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3,591,374

**PYRYLIUM DYE OVERCOATING OF PYRYLIUM DYE SENSITIZED PHOTOCONDUCTIVE ELEMENTS**

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No Drawing. Continuation-in-part of application Ser. No. 708,805, Feb. 28, 1968. This application Oct. 1, 1968, Ser. No. 764,302

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U.S. Cl. 96-1.6

12 Claims

**ABSTRACT OF THE DISCLOSURE**

High speed electrophotographic elements are prepared by forming a photoconductive composition comprising an organic photoconductor sensitized with a two-phase heterogeneous combination of a sensitizing dye and a film-forming hydrophobic polymer, coating this composition onto a conducting support and then overcoating the composition with a solution of a sensitizing dye in a volatile halogenated hydrocarbon solvent.

This application is a continuation-in-part application based on U.S. application Ser. No. 708,805, filed Feb. 28, 1968, now abandoned.

This invention relates to electrophotography and to photoconductive elements and structures useful in electrophotography. In addition, this invention relates to methods for preparing electrophotographic elements.

Electrophotographic imaging processes and techniques have been extensively described in both the patent and other literature, for example, U.S. Pat. Nos. 2,221,776; 2,277,013; 2,297,691; 2,357,809; 2,551,582; 2,825,814; 2,833,648; 3,220,324; 3,220,831; 3,220,833 and many others. Generally, these processes have in common the steps of employing a normally insulating photoconductive element which is prepared to respond to imagewise exposure with electromagnetic radiation by forming a latent electrostatic charge image. A variety of subsequent operations, now well known in the art, can then be employed to produce a permanent record of the image.

One type of photoconductive insulating structure or element particularly useful in electrophotography utilizes a composition containing a photoconductive insulating material. A unitary electrophotographic element is generally produced in a multilayer type of structure by coating a layer of the photoconductive composition onto a film support previously overcoated with a layer of conducting material or the photoconductive composition may be coated directly onto a conducting support of metal or other suitable conducting material. Such photoconductive compositions have shown improved speed and/or spectral response, as well as other desired electrophotographic characteristics when one or more photosensitizing materials or addenda are incorporated into the photoconductive composition. Typical addenda of this latter type are disclosed in U.S. Pat. Nos. 3,250,615, 3,141,770 and 2,987,395. Generally photosensitizing addenda to photoconductive compositions are incorporated to effect a change in the sensitivity or speed of a particular photoconductor system and/or a change in its spectral response characteristics. Such addenda can enhance the sensitivity of an element to radiation at a particular wavelength or to a broad range of wavelengths where desired. The mechanism of such sensitization is presently not fully understood. The phenomenon, however, is extremely useful. The importance of such effects is evidenced by the extensive search currently conducted by workers in the art for compositions and compounds which are capable of photosensitizing photoconductive compositions in the manner described.

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Usually the desirability of a change in electrophotographic properties is dictated by the end use contemplated for the photoconductive element. For example, in document copying applications the spectral electrophotographic response of the photoconductor should be capable of reproducing the wide range of colors which are normally encountered in such use. If the response of the photoconductor falls short of these design criteria, it is highly desirable if the spectral response of the composition can be altered by the addition of photosensitizing addenda to the composition. Likewise, various applications specifically require other characteristics such as the ability of the element to accept a high surface potential, and exhibit a low dark decay of electrical charge. It is also desirable for the photoconductive element to exhibit high speed as measured in an electrical speed or characteristic curve, a low residual potential after exposure, and resistance to fatigue. Sensitization of many photoconductive compositions by the addition of certain dyes selected from the large number of dyes presently known has hitherto been widely used to provide for the desired flexibility in the design of photoconductive elements in particular photoconductor-containing systems. At the present time, however, no photosensitizer addenda to photoconductor compositions or elements have been shown to the art which are capable of producing a significant improvement in substantially all of the aforementioned desirable characteristics. Conventional dye addenda to photoconductor compositions have generally shown only a limited capability for over-all improvement in the totality of electrophotographic properties which cooperate to produce a useful electrophotographic element or structure. The art is still searching for improvements in shoulder and toe speeds, improved solid area reproduction characteristics, rapid recovery and useful electrophotographic speed from either positive or negative electrostatic charging.

