino)-2',2''-dimethyltriphenylmethane
- 4',4''-bis(diethylamino)-2',2''-diethoxytriphenylmethane
- 4,4'-bis(dimethylamino)-1,1,1-triphenylethane
- 25 1-(4-N,N-dimethylaminophenyl)-1,1-diphenylethane
- 4-dimethylaminotetraphenylmethane
- 4-diethylaminotetraphenylmethane
- 4,4'-bis(diphenylamino) chalcone
- 4-diphenylamino-4'-dimethylaminochalcone
- 30 4-dimethylamino-4'-diphenylaminochalcone
- 4,4'-bis(dimethylamino) chalcone
- 4,4'-bis(diethylamino) chalcone
- 4-diethylamine-4'-diphenylaminochalcone
- 4-diphenylaminochalcone
- 35 4-dimethylaminochalcone
- 4'-diphenylaminochalcone
- 4'-dimethylaminochalcone
- bis-[5-(5H-dibenzo[a,d]cycloheptenyl)] ether
- 5-hydroxy-5H-dibenzo[a,d]cycloheptene
- 40 1-{5-(5H-dibenzo[a,d]cycloheptenyl)}-4,5-dicarbo-methoxy-1,2,3-triazole
- 1-{5-(5H-dibenzo[a,d]cycloheptenyl)}-4,5-dibenzoyl-1,2,3-triazole
- 5-azido-5H-dibenzo[a,d]cycloheptene
- 45 1-{5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)}-4,5-dicarbomethoxy-1,2,3-triazole
- 1-{5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)}-4,5-dibenzoyl-1,2,3-triazole
- 4-[5-(5H-dibenzo[a,d]cycloheptenyl)]-N,N-dimethyl aniline
- 50 N,N-diethyl-3-methyl-4-[5-(5H-dibenzo[a,d]cycloheptenyl)]-aniline
- 4-[5-(5H-dibenzo[a,d]cycloheptenyl)]-1-dimethylamino-naphthalene
- 55 N,N-diethyl-3-methyl-4-[5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)] aniline
- 3-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene
- 3-(4-diethylamino-2-methylphenyl)-1,3,5-cycloheptatriene
- 60 3-(4-dimethylaminonaphthyl)-1,3,5-cycloheptatriene
- N,N-diethyl-3-methyl-4-[5-(5H-dibenzo[a,d]cycloheptenyl)]-aniline
- tetra-α-naphthylhydrazine
- tetra(3-methyl-4-hydroxyphenyl) hydrazine
- 65 tetra(m-hydroxyethylphenyl) hydrazine
- tetra(2-methyl-5-chloroethylphenyl) hydrazine
- tetra(2-methyl-5-hydroxyphenyl) hydrazine
- tetra(1-imidazolyl) hydrazine
- N,N-di-α-naphthyl-N',N'-di(3-methyl-4-hydroxyphenyl) hydrazine
- 70 N-3-furyl-N-(2-methyl-4-hydroxyphenyl)-N',N'-di-β-naphthylhydrazine
- tetra-β-naphthylhydrazine
- N,N'-di-β-naphthyl-N,N'-diphenylhydrazine
- 75 tetra-4-tolylhydrazine

N,N'-diphenyl-N,N'-di(3-methyl-4-hydroxyphenyl) hydrazine
 N,N'-diphenyl-N,N'-di-p-chlorophenyl hydrazine
 phenyltri-(2-methyl-5-hydroxyphenyl) hydrazine
 N,N'-bicarbaryl
 cyclotetakis(3,9-carbazolyene)
 6-(3-carbazolyl)-cyclotetakis(3,9-carbazolyene)
 6-(9-carbazolyl)-cyclotetakis(3,9-carbazolyene)
 3,3'-bis(3-carbazolyl)-9,9'-bicarbazolyl
 3-(3-carbazolyl)-9-(carbazolyl) carbazole
 3-(9-carbazolyl)-9,9'-bicarbazolyl
 3,3'-diethyl-9,9'-bicarbazolyl
 3,3'-diphenyl-9,9'-bicarbazolyl
 3,3'-dichloro-9,9'-bicarbazolyl
 4,4'-bis(diethylamino)-9,9'-bicarbazolyl
 3,3'-diethoxy-9,9'-bicarbazolyl
 1,1'-dihydroxy-9,9'-bicarbazolyl
 2,2'-dicyano-9,9'-bicarbazolyl
 tetra(p-diethylaminophenyl) hydrazine
 3,3'-bis(1,5-diphenyl-2-pyrazoline)
 3,3'-bis(1-p-tolyl-5-phenyl-2-pyrazoline)
 3,3'-bis(1,5-[1-naphthyl]-2-pyrazoline)
 1,5-diphenyl-3-[3'-(1'-p-tolyl-5'-phenyl)-2'-pyrazolyl]-2-pyrazoline
 3,3'-bis(1,5-diphenyl-4,5-dimethyl-2-pyrazoline)
 3,3'-bis(1,4,5-triphenyl-2-pyrazoline)
 3,3'-bis(1,5-di-p-tolyl-4-methoxy-2-pyrazoline)
 3,3'-bis(1,5-diphenyl-4-dimethylamino-2-pyrazoline)
 3,3'-bis[1,5-diphenyl-4-(p-chlorophenyl)-2-pyrazoline]
 3,3'-bis[1,5-diphenyl-4,5-di-(p-diethylaminophenyl)-2-pyrazoline]
 3,3'-bis[1,5-diphenyl-4-(p-methoxyphenyl)-5-ethyl-2-pyrazoline]
 3,3'-bis(1,5-diphenyl-4-chloromethyl-2-pyrazoline)
 1,5-diphenyl-4,5-dimethyl-3-[3'-(1'-p-tolyl-4'-diethyl-5'-methylphenyl)-2'-pyrazolyl]-2-pyrazoline
 4-(p-diphenylaminophenyl)-3-buten-1-yne
 p-diphenylaminostyrene
 ethyl-p-diphenylaminocinnamate
 methyl p-diphenylaminocinnamate
 p-diphenylaminocinnamoyl chloride
 p-diphenylaminocinnamic acid N,N-diphenylamide
 p-diphenylaminocinnamic acid anhydride
 3-(p-diphenylaminophenyl)-2-butenic acid
 bis(p-diphenylaminobenzal)succinic acid
 4-N,N-bis(p-bromophenyl)aminocinnamic acid
 1-(4-diphenylamino)naphthacrylic acid
 p-diphenylaminocinnamic acid
 p-diphenylaminocinnamionitrile
 7-diphenylamino coumarin
 p-diphenylaminophenylvinylacrylic acid
 p-diphenylaminobenzyl p'-diphenylaminocinnamate
 7-(p-diphenylaminostyryl) coumarin
 p-diphenylaminocinnamyl alcohol
 4-diphenylaminocinnamaldehyde semicarbazone
 O-p-diphenylaminocinnamoyl p'-diphenylaminobenzaldehyde oxime
 p-diphenylaminocinnamaldehyde oxime
 1,3-bis(p-diphenylaminophenyl)-2-propen-1-ol
 methyl p-diphenylaminobenzoate
 N,N'-diphenylanthranilic acid
 3-p-diphenylaminophenyl-1-propanol
 4-acetyltriphenylamine semicarbazone
 ethyl 2,6-diphenyl-4-(p-diphenylaminophenyl) benzoate
 1-(p-diphenylaminophenyl)-1-hydroxy-3-butyne
 4-hydroxymethyltriphenylamine
 1-(p-diphenylaminophenyl) ethanol
 4-hydroxytriphenylamine
 2-hydroxytriphenylamine
 4-formyltriphenylamine oxime
 4-acetyltriphenylamine oxime
 1-(p-diphenylaminophenyl) hexanol
 1-(p-diphenylaminophenyl) dodecanol
 p-diphenylaminobenzoic acid anhydride
 4-cyanotriphenylamine