A high speed "aggregate" photoconductive system was developed by William A. Light which overcomes many of the problems of the prior art. This aggregate composition is the subject matter of copending application Ser. No. 674,005, filed Oct. 9, 1967, now abandoned. However, there is a need for photoconductive elements of even higher electrophotographic speeds.

It is, therefore, an object of this invention to provide the art of electrophotography with novel photoconductive elements having improved electrophotographic speeds.

It is a further object of this invention to provide a novel method for preparing higher speed photoconductive elements.

It is another object of this invention to provide a novel means for increasing the electrophotographic speeds of aggregate photoconductive compositions.

It is likewise an object of this invention to provide novel photoconductive elements having high relative efficiency when electrically charged to a negative potential.

These and further objects and advantages of the invention will become apparent from the following description of the invention.

It has been discovered that when the heterogeneous or aggregate photoconductive compositions of William A. Light are overcoated in a certain manner, a large increase in electrophotographic speed can be effected. In particular, when such aggregate compositions are overcoated with one or more coatings of a solution of a sensitizing dye of the type useful in the aggregate composition, the electrophotographic speed can be substantially increased.

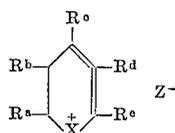
The aggregate photoconductive compositions are in general composed of a photoconductor sensitized with a sensitizing composition comprising a two-phase heterogeneous combination of a sensitizing dye and a film-forming hydrophobic polymer. Many dyes and mixtures of dyes, such as pyrylium dyes, including pyrylium, selen-

pyrylium and thiapyrylium dye salts, are useful in forming these heterogeneous compositions. These heterogeneous compositions are formed by combining the sensitizing dye with the hydrophobic polymer under conditions which result in the formation of a separately identifiable two-phase state having a radiation absorption maximum that is substantially shifted from the radiation maximum characteristic of the dye simply dissolved in the polymer.

The aggregate photoconductive compositions can be prepared in a variety of ways. A solution containing the constituents of the aggregate photoconductive compositions can be coated in the form of a layer in a conventional manner onto a suitable support and the formation of the aggregate composition of the invention achieved in situ in the formed layer. One technique for converting a homogeneous coating of dye and polymer to the heterogeneous system is by prolonged contact of the coating to vapors of solvent which are capable of softening the layer, the dye being caused to migrate and form aggregates in a two phase system. Usually such vapor exposure is effective to permit formation of a substantial amount of the heterogeneous compositions from the dye and polymer in about two minutes at about 70° F. Likewise, inhibition of solvent removal in an otherwise normal coating operation of a dope solution made up of the dye and polymer can form the heterogeneous compositions. Similarly, immersing the homogeneous coating in a solvent, or coating from an original solvent mixture which contains a high boiling solvent which persists in the coating during drying, are among other methods of forming the heterogeneous compositions. Still another useful method of forming the aggregate photoconductive compositions is by vigorous, high speed shearing of the constituents, coating of the sheared solution, and drying.

The compositions when formed in situ in a photoconductive layer have an identifiable heterogeneous appearance when viewed under 2500× magnification, although such compositions may appear to be substantially optically clear to the naked eye in the absence of magnification. The aggregate compositions can, however, exhibit a macroscopic heterogeneity. Typically the aggregate in the discontinuous phase is predominantly in the size range of about .1 to 25 microns.

Sensitizing dyes and hydrophobic polymeric materials are used in forming these heterogeneous compositions. Typically, pyrylium dyes, including pyrylium, thiapyrylium and selenapyrylium dye salts are useful in forming such compositions. Such dyes include those which can be represented by the following general formula:



wherein R<sup>a</sup>, R<sup>b</sup>, R<sup>c</sup>, R<sup>d</sup>, and R<sup>e</sup> 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, onyl, dodecyl, styryl, methoxystyryl, diethoxystyryl, dimethylaminostyryl, 1-butyl-4-p-dimethylaminophenyl-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,

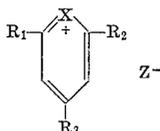
oxygen or selenium atom, and Z is an anionic function, including such anions as perchlorate, fluoroborate, iodide, chloride, bromide, sulfate, sulfonate, periodate, p-toluenesulfonate, hexafluorophosphate, and the like. In addition, the pair R<sup>a</sup> and R<sup>b</sup> as well as the pair R<sup>d</sup> and R<sup>e</sup> can together be the necessary atoms to complete an aryl ring fused to the pyrylium nucleus. 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-amylistyryl)-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.