p-diphenylaminobenzoic acid N,N-diphenylamide
 p-diphenylaminobenzoic acid
 p-diphenylaminobenzoic chloride
 3-p-diphenylaminophenylpropionic acid
 4-formyltriphenylamine semicarbazone
 triphenyl-p-diethylaminophenylsilane
 methyl-diphenyl-p-diethylaminophenylsilane
 triphenyl-p-diethylaminophenylgermane
 triphenyl-p-dimethylaminophenylstannane
 triphenyl-p-diethylaminophenylstannane
 diphenyl-di-(p-diethylaminophenyl) stannane
 triphenyl-p-diethylaminophenylplumbane
 tetra-p-diethylaminophenylplumbane
 phenyl-di-(p-diethylaminophenyl) phosphine
 bis(p-diethylaminophenyl) phosphine oxide
 tri-p-dimethylaminophenylarsine
 tri-p-diethylaminophenylarsine
 2-methyl-4-dimethylaminophenylarsine oxide
 tri-p-diethylaminophenylbismuthine
 methyl-di-(p-diethylaminophenyl) arsine
 methyl-di-(p-diethylaminophenyl) phosphine
 phenyl-tri(p-diethylaminophenyl) stannane
 methyl-tri(p-diethylaminophenyl) stannane
 tetra-p-diethylaminophenylgermane
 diphenyl-p-diethylaminophenylsilane
 p-diethylaminophenylarsine
 tetrakis-[diphenyl-(p-diethylaminophenyl) plumbyl]-methane
 tetrakis-[diphenyl-(p-diethylaminophenyl) stannyl]-stannane
 bis-[phenyl-(p-diethylaminophenyl)] dibismuthine
 tri-(p-diethylaminophenyl) phosphine sulfide
 di-(p-diethylaminophenyl) thioxotin.

Other useful photoconductors include various polymeric photoconductors such as polyvinyl carbazoles and halogenated polyvinyl carbazoles. Various polymeric photoconductors are described more fully in Inami et al. U.S. Pat. No. 3,421,891, issued Jan. 14, 1969 and Leistner U.S. Pat. No. 3,037,961, issued Jan. 5, 1962. For certain uses, it may be desirable to omit the polymeric binder or vehicle described above when a polymeric photoconductor is used.

Suitable supporting materials for use in the practice of this invention can include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foils such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass and galvanized plates; vapor deposited metal layers such as silver, nickel, aluminum and the like coated on paper or conventional photographic film bases such as cellulose acetate, polystyrene, etc. Such conducting materials as nickel can be coated by vacuum deposition on transparent film supports in sufficiently thin layers to allow electrophotographic elements prepared therewith to be exposed from either side of such elements. An especially useful conducting support can be prepared by coating a support material such as poly(ethylene terephthalate) with a conducting layer containing a semiconductor dispersed in a resin. Such conducting layers are described in U.S. Pat. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone of maleic anhydride and a vinyl acetate polymer. Such kinds of conducting layers and methods for their optimum preparation and use are disclosed in U.S. 3,007,901 and 3,267,807.

After the conductive layer is deposited, it is overcoated with a layer of a solvent swellable, electrically insulating polymeric layer characterized in that it has a greater affinity for the sensitizing dye than does the photoconductive layer. Useful subcoating materials are three- and four-component addition copolymers prepared by aqueous emulsion co-polymerization. Preferred polymers are certain hydrosol terpolymers containing vinylidene chloride

as a major constituent, such as a terpolymer derived from methyl acrylate, vinylidene chloride and an unsaturated diacid such as acrylic acid or itaconic acid. Particularly preferred polymers are hydrosol tetrapolymers containing acrylonitrile in addition to the above constituents. Of the terpolymers, the preferred polymers have a weight composition of from about 4 to about 20 percent of units derived from methyl acrylate, from about 15 to about 90 percent of units derived from vinylidene chloride, and from about 0.5 to about 10 percent of units derived from itaconic acid. Of the tetrapolymers, the most preferred polymers have a weight composition of from about 5 to about 20 percent of units derived from methyl acrylate, from about 5 to about 20 percent of units derived from acrylonitrile, from about 15 to about 90 percent of units derived from vinylidene chloride, and from about 0.5 to about 10 percent of units derived from acrylic acid or itaconic acid. Polymers of this type are disclosed in U.S. Pat. 3,143,421. Other useful materials also include the so-called tergels which are the subject of Nadeau et al. U.S. Pat. 3,501,301, issued Mar. 17, 1970.

The polymeric subbing layers useful for the practice of this invention have in common the property of being readily swollen but not dissolved by the solvent contained in the photoconductive composition to be coated over them. While they are so swollen, the dye contained in the overlying photoconductive layer preferentially migrates from the photoconductive layer into the subbing layer to cause partitioning of the dye between the photoconductive layer and the subbing layer. This can be more readily understood by reference to the drawings. FIG. 1 shows in schematic cross-section typical dye-sensitized organic photoconductor-containing element according to the prior art. It is seen that the dye is substantially uniformly distributed throughout the depth of the photoconductive layer. Elements having this structure in general do not show the enhanced speeds obtainable with elements prepared according to this invention.

FIG. 2 shows in schematic cross-section a dye-sensitized organic photoconductor-containing element according to this invention. The element comprises a conductive support as in FIG. 1, over which is coated a subbing layer which, in turn, carries the photoconductive layer. During coating of the photoconductive layer from a dye-sensitized photoconductor-containing solution, it is found that the subbing layer serves to concentrate the dye from the solution into the subbing layer, so that a major portion of the dye is present in the subbing layer after the solvent has been removed from the photoconductive layer.

The extent of the partitioning of the dye depends to some extent on the concentration of the dye in the photoconductor-containing solution. If the concentration is relatively low, that is, less than about 3 percent by weight based on the dry weight of photoconductor plus binder, substantially all of the dye appears to be present in the subbing layer, as judged by the appearance of color cross-section photomicrographs. When the weight concentration of the dye is substantially greater than this level, a significant portion of the dye is seen to remain in the photoconductive layer. Additionally, a gradient of dye concentration is noticed in the photoconductive layer at these higher dye levels, with the portion of the photoconductive layer furthest removed from the subbing layer containing relatively more dye than the portion closest to the subbing layer.

It will be realized, of course, that it is possible to concentrate sensitizing dye in the first polymeric layer by merely coating a solution containing the dye onto the layer directly before coating the organic photoconductor-containing solution onto the layer. This, however, would involve an extra coating step, which is avoided by the method of this invention.

While it is not intended that the invention be bound to a particular theory or mechanism, the following explanation may serve to clarify the reasons for the speed

increases obtained using the method and elements of this invention. Many organic photoconductive compounds in common use are p-type, that is, they operate by the generation and conduction of positive holes (as the majority carriers) during exposure to actinic radiation. When such compounds are coated in the form of a layer on a conductive support and the layer is electrically charged, the surface of the layer at which a positive charge resides is the surface at which the absorption of light should be a maximum for optimum results. If the external surface of the layer is negatively charged, the positively charged surface is the interface of the photoconductive layer with the conductive substrate. Optimum results with negative charging should therefore be obtained if the dye can be concentrated at this interface. What has been discovered is a method for concentrating the dye in the desired position, using no special or additional coating or treatment operations. As will be seen in the examples, the effect of dye localization on increased negative speeds becomes less as the dye concentration in the photoconductor-containing solution is raised. This is because there is a limit to the amount of dye which the subbing layer can absorb out of the solution. When the layer has absorbed all that it can, most of the dye is, of course, absorbed from that portion of the photoconductor-containing layer adjacent to the subbing layer, while a decreasing amount is absorbed from those portions of the photoconductor-containing layer further removed from the subbing layer. If n-type photoconductors are used, of course, the same effect should be noticed when positive polarity of surface charge is employed.

After the first polymeric layer or subbing layer has been coated, it is overcoated with a photoconductive composition comprising an organic photoconductor, a sensitizing dye and, when necessary, a polymeric binder. Preferred binders useful in the practice of this invention comprise polymers having fairly high dielectric strength which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly(isobutylmethacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylene alkaryloxyalkylene terephthalate); phenolformaldehyde resins; ketoneresins; polyamides; polycarbonates; polythiocarbonates; poly(ethyleneglycol-cobishydroxyethoxyphenylpropane terephthalate); nuclear substituted polyvinyl haloarylates; etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Pats. 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of the invention are sold under such trade names as Vitel PE-101, Cymac, Piccopale 100, Saran F-220 and Lexan 105. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

Solvents of choice for preparing the photoconductive layers in accordance with this invention can include a number of solvents such as benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc. Preferred solvents are halogenated lower alkanes having from 1 to about 3 carbon atoms, with dichloromethane being particularly preferred.