Compound No.	Name of compound
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.
59	2,6-bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
60	4-anisyl-2,6-bis(4-n-amyloxyphenyl)thiapyrylium chloride.
61	2-[ $\beta$ , $\beta$ -bis(4-dimethylaminophenyl)vinylene]-4,6-diphenylthiapyrylium perchlorate.
62	6-( $\beta$ -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-[ $\beta$ , $\beta$ -bis(4-dimethylaminophenyl)vinylene]-2,4-di-(4-ethylphenyl)pyrylium perchlorate.
68	2,6-bis(4-amyloxyphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
69	6-(3,4-diethoxy- $\beta$ -ethylstyryl)-2,4-diphenylpyrylium fluoroborate.
70	6-(4-methoxy- $\beta$ -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-amyloxyphenyl)thiapyrylium perchlorate.
75	2,6-bis(4-methoxyphenyl)-4-(4-n-amyloxyphenyl)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-phenylbenzo(b)selenapyrylium perchlorate.
79	2-(2,4-dimethoxyphenyl)-4-(4-dimethylaminophenyl)benzo(b)selenapyrylium perchlorate.
80	4-(4-dimethylaminophenyl)-2,6-diphenylselenapyrylium perchlorate.
81	4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenylselenapyrylium perchlorate.
82	4-(4-bis(2-chloroethyl)aminophenyl)-2,6-diphenylselenapyrylium perchlorate.
83	4-(4-dimethylaminophenyl)-2,6-bis(4-ethylphenyl)-selenapyrylium perchlorate.
84	4-(4-dimethylamino-2-methylphenyl)-2,6-diphenylselenapyrylium perchlorate.
85	3-(4-dimethylaminophenyl)naphtho(2,1-b)selenapyrylium perchlorate.
86	4-(4-dimethylaminostyryl)-2-(4-methoxyphenyl)benzo(b)selenapyrylium perchlorate.
87	2,6-di(4-diethylaminophenyl)-4-phenylselenapyrylium perchlorate.
88	4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenylthiapyrylium fluoroborate.
89	4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium hexafluorophosphate.

Particularly useful dyes in forming the feature aggregates are pyrylium dye salts having the formula:



wherein:

$R_1$  and  $R_2$  can each be aryl radicals, such as phenyl and naphthyl, including substituted aryl radicals having at least one substituent chosen from alkyl radicals of from 1 to 6 carbon atoms and alkoxy radicals having from 1 to 6 carbon atoms;

$R_3$  can be an arylamino or alkylamino-substituted aryl radical of from 1 to 6 carbon atoms, including halogenated alkylamino aryl radicals of from 1 to 6 carbon atoms in the alkyl moiety; and

X and Z are the same as above.

While the pyrylium dyes are preferred in preparing the present two phase heterogeneous or aggregate systems, other photographic spectral sensitizing dyes that activate light exposed areas of photographic compositions can be utilized in the hydrophobic polymer of such a system.

Hydrophobic polymers suitable for the formation of the aggregate photoconductive compositions include polydiarylanes such as polycarbonates and polythiocarbonates, polyvinyl ethers, polyesters, poly- $\alpha$ -olefins, phe-

nolic resins, and the like. Typical polymeric materials from these classes are set out in Table 2.