In preparing the photoconductive coating composition, useful results are obtained where the photoconductor substance is present in an amount equal to at least about 1

weight percent of the coating composition. The upper limit in the amount of photoconductor substance present can be widely varied in accordance with usual practice. In those cases where a binder is employed, it is normally required that the photoconductor substance be present in an amount from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductor substance in the coating composition is from about 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally, a coating in the range of about 0.001 inch to about 0.01 inch before drying is useful for the practice of this invention. The preferred range of coating thickness is found to be in the range from about 0.002 inch to about 0.006 inch before drying although useful results can be obtained outside of this range.

In the same manner, the coating thickness of the subbing layer can vary widely. Normally, the dry thickness can vary between about 0.03 micron to about 1.0 micron, with a thickness between about 0.05 micron to about 0.5 micron being preferred. Of course, it will be understood that useful results can be obtained outside of this range, and that the particular thickness chosen depends also on the thickness of the photoconductive layer to be coated over the subbing layer. Best results are normally obtained when the thickness of the subbing layer is no greater than about ten percent of the thickness of the photoconductive layer, although for certain applications, dimensions outside of these limits may be useful or even preferred.

The elements of the present invention can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the xerographic process. In a process of this type, an electrophotographic element is held in the dark and given a blanket electrostatic charge by placing it under a corona discharge. This uniform charge is retained by the layer because of the substantial dark insulating property of the layer, i.e., the low conductivity of the layer in the dark. The electrostatic charge formed on the surface of the photoconductive layer is then selectively dissipated from the surface of the layer by imagewise exposure to light by means of a conventional exposure operation such as, for example, by a contact-printing technique, or by lens projection of an image, and the like, to thereby form a latent electrostatic image in the photoconductive layer. Exposing the surface in this manner forms a pattern of electrostatic charge by virtue of the fact that light energy striking the photoconductor causes the electrostatic charge in the light struck areas to be conducted away from the surface in proportion to the intensity of the illumination in a particular area.

The charge pattern produced by exposure is then developed or transferred to another surface and developed there, i.e., either the charged or uncharged areas rendered visible, by treatment with a medium comprising electrostatically responsive particles having optical density. The developing electrostatically responsive particles can be in the form of a dust, i.e., powder, a pigment in a resinous carrier, i.e., toner. A preferred method of applying such toner to a latent electrostatic image for solid area development is by the use of a magnetic brush. Methods of forming and using a magnetic brush toner applicator are described in the following U.S. Pat.: 2,786,439; 2,786,440; 2,786,441; 2,811,465; 2,874,063; 2,984,163; 3,040,704; 3,117,884; and Reissue 25,779. Liquid development of the latent electrostatic image may also be used. In liquid development, the developing particles are carried to the image-bearing surface in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature, for example, U.S. Pat. 2,907,674 and in Australian Pat. 212,315. In dry develop-

ing processes, the most widely used method of obtaining a permanent record is achieved by selecting a developing particle which has as one of its components a low-melting resin. Heating the powder image then causes the resin to melt or fuse into or on the element. The powder is, therefore, caused to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the electrostatic charge image formed on the photoconductive layer can be made to a second support such as paper which would then become the final print after development and fusing. Techniques of the type indicated are well known in the art and have been described in a number of U.S. and foreign patents, such as U.S. Pat. 2,297,691 and 2,551,582 and in "RCA Review," vol. 15 (1954), pp. 469-484.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A series of coating dopes is prepared, each of which contains the following ingredients:

Binder — poly(4,4' - isopropylidenediphenylene carbonate) -----g--	1.6
Photoconductor—triphenylamine -----g--	0.4
Sensitizer—6,6' - dichloro - 1,1',3,3' - tetraphenyl-imidazo[4,5 - b]quinoxalinocarbocyanine p-toluenesulfonate -----	Varies
Solvent—dichloromethane -----ml--	11.7

The dye concentration in the dopes is set at four different levels of 0.01%, 0.02%, 0.04% and 0.08% by weight based on the weight of solids in the dopes. The ingredients are combined with mild stirring until a uniform solution results. The dope is coated at a wet thickness of 0.004 inch on a conducting support comprising poly(ethylene terephthalate) film base bearing a layer of evaporated nickel having an optical density of about 0.4, which in turn bears a layer of one of two polymeric materials. The first material, identified as "A" in Table III, comprises a terpolymer of about 15 weight percent of methyl acrylate units, about 83 weight percent of vinylidene chloride units, and about 2 weight percent of itaconic acid units. The second material, identified as "B" in Table III, comprises a tetrapolymer of about 10 weight percent of methyl acrylate units, about 15 weight percent of acrylonitrile units, about 69 weight percent of vinylidene chloride units, and about 6 weight percent of acrylic acid units. As a control, another piece of film support is coated with a conducting layer comprising the sodium salt of a carboxy ester lactone of a copolymer of maleic anhydride and vinyl acetate, as disclosed in Minsk et al. U.S. Pat. 3,260,706, issued July 12, 1966. After coating, the elements are dried by holding them at room temperature for at least 24 hours to remove residual solvent. The thus cured elements are each charged in turn under a negative corona source until the surface potential, as measured by an electrometer probe, reaches about 600 volts. The charged element is then exposed to a 3000° K. tungsten light source through a stepped density gray scale. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential, V_0 , to some lower potential, V , whose exact value depends on the actual amount of exposure in meter-candle-seconds received by the area. The results of these measurements are then plotted on a graph of surface potential V vs. log exposure for each step. The actual negative speed of the photoconductive composition can then be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily selected value. Herein, unless otherwise stated, the actual negative speed is the numerical expression of 10^4 divided by the exposure in meter-candle-seconds required to reduce the 600 volt charged surface potential

to a value of 100 volts. Speeds thus determined are referred to as negative 100 volt toe speeds. Speeds obtained in this manner are listed in Table III below.

TABLE III

Dye concentrate	Speed of—		Speed control
	Sub "A"	Sub "B"	
Grams			
0.01-----		12	
0.02-----		29	1.
0.04-----	29	45	1.
0.08-----	29	50	5.

The table clearly shows the speed advantage gained using the method and improved elements of this invention.

EXAMPLE 2

The procedure of Example 1 is followed using instead the sensitizer 6-chloro-1'-methyl-1,2',3'-triphenylimidazo[4,5-b]quinoxalino-3'-indolocarbocyanine p-toluenesulfonate at a concentration of 0.016 gram in the same composition. The speed of an element containing Sub "B" of Example 1 is measureably greater than that of an element comprising the control sub of Example 1. Again, the advantage gained using the method and improved elements of this invention is clearly seen.

EXAMPLE 3

The procedure of Example 1 is followed using instead the binder poly[4,4'-isopropylidenebis(phenyleneoxyethylene)-co-ethylene terephthalate] and the sensitizer of Example 1 in an amount of 0.016 gram. The speed of an element comprising Sub "A" of Example 1 is 70, while the speed of an element comprising the control sub of Example 1 is 40. Again, there is seen to be a clear advantage to the use of the method and element of this invention.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method for preparing a homogeneous dye-sensitized electrophotographic element comprising a conductive support, a layer of dye and a photoconductive composition, said process comprising the steps of:

- coating on said conductive support a first layer comprising a film-forming polymeric material having a greater affinity for the dye than does the photoconductive composition;
- coating a thin film of a solution onto the first layer, said solution comprising an organic photoconductor, an electrically insulating film-forming polymeric binder having a lower affinity for the dye than does the polymeric material of the first layer, and a sensitizing amount of a sensitizing dye for the photoconductor in a mutual solvent capable of causing at least limited swelling of the first layer; and
- allowing the dye to be preferentially absorbed out of at least the zone of the photoconductive layer adjacent to the first polymeric layer into the first polymeric layer after the photoconductive layer is coated.