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TABLE 2

No.	Hydrophobic polymeric material
1	Polystyrene.
2	Polyvinyltoluene.
3	Polyvinylanisole.
4	Polychlorostyrene.
5	Poly $\alpha$ -methylstyrene.
6	Polyacenaphthalene.
7	Poly(vinyl isobutyl ether).
8	Poly(vinyl cinnamate).
9	Poly(vinyl benzoate).
10	Poly(vinyl naphthoate).
11	Polyvinyl carbazole.
12	Poly(vinylene carbonate).
13	Polyvinyl pyridine.
14	Poly(vinyl acetal).
15	Poly(vinyl butyral).
16	Poly(ethyl methacrylate).
17	Poly(butyl methacrylate).
18	Poly(styrene-co-butadiene).
19	Poly(styrene-co-methyl methacrylate).
20	Poly(styrene-co-ethyl acrylate).
21	Poly(styrene-co-acrylonitrile).
22	Poly(vinyl chloride-co-vinyl acetate).
23	Poly(vinylidene chloride-co-vinyl acetate).
24	Poly(4,4'-isopropylidenediphenyl-co-4,4'-isopropylidenedicyclohexyl carbonate).
25	Poly(4,4'-isopropylidenebis(2,6-dibromophenyl)carbonate).
26	Poly(4,4'-isopropylidenebis(2,6-dichlorophenyl)carbonate).
27	Poly(4,4'-isopropylidenebis(2,6-dimethylphenyl)carbonate).
28	Poly(4,4'-isopropylidenediphenyl-co-1,4-cyclohexyldimethylcarbonate).
29	Poly(4,4'-isopropylidenediphenyl terephthalate-co-isophthalate).
30	Poly(3,3'-ethylenedioxyphenyl thiocarbonate).
31	Poly(4,4'-isopropylidenediphenyl carbonate-coterephthalate).
32	Poly(4,4'-isopropylidenediphenyl carbonate).
33	Poly(4,4'-isopropylidenediphenyl thiocarbonate).
34	Poly(2,2-butanebis-4-phenyl carbonate).
35	Poly(4,4'-isopropylidenediphenyl carbonate-blockethylene oxide).
36	Poly(4,4'-isopropylidenediphenyl carbonate-blocktetramethyleneoxide).
37	Poly(4,4'-isopropylidenebis(2-methylphenyl)carbonate).
38	Poly(4,4'-isopropylidenediphenyl-co-1,4-phenylene carbonate).
39	Poly(4,4'-isopropylidenediphenyl-co-1,3-phenylene carbonate).
40	Poly(4,4'-isopropylidenediphenyl-co-4,4'-diphenyl carbonate).
41	Poly(4,4'-isopropylidenediphenyl-co-4,4'-oxydiphenyl carbonate).
42	Poly(4,4'-isopropylidenediphenyl-co-4,4'-carbonyldiphenyl carbonate).
43	Poly(4,4'-isopropylidenediphenyl-co-4,4'-ethylenediphenyl carbonate).
44	Poly(4,4'-methylene bis(2-methylphenyl)carbonate).
45	Poly[1,1-(p-bromophenylethane)bis(4-phenyl)carbonate].
46	Poly(4,4'-isopropylidenediphenyl-co-sulfonyl bis(4-phenyl)carbonate).
47	Poly[1,1-cyclohexane bis(4-phenyl)carbonate].
48	Poly(4,4'-isopropylidenediphenoxydimethylsilane).
49	Poly[4,4'-isopropylidene bis(2-chlorophenyl)carbonate].
50	Poly( $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-p-xylylene bis(4-phenyl carbonate)).
51	Poly(hexafluoroisopropylidenedi-4-phenyl carbonate).
52	Poly(dichlorotetrafluoroisopropylidenedi-4-phenyl carbonate).
53	Poly(4,4'-isopropylidenediphenyl-4,4'-isopropylidenedibenzoate).
54	Poly(4,4'-isopropylidenedibenzyl-4,4'-isopropylidenedibenzoate).
55	Poly(4,4'-isopropylidenedi-1-naphthyl carbonate).
56	Poly(4,4'-isopropylidene bis(phenoxy-4-phenyl sulfonate)).
57	Acetophenone-formaldehyde resin.
58	Poly(4,4'-isopropylidene bis(phenoxyethyl)-coethylene terephthalate).
59	Phenol-formaldehyde resin.
60	Polyvinyl acetophenone.
61	Chlorinated polypropylene.
62	Chlorinated polyethylene.
63	Poly(2,6-dimethylphenylene oxide).
64	Poly(neopentyl-2,6-naphthalenedicarboxylate).
65	Poly(ethylene terephthalate-co-isophthalate).
66	Poly(1,4-phenylene-co-1,3-phenylene succinate).
67	Poly(4,4'-isopropylidenediphenyl phenylphosphonate).
68	Poly(m-phenylcarboxylate).
69	Poly(1,4-cyclohexanedimethyl terephthalate-co-isophthalate).
70	Poly(tetramethylene succinate).
71	Poly(phenolphthalein carbonate).
72	Poly(4-chloro-1,3-phenylene carbonate).
73	Poly(2-methyl-1,3-phenylene carbonate).
74	Poly(1,1-bi-2-naphthyl thiocarbonate).
75	Poly(diphenylmethane bis-4-phenyl carbonate).
76	Poly[2,2-(3-methylbutane)bis-4-phenyl carbonate].
77	Poly[2,2-(3,3-dimethylbutane)bis-4-phenyl carbonate].
78	Poly[1,1-(1-naphthyl)bis-4-phenyl carbonate].
79	Poly[2,2-(4-methylpentane)bis-4-phenyl carbonate].
80	Poly(4,4'-(2-norbornylidene)diphenyl carbonate).
81	Poly(4,4'-(hexahydro-4,7-methanoindan-5-ylidene) diphenyl carbonate).

Included among the preferred polymers used for preparing the two phase heterogeneous compositions, in-



Inventor:	U.S. Pat. No.
Sues et al. -----	3,127,266
Schlesinger -----	3,130,046
Cassiers -----	3,131,060
Schlesinger -----	3,139,338
Schlesinger -----	3,139,339
Cassiers -----	3,140,946
Davis et al. -----	3,141,770
Ghys -----	3,148,982
Cassiers -----	3,155,503
Cassiers -----	3,131,060
Cassiers -----	3,158,475
Tomanek -----	3,161,505
Schlesinger -----	3,163,530
Schlesinger -----	3,163,531
Schlesinger -----	3,163,532
Hoegl -----	3,169,060
Stumpf -----	3,174,854
Klupfel et al. -----	3,180,729
Klupfel et al. -----	3,180,730
Neugebauer -----	3,189,447
Neugebauer -----	3,206,306
Fox -----	3,240,597
Schlesinger -----	3,257,202
Sues et al. -----	3,257,203
Sues et al. -----	3,257,204
Fox -----	3,265,496
Kosche -----	3,265,497
Noe et al. -----	3,274,000

The electrophotographic speeds of such aggregate photoconductive compositions can be substantially increased in accordance with this invention by overcoating the compositions with at least one coating of a solution of a sensitizing dye of the type described above used in preparing the aggregate compositions. Many dyes and mixtures thereof, such as pyrylium dyes, including such pyrylium dyes as pyrylium, selenapyrylium and thiapyrylium dye salts, listed above, are useful in the overcoating procedure of this invention. Although the dyes useful in the overcoating solution include any of the dyes that will form the so-called aggregate with a hydrophobic polymer, the dye used in a particular overcoat application need not be exactly the same as the dye in the aggregate base layer. Preferably, however, the dye used in the overcoat is comparable in structure to the dye in the aggregate photoconductive layer.

The solvents useful for preparing the overcoating solutions of this invention can be widely varied among polar hydrocarbon coating solvents. Preferred solvents are halogenated hydrocarbon coating solvents. The solvent, of course, must be one which will dissolve the dye chosen. In addition, the solvent must be such that it is capable of at least causing swelling of the polymer component of the aggregate photoconductive composition. The solvent must be volatile and preferably has a boiling point of less than 200° C. Particularly useful solvents include halogenated lower alkanes having from 1 to 3 carbon atoms, such as dichloromethane, dichloroethane, dichloropropane, trichloromethane, trichloroethane, tribromomethane, trichloromonofluoromethane, trichlorotrifluoroethane, etc.; halogenated benzene compounds such as chlorobenzene, bromobenzene, dichlorobenzene, etc.; and the like.

The present invention is not limited to only one overcoating step. In fact, aggregate photoconductive elements overcoated a number of times with the dye solutions of this invention show electrophotographic speed increases with each new overcoat. However, from the point of practicality, more than about eight overcoats may not be justified by the decreasing effective speed increase attributable to an additional overcoat.

The concentration of dye in the overcoating solution can be varied considerably, being limited, of course, by

the solubility of a particular dye in a particular solvent. Higher concentrations of dye are preferred as low dye concentrations give only small speed increases. In addition, the dye solution can contain other materials in order to facilitate coating, such as a material to increase the solution viscosity. Polymeric materials, such as high viscosity carbonates prepared with Bisphenol A are just one example of materials that can be used to increase the solution viscosity. When coating these solutions, it has been found that the coating rate can be varied. However, coverage rates greater than about 3 ml./ft.<sup>2</sup> are typically avoided to minimize mottling in the coating. Also, it has been noted that the coating rate is substantially independent of dye concentration or solution viscosity.

It has further been found that the total dye concentration in an overcoated aggregate composition of this invention is not the sole reason for the increased electrophotographic speeds. A typical comparison of an ordinary non-overcoated photoconductive element having an aggregate photoconductive composition coating containing dye in a concentration equal to the total dye concentration of an overcoated aggregate photoconductive composition of this invention shows the latter to be faster by a factor of four times the speed of the former. Such a comparison clearly shows that the speed increases obtained in accordance with the invention are not merely dependent upon dye concentration but, rather the speed increases are a result of the cooperating combination of an overcoat of sensitizing dye on an aggregated photoconductive composition.

The dye overcoats of this invention are imbibed into the photoconductive layer such that there is little or no dimensional change in the thickness of the layer after overcoating. Normally the base photoconductive layers, which are overcoated in accordance with this invention, range in thickness from about 5 to about 15 $\mu$ .

Another feature of this invention is the fact that the dye in the overcoat solution changes its radiation absorption characteristics after being imbibed into the base photoconductive layer. The radiation absorption maximum of the dye or dyes after imbibition in accordance with this invention is substantially shifted from the radiation absorption maximum of the dye or dyes when merely in solution. Such an absorption maximum shift after imbibition is generally of the magnitude of at least about 10  $m\mu$ .

In general, the present invention is practiced by forming a layer of an aggregate photoconductive composition on a conducting support and then overcoating the photoconductive layer one or more times with a solution containing a sensitizing dye of the type referred to above. The dye solution is imbibed into the photoconductive layer and the solvent is evaporated. The resultant electrophotographic element can then 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, and 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 are using a magnetic brush toner applicator are described in the following U.S. Pats.: 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 Australian Pat. 212,315. In dry developing 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) pages 469-484.

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

#### EXAMPLE 1

An aggregate photoconductive composition is prepared in accordance with the method disclosed in E. P. Gramza U.S. application Ser. No. 674,006, filed Oct. 9, 1967, now abandoned, by vigorous, high speed shearing of a solution having a solids content of about 10% of a mixture of approximately 3% by weight of 4-(4-dimethylamino-phenyl)-2,6-diphenylthiapyrylium perchlorate sensitizing dye salt, 39% of 4,4'-diethylamino-2,2'-dimethyltriphenylmethane photoconductor and 58% of a polycarbonate resin formed from the reaction between phosgene and a dihydroxydiarylalkane or from the ester exchange between diphenylcarbonate and 2,2-bis-4-hydroxyphenyl propane ("Lexan 105" polycarbonate resin, General Electric Company). This composition is then wet-coated onto a conducting support which comprises high vacuum evaporated nickel film coated on a poly(ethylene terephthalate) film base which is subbed with a terpolymer of 2% by weight itaconic acid, 15% methylacrylate and 83% vinylidene chloride. The coating is allowed to dry and when dry has a thickness of about 10 $\mu$ . The resultant electrophotographic element is then electrostatically charged under a 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. All exposures are also through a short wavelength pass interference filter having 30% transmittance at 600 m $\mu$ . The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential, V<sub>0</sub>, 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 positive or negative speed of the photoconductive composition can then be expressed in terms of the recip-

rocal of the exposure required to reduce the surface potential to any fixed arbitrarily selected value. Herein, unless otherwise stated, the actual positive or negative speed is the numerical expression of 10<sup>4</sup> divided by the exposure in meter-candle-seconds required to reduce the 600 volt charged surface potential to a value of 50 volts. Speeds thus determined are referred to as positive or negative 50 volt toe speeds. The speed of the non-overcoated element is recorded in Table 5 below. Next, the photoconductive composition on the above element is overcoated from an extrusion hopper with a 0.45% solution of 4-(4 - dimethylamino-phenyl)-2,6-diphenylthiapyrylium perchlorate in dichloromethane. The dye solution is coated at a rate of 2 ml./ft.<sup>2</sup>/pass which is equal to 12 mg. dye/ft.<sup>2</sup>/pass. The speed is then measured in accordance with the above procedure. Next, the element is overcoated a second and third time measuring the speeds after each overcoat. The speeds are shown in the table below.

TABLE 5

	Optical density at 600 m $\mu$	Speed - 50 v. (toe speed)
No overcoat (control).....	0.98	900
1 overcoat.....	1.55	1,400
2 overcoats.....	2.07	1,800
3 overcoats.....	2.68	2,000

The above comparison shows that increases in speed can be obtained with each new coating. Similar results are obtained using 1,1,2-trichloroethane, mixtures of methylene chloride and trichloroethane or using bromoform as the solvent in the dye overcoat. In addition, similar results are obtained when the dye in the overcoat solution is not the same as the dye in the aggregate photoconductive composition. For example, when 4-(4-dimethylamino-phenyl)-2,6-diphenylthiapyrylium fluoroborate is used in solution to overcoat an element identical to the one above, similar increases in speed are seen with each overcoat. The charged and exposed electrophotographic elements described can be developed to form visible images with liquid developers of the type described in U.S. Pat. 2,907,674.

#### EXAMPLE 2

A first electrophotographic element with no overcoat is prepared in accordance with the procedure of Example 1, only 10 parts of the sheared photoconductive composition are added to 90 parts of the unsheared composition followed by a brief period of shearing. The resultant composition is then coated as in Example 1. Next, a solution of 0.45 weight percent of 4-(4-dimethylamino-phenyl)-2,6-diphenylthiapyrylium perchlorate in methylene chloride is coated over the photoconductive layer of the element. The solution is coated at a rate of 2 cc./ft.<sup>2</sup> per pass. The photoconductive layer is given three of these overcoats. The overcoated element is then measured for optical density. The absolute value for the optical density of the overcoated photoconductive layer is shown in Table 6. The absolute value is the optical density of the completed element less the value (0.5) of the nickel-coated substrate. The completed element is then charged and exposed in the manner of Example 1. The 50 volt negative toe speed is shown in the table below. Next, a second element is prepared having a dye concentration, as measured by the optical density of the photoconductive layer, similar to that of the first element above. The photoconductive composition for the second element contains 55% by weight of a polymeric mixture of 50% by weight of the polycarbonate resin of Example 1 and 50% by weight of high viscosity polycarbonate prepared with Bisphenol A and having a viscosity of 2.70 centipoises, 40% of 4,4'-diethylamino-2,2'- dimethyltriphenylmethane photoconductor and 5% of 4 - (4-dimethylamino-phenyl)-2,6-diphenylthiapyrylium perchlorate sensitizing dye salt. This composition is then subjected to vigorous, high-speed shearing and then used to prepare an electrophotographic

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element by coating onto a support as in Example 1. This second element is allowed to dry thus forming an aggregated photoconductive composition and is measured for optical density and for the 50 volt toe speed as with the first element. The results of these measurements are shown in Table 6 below.

TABLE 6

	Absolute optical density at 600 m $\mu$	Speed -50 v. (toe speed)
Second element, no overcoat.....	1.43	450
First element, overcoated.....	1.40	1,800

This comparison shows that the increase in electrophotographic speed is not simply a function of dye concentration as the second element has a slightly greater dye concentration but is four times slower than the first element.

## EXAMPLE 3

A non-overcoated electrophotographic element is prepared as in Example 1 and used as a control. Next, a second element is prepared similar to the first and overcoated as in Example 1 using only the dye solvent, methylene chloride, with no dye present. Finally, a third electrophotographic element is prepared as above and overcoated with a solution of about 0.4 weight percent of 4-(4-dimethylaminophenyl) - 2,6 - diphenylthiapyrylium perchlorate in methylene chloride. Both are second and third elements are overcoated at a rate of 2 ml./ft.<sup>2</sup>. Next, all three electrophotographic elements are measured for electrical speed in accordance with the procedure of Example 1. The positive and negative speeds are shown in Table 7 below.

TABLE 7

	Electrical speed	
	+50 toe	-50 toe
First element (no overcoat).....	900	1,000
Second element (solvent overcoat).....	630	900
Third element (solvent plus dye overcoat).....	1,200	1,800

This example shows that the coating solvent itself does not contribute to the speed increase of a fully aggregated photoconductive composition.

## EXAMPLE 4

Example 1 is repeated using bis(4-diethylamino)-1,1,1-triphenylethane in place of the 4,4'-diethylamino-2,2'-dimethyltriphenylmethane as the photoconductor. The resultant non-overcoated electrophotographic element is measured for electrical speed and is then overcoated as in Example 1 with two coatings of the dye solution and measured again for electrical speed. Optical density and electrical speed measurements are shown in Table 8 below.

TABLE 8

	Total optical density at 600 m $\mu$	Speed -50 v. (toe speed)
Control (no overcoat).....	0.76	710
2 overcoats.....	1.79	1,400

## EXAMPLE 5

Example 1 is repeated with the aggregate photoconductive composition being coated without an overcoat to produce a layer thickness of 12.5 m $\mu$  dry. The resultant electrophotographic element is then measured for total optical density and electrical speed. Next, the element is given one overcoat of dye as in Example 1 and measured again for density and speed. The element is then overcoated two more times and measured for optical

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density and electrical speed. The results of these measurements are shown in Table 9 below.

TABLE 9

	Total optical density at 600 m $\mu$	Speed -50 v. (toe speed)
Control (no overcoat).....	1.25	1,100
1 overcoat.....	2.00	1,800
3 overcoats.....	2.95	2,500

## EXAMPLE 6

A non-overcoated electrophotographic element is prepared and measured as in Example 1. Next, the element is given an overcoat of a 1.25% solution of 4-(4-dimethylaminophenyl) - 2,6 - diphenylthiapyrylium fluoroborate in methylene chloride. The dye solution is coated at a rate of 1.5 cc./ft.<sup>2</sup>. After allowing the overcoat to dry, the element is measured for optical density and electrical speed. Table 10 shows the density and speed measurements.

TABLE 10

	Total optical density at 600 m $\mu$	Speed -50 v. (toe speed)
Control (no overcoat).....	0.96	1,000
1 overcoat.....	1.76	1,400

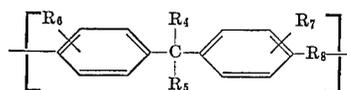
## EXAMPLE 7

A non-overcoated electrophotographic element is prepared in accordance with the procedure of Example 1 using 4 - (4-dimethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate as the dye in the aggregated photoconductive composition. After drying, the photoconductive layer is overcoated with two coatings of the dye overcoat solution of Example 1. After final drying the element is charged as previously described and imaged exposed. The latent electrostatic image is then developed by cascade development, as described in U.S. Pat. No. 2,618,552, using a developer mix composed of glass beads and a toner powder of polystyrene and carbon black. This mix is cascaded across the surface of the photoconductive layer and the electroscopic toner powder adheres to the charged areas of the latent electrostatic image. The resultant developed image is then transferred to a receiving sheet and the powder image is fused by heating. A good image results.

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 as described hereinabove and as defined in the appended claims.

I claim:

1. A method of increasing the electrophotographic speed of a heterogeneous photoconductive composition comprising an organic photoconductor and a two phase combination of a pyrylium dye and a polymer having the following recurring unit:



wherein:

each of R<sub>4</sub> and R<sub>5</sub>, when taken separately, is selected from the group consisting of a hydrogen atom, an alkyl radical of from 1 to 10 carbon atoms and a phenyl radical and R<sub>4</sub> and R<sub>5</sub>, when taken together, are the carbon atoms necessary to form a cyclic hydrocarbon radical, the total number of carbon atoms in R<sub>4</sub> and R<sub>5</sub> being up to 19;

R<sub>6</sub> and R<sub>7</sub> are each selected from the group consisting of hydrogen, alkyl radicals of from 1 to 5 carbon atoms, alkoxy radicals of from 1 to 5 carbon atoms and a halogen; and