2. The method as described in claim 1 including the step of removing the solvent after the thin film is coated.

3. The method as described in claim 1 wherein the sensitizing dye is present in the solution in a concentration of from about 0.01 percent to about 15 percent by weight based on the combined weight of photoconductor and binder.

4. The method as described in claim 1 wherein the sensitizing dye is a cyanine dye.

5. The method as described in claim 4 wherein the sensitizing dye is selected from the group consisting of 6,6'-dichloro-1,1',3,3'-tetraphenylimidazo[4,5-b]quinoxalinocarbocyanine p-toluenesulfonate and 6-chloro-1'-methyl-1,2',2'-triphenylimidazo[4,5-b]quinoxalino-3'-indolocarbocyanine p-toluenesulfonate.

6. The method as described in claim 1 wherein the first layer has a dry thickness between about 0.05 and about 0.5 micron.

7. The method as described in claim 1 wherein the film-forming polymeric binder for the photoconductor is selected from the group consisting of poly(4,4'-isopropylidenediphenylene carbonate) and poly[4,4'-isopropylidenebis(phenyleneoxyethylene)-co-ethylene terephthalate].

8. The method as described in claim 1 wherein the photoconductor is selected from the group consisting of arylamines, polyaryl alkanes, 4-diarylamino-substituted chalcones, non-ionic cycloheptenyl compounds, compounds containing an



nucleus, 3,3'-bis-aryl-2-pyrazolines, triarylamines containing an active hydrogen-containing group, and organo-metallic compounds having at least one aminoaryl substituent attached to a Group IVa or Group Va metal atom.

9. A method for preparing a homogeneous dye-sensitized electrophotographic element comprising a conductive support, a layer of dye and a photoconductive composition, said process comprising the steps of:

- providing a conductive support;
- coating on the support a first layer comprising a film-forming polymeric material having a greater affinity for the dye than does the photoconductive composition and comprising a hydrosol polymer of vinylidene chloride groups as the major constituent and methyl acrylate groups and acid groups selected from the group consisting of itaconic acid groups and acrylic acid groups as minor constituents;
- preparing a solution of an organic photoconductor, an electrically insulating film-forming polymeric binder having a lower affinity for the dye than does the polymeric material of the first layer, and a sensitizing amount of a sensitizing dye for the photoconductor in a mutual solvent;
- coating a thin film of the solution onto the first layer; and
- allowing the dye to be preferentially absorbed out of at least the zone of the photoconductive layer adjacent to the first polymeric layer into the first polymeric layer after the photoconductive layer is coated.

10. The method as described in claim 9 wherein the hydrosol polymer additionally contains acrylonitrile groups as a minor constituent.

11. The method as described in claim 10 wherein the hydrosol polymer comprises from about 5 to about 20 percent by weight of methyl acrylate groups, from about 5 to about 20 percent by weight or acrylonitrile groups, from about 15 to about 90 percent by weight of vinylidene chloride groups, and from about 0.5 to about 10 percent by weight of acrylic acid groups.

12. The method as described in claim 9 wherein the solvent is a volatile halogenated hydrocarbon.

13. The method as described in claim 12 wherein the solvent is a halogenated lower alkane having from 1 to about 3 carbon atoms.

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14. The method as described in claim 13 wherein the solvent is dichloromethane.

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CHARLES E. VAN HORN, Primary Examiner

U.S. Cl. X.R.

96—1.5, 1.6; 117—215, 218

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,548 Dated August 15, 1972

Inventor(s) L. E. Contois

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 8, "carbazoyl" should read ---carbazolyl---;
line 25, "substituted" (second occurrence) should read
---unsubstituted---.

Column 10, line 67, that part of formula reading "Ar"
should read ---Ar₂---.

Column 15, line 10, that part of formula reading
"9-(carbazolyl)" should read --- 9-(9-carbazolyl) ---.

Column 21, lines 10-13, under table heading "Speed
control", the numbers set forth as:

1.	should read	0
1.		1.2
5.		1.6
		5.7

Claim 11, column 22, line 67, "or" should read ---of---.

Signed and sealed this 6th day of March 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents