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3,141,770

ELECTROPHOTOGRAPHIC LAYERS AND SENSITIZERS FOR SAME

Dale R. Davis, Cornelia C. Natale, and Charles J. Fox, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
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The present invention relates to electrophotography and to photoconductive substances for preparing photoconductive layers for use in processes of electrophotography. More particularly, the present invention relates to such layers having incorporated novel sensitizing compounds.

Electrophotographic processes which depend on photoconductive layers include (a) xerographic processes in which, for example, a photoconductive layer on an electrically conducting support is provided with a uniform electrostatic charge in the dark, given an image exposure to light which causes the charge to be selectively dissipated in proportion to the intensity of the incident radiation, and then toned with a powder having optical density which adheres in the areas of residual charge, and (b) photoconductographic processes in which, for example, a photoconductive layer provides in areas of image exposure sufficient conductivity to enable formation of a visible image by an electrolytic process activated by an externally applied source of electric current. Processes of these types have been described in such U.S. and foreign patents as U.S. 2,297,691; 2,551,582 and in British 188,030 and 464,112.

Photoconductive layers for use in electrophotographic processes of the present type have been prepared in the past using such photoconductors as selenium, cadmium sulfide and zinc oxide. More recently, certain organic compounds have been proposed for use as photoconductors in photoconductive layers. Organic compounds, although preferred for other reasons, such as their capacity to form transparent layers and the like, have not shown in many cases a sensitivity to light to give the speed values desired in layers of this type. A number of sensitizing compounds have been disclosed recently in the prior art for use with certain of the organic-type photoconductor compounds. It is an object of the present invention to disclose still other classes of sensitizing compounds for use in combination with certain organic photoconducting compounds so that improved speed in photoconducting layers is obtained. An object of the present invention, accordingly, is to provide novel sensitizing compounds for use in photoconductive electrophotographic layers. Another object is to provide novel photoconductive layers having improved photoelectric speed. Other objects will become apparent from a reading of the specification and appended claims.

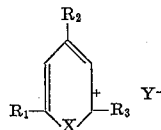
These objects are accomplished by incorporating in arylamine-incorporated photoconductive layers a sensitizing compound for said arylamine comprising a member selected from the group consisting of pyrylium salts and thiapyrylium salts. Arylamines to which we refer in the present specification comprises (1) diarylamines such as 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-phenylene diamine, and the like, and (2) triarylamines including (a) nonpolymeric triarylamines, such as triphenylamine, N,N,N',N'-tetraphenylbenzidine, N,N,N',N'-tetraphenyl-p phenylenediamine, N,N,N',N'-tetraphenyl-m-phenylenediamine, acetyltriphenylamine, hexanoyltriphenylamine, lauroyltriphenylamine, hexyltriphenylamine, dodecyltriphenylamine, hexaphenylpara-

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rosaniline, 4,4'-bis(diphenylamino)benzil, 4,4'-bis(diphenylamino)benzophenone, and the like, and (b) polymeric triarylamines such as poly[N,4'-(N,N',N'-triphenylbenzidine)], polyadipyltriphenylamine, polysebacyltriphenylamine, polydecamethylenetriphenylamine, poly-N-(4-vinylphenyl)diphenylamine, poly-N-(4-vinylphenyl)- α,α' -dinaphthylamine, and the like.

Arylamine compounds of the type described and methods for preparing them have been described in our two copending applications filed on even date herewith in the names of C. J. Fox et al. and C. J. Fox, respectively.

Pyrylium salts and thiapyrylium salts of the present invention comprise compounds represented by the following general formula:



wherein R₁, R₂ and R₃ may each represent an aliphatic group having from 1 to 15 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl, isoamyl, hexyl, octyl, nonyl, dodecyl, vinyl, styryl, alkoxy-styryl, diethoxystyryl, dimethylaminostyryl, 1-butyl-4-p-dimethylaminophenyl-1,3-butadienyl, β -ethyl-4-dimethylaminostyryl; an alkoxy group such as methoxy, ethoxy, propoxy, butoxy, amyloxy, hexoxy, octoxy, etc.; aryl, such as phenyl, 4-biphenyl, alkphenyl, such as 4-ethylphenyl, 4-propylphenyl, etc., alkoxyphenyl, e.g., 4-ethoxyphenyl, 4-methoxyphenyl, 4-amyloxyphenyl, 2-hexoxyphenyl, 2-methoxyphenyl, 2-amylloxyphenyl, 3,4-dimethoxyphenyl, etc.; ω -hydroxy alkoxyphenyl, e.g., 2-hydroxyethoxyphenyl, 3-hydroxyethoxyphenyl, etc., 4-hydroxyphenyl, halophenyl, e.g., 3,4-dichlorophenyl, 3,4-dibromophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, etc., azidophenyl, nitrophenyl, etc., aminophenyl, e.g., 4-diethylaminophenyl, 4-dimethylaminophenyl, etc.; X is a hetero atom, such as oxygen, sulfur and selenium; and Y is an anionic function.

Typical members of the present pyrylium and thiapyrylium salts include the following:

Compound Number	Name of Compound
1	2,4,6-Triphenylpyrylium perchlorate.
2	4-(4-Methoxyphenyl)-2,6-diphenylpyrylium perchlorate
3	4-(2,4-Dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
4	4-(3,4-Dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
5	2,6-Bis(4-methoxyphenyl)-4-phenylpyrylium perchlorate.
6	6-(4-Methoxyphenyl)-2,4-diphenylpyrylium perchlorate.
7	2-(3,4-Dichlorophenyl)-4-(4-methoxyphenyl)-6-phenylpyrylium perchlorate.
8	4-(4-Amyloxyphenyl)-2,6-bis(4-ethylphenyl)pyrylium perchlorate.
9	4-(4-Amyloxyphenyl)-2,6-bis(4-methoxyphenyl)pyrylium perchlorate.
10	2,4,6-Triphenylpyrylium fluoborate.
11	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium perchlorate.
12	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium fluoborate.
13	6-(3,4-Diethoxystyryl)-2,4-diphenylpyrylium perchlorate.
14	6-(3,4-Diethoxy- β -amylstyryl)-2,4-diphenylpyrylium fluoborate.
15	6-(4-Dimethylamino- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
16	6-(1-n-Amyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
17	6-(4-Dimethylaminostyryl)-2,4-diphenylpyrylium fluoborate.
18	6-(α -Ethyl- β , β -dimethylaminophenyl vinylene)-2,4-diphenylpyrylium fluoborate.
19	6-(1-Butyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
20	6-(4-Dimethylaminostyryl)-2,4-diphenylpyrylium perchlorate.
21	6-[β , β -Bis(4-dimethylaminophenyl) vinylene]-2,4-diphenylpyrylium perchlorate.

Compound Number	Name of Compound
22	2,6-Bis(4-dimethylaminostyryl)-4-phenylpyrylium perchlorate.
23	6-(β -Methyl-4-dimethylaminostyryl)-2,4-diphenylpyrylium fluoborate.
24	6-(1-Ethyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
25	6- β -Bis(4-dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium fluoborate.
26	6-(1-Methyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
27	4-(4-Dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate.
28	2,6-Bis(4-ethylphenyl)-4-phenylpyrylium perchlorate.
29	2,6-Bis(4-ethylphenyl)-4-methoxyphenylthiapyrylium fluoborate.
30	2,4,6-triphenylthiapyrylium perchlorate.
31	4-(4-Methoxyphenyl)-2,6-diphenylthiapyrylium perchlorate.
32	6-(4-Methoxyphenyl)-2,4-diphenylthiapyrylium perchlorate.
33	2,6-Bis(4-methoxyphenyl)-4-phenylthiapyrylium perchlorate.
34	4-(2,4-Dichlorophenyl)-2,6-diphenylthiapyrylium perchlorate.
35	2,4,6-Tri(4-methoxyphenyl)thiapyrylium perchlorate.
36	2,6-Bis(4-ethylphenyl)-4-phenylthiapyrylium perchlorate.
37	4-(4-Amyloxyphenyl)-2,6-bis(4-ethylphenyl)thiapyrylium perchlorate.
38	6-(4-Dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
39	2,4,6-Triphenylthiapyrylium fluoborate.
40	2,4,6-Triphenylthiapyrylium sulfate.
41	4-(4-Methoxyphenyl)-2,6-diphenylthiapyrylium fluoborate.
42	2,4,6-Triphenylthiapyrylium chloride.
43	2-(4-Amyloxyphenyl)-4,6-diphenylthiapyrylium fluoborate.
44	4-(4-Amyloxyphenyl)-2,6-bis(4-methoxyphenyl)thiapyrylium perchlorate.
45	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
46	4-Anisyl-2,6-bis(4-n-amylxyphenyl)thiapyrylium chloride.
47	2- β -Bis(4-dimethylaminophenyl)vinylene]-4,6-diphenylthiapyrylium perchlorate.
48	6-(β -Ethyl-4-dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
49	2-(3,4-Diethoxystyryl)-4,6-diphenylthiapyrylium perchlorate.
50	2,4,6-Triphenylthiapyrylium perchlorate.
51	6-Ethyl-2,4-diphenylpyrylium fluoborate.
52	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium chloride.
53	6- β -Bis(4-dimethylaminophenyl)vinylene]-2,4-di(4-ethylphenyl)pyrylium perchlorate.
54	2,6-Bis(4-amylxyphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
55	6-(3,4-Diethoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
56	6-(4-Methoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
57	2-(4-ethylphenyl)-4,6-diphenylthiapyrylium perchlorate.
58	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium perchlorate.
59	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium fluoborate.
60	2,6-bis(4-ethylphenyl)-4-(4-n-amylxyphenyl)thiapyrylium perchlorate.
61	2,6-bis(4-methoxyphenyl)-4-(4-n-amylxyphenyl)thiapyrylium perchlorate.
62	2,4,6-tri(4-methoxyphenyl)thiapyrylium fluoborate.
63	2,4-diphenyl-6(3,4-diethoxystyryl)pyrylium perchlorate.

In preparing photoconductive layers of the present invention, it is the usual practice to dissolve the photoconductive substance in a suitable solvent in the presence of an electrically insulating binder and then to dissolve the sensitizing compound in this composition prior to coating on a conducting support. In those cases where certain polymeric triarylamines of the invention are employed, it is often unnecessary to employ a binder since compositions of this sort usually form self-supporting hydrophobic layers. Where the self-supporting layers are prepared, the sensitizing compound is added to the coating composition prior to coating in the usual manner.

The amount of sensitizer which can be added to a particular composition to give optimum sensitization can vary widely. The optimum amount will, of course, vary with the arylamine photoconductor employed as well as with the particular sensitizing compound. In general, substantial speed gains can be obtained where an appropriate sensitizer is added at a concentration in a range from about 0.0001 to 30 percent by weight based on the weight of the film-forming hydrophobic composition.

Preferred binders for use in preparing the photoconductive layers comprise polymers having fairly high dielectric strength and which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-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(methyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylene-alkaryloxyalkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamide; polycarbonates; 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. Patents 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of this invention are sold under such trade names as Vitel PE-101-X, Cymac, Piccopale 100, and Saran F-220. 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 coating compositions of the present 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.

Photoconductive layers of the present invention can be coated on a conducting support in any well-known manner such as doctor-blade coating, swirling, dip-coating, and the like. Photoconductive layers of the invention in some cases do not require a binder, for example, where certain polymeric arylamines are employed. However, it has been found beneficial sometimes to include in a coating composition of this type at least some binder, for example, as little as 1 weight percent.

In preparing the coating composition, useful results were obtained where the photoconductor substance was 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 is not critical. As indicated previously, the polymeric materials of the present invention in many cases do not require a binder in order to obtain a self-supporting coating on the support. 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 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally a wet coating in the range from about 0.001 inch to about 0.01 inch was useful for the invention. The preferred range of wet coating thickness was found to be in the range from about 0.002 inch to about 0.006 inch.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of the 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; regenerated cellulose and cellulose derivatives; certain polyesters, especially polyesters having a thin electroconductive layer (e.g., cuprous iodide) coated thereon; etc. Suitable supporting materials can also include the humidity-independent conducting layers of semiconductors dispersed in poly-

meric binders, as described in U.S. application Serial No. 56,648, filed September 19, 1960.

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, the electrophotographic element is given a blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer owing to the substantial 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 photoconducting layer is then selectively dissipated from the surface of the layer by exposure to light through a negative by a conventional exposure operation such as, for example, by contact-printing technique, or by lens projection of an image, etc., to form a latent image in the photoconducting layer. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that light causes the charge to leak away in proportion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then developed, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust, i.e., powder, a pigment in a resinous carrier, i.e., toner, or a liquid developer may be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature in such patents, for example, as U.S. Patent 2,296,691 and in Australian Patent 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has as one of its components, a low-melting resin, it is possible to treat the developed photoconductive material with heat and cause the powder to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the image formed on the photoconductive layer can be made to a second support which would then become the final print. 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. Patent 2,297,691 and 2,551,582 and in "RCA Review," vol. 15 (1954), pages 469-484.

The invention will now be further described by reference to the following examples.

EXAMPLE 1

0.056 gram of 4-anisyl-2,6-diphenylthiapyrylium perchlorate sensitizer was dissolved in 8 grams of solvent comprising equal weights of cyclohexanone and methyl alcohol. To this solution was then added with stirring 39 grams of 1,2-dichloropropane and 6 grams of triphenylamine photoconductor followed by 37 grams of 1,2-dichloropropane containing 30 percent of a polyester sold under the trade name of Vitel PE-101-X by the Good-year Tire and Rubber Company. The solution was coated on thin aluminum foil with a 0.002 inch coating knife. The coating block was maintained at 130° F. to promote rapid drying. Alternatively, this solution was coated onto transparent base coated with a transparent conducting layer, such as evaporated aluminum.

In either case, the dried coating was given a negative corona discharge in a well-known manner and exposed for 8 seconds through a positive image transparency to a Kodak No. 1 Photoflood Lamp at a distance of 5 feet. The resulting electrostatic latent image was rendered visible by dusting with an electrostatically attractable powder having optical density according to the method described in U.S. Patent 2,297,691. A high quality positive image of the transparency was obtained.

EXAMPLE 2

In a manner similar to Example 1, good image results were obtained using the following photoconductor substances separately sensitized with 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate at a 0.4 mole percent concentration of sensitizer based on the amount of arylamine present in the coating. The photoconductor substances in the coatings comprised diphenylamine, triphenylamine, N,N'-diphenylbenzidine, α,α' -dinaphthylamine, N-phenyl-1-naphthylamine, N-phenyl-2-naphthylamine, N,N'-diphenyl-p-phenylenediamine, 2-carboxy-5-chloro-4'-methoxydiphenylamine, and p-anilino-phenol. No image was obtained in unsensitized coatings.

EXAMPLE 3

This example shows the improved speed obtained using various sensitizers in electrophotographic materials of the invention where triphenylamine is employed at a 30 percent by weight concentration as the photoconductor substance in a 70 percent polyester photoconductive layer. The polyester is a copolymer obtained from terephthalic acid and a glycol mixture of 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane and ethylene glycol (9:1).

The photoelectric speed values given in the following table are based on the following arbitrary speed scale. The relative speed value of 20 was given to a coating when 57 foot candle seconds of illumination from a 3000° K. tungsten source reduced an electrostatic charge just to the point where no toner would be held by the coating on development. Thus, a coating which required twice this amount of illumination or 114 foot candle seconds to discharge would have a relative speed of 10 and coatings requiring less than 57 foot candle seconds would have speed values greater than 20.

Table 1

Arylamine Photoconductor	Sensitizer	Sensitizer Concentration in Moles/100 Moles of Nitrogen in Layer	Speed
Triphenylamine	None	None	.01
Do	2,4,6-Triphenyl-thiapyrylium fluoborate.	0.5	8
Do	2-(4-ethylphenyl)-4,6-diphenyl thiapyrylium perchlorate.	0.5	15
Do	2,6-diphenyl-4-(4-methoxyphenyl)-thiapyrylium perchlorate.	0.5	20
Do	2,6-diphenyl-4-(4-methoxyphenyl)-thiapyrylium fluoborate.	1.0	60
Do	2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)-thiapyrylium perchlorate.	2.0	80
Do	2,6-bis(4-methoxyphenyl)-4-phenyl-thiapyrylium chloride.	0.5	12
Do	2,6-bis(4-methoxyphenyl)-4-(4-n-amyloxyphenyl)-thiapyrylium perchlorate.	0.1	8
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	0.2	12
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	0.3	30
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	0.4	40
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	0.5	60
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	0.5	6
Do	2,6-bis(4-methoxyphenyl)-4-phenyl-thiapyrylium chloride.	0.5	60
Do	2,6-bis(4-methoxyphenyl)-4-(4-n-amyloxyphenyl)-thiapyrylium perchlorate.	0.5	50
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	1.0	80
Do	2,4,6-tris(4-methoxyphenyl)-thiapyrylium perchlorate.	2.0	100
Do	2,4-diphenyl-6(3,4-diehoxystryryl) pyrylium perchlorate. ¹	0.5	10

¹ Polystyrene replaced Vitel PE-101-X as binder.

EXAMPLE 4

Coatings of triphenylamine derivatives were prepared and sensitized as follows:

In coatings of the example containing a binder, 0.5 gram of the particular photoconductor compound was dissolved in a solution of 2 grams of either polystyrene or Vitel PE-101-X in 15 ml. of tetrahydrofuran. To the resulting dope was added 0.025 g. of 2,6-bis(4-ethylphenyl)-4-(4-amyloxyphenyl)thiapyrylium perchlorate in

0.5 ml. of tetrahydrofuran. This dope was then coated on a conducting support and dried. The resulting element was then charged as in Example 1 and exposed from behind a 0.16 log E step tablet to a 300-watt tungsten exposure source at 9 inches for 30 seconds. The results are shown in Table II. Compounds of the example which would not require a binder were prepared and processed in the same manner except that the coating was prepared by dissolving 2 grams of the photoconductor in tetrahydrofuran to which the same amount of sensitizer was added. Coatings 14 and 15 were prepared in dichloromethane.

Table II

Coating No.	Derivative	Image obtained	Visible steps	
			Poly-styrene	Vitel
1	Triphenylamine	Yes		24
2	Acetyltriphenylamine	Yes		
3	Hexanoyltriphenylamine	Yes	16	11
4	Lauroyltriphenylamine	Yes	15	13
5	Hexyltriphenylamine	Yes	15	14
6	Dodecyltriphenylamine	Yes	11	5
7	Polyadipyltriphenylamine	Yes	124	
8	Polysebacyltriphenylamine	Yes	118	
9	Poly-1,10-decylene triphenylamine	Yes	9	6
10	Poly[N,4'-(N,N',N'-triphenylbenzidine)]	Yes		6
11	N,N,N',N'-tetraphenylbenzidine	Yes		18
12	N,N,N',N'-tetraphenyl-p-phenylenediamine	Yes		19
13	N,N,N',N'-tetraphenyl-m-phenylenediamine	Yes		14
14	Poly-N-(4-vinylphenyl)diphenylamine	Yes	24	
15	Poly-N-(4-vinylphenyl)- α,α' -dimaphthylamine	Yes		

¹ No binder.

Substantially no image was obtained at the exposure level used in the example in control coatings where the coatings were prepared in the same manner as those of Table II except without the use of a thiapyrylium salt sensitizing compound.

Methods for preparing pyrylium and thiapyrylium salts suitable for use in the present invention has been described in the prior art, for example, in *Helvetica Chimica Acta*, 39, 214-216 (1956).

A method of preparation, for example, of 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate comprises mixing 11 grams (0.02 mole) of 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)pyrylium perchlorate in 400 ml. of acetone to which was added a solution of 10 grams Na₂S₉H₂O in 100 ml. of water and allowing the preparation to stand at room temperature for one-half hour after which a 100 ml. solution of 20 percent perchloric acid diluted with 400 ml. of water was added with good stirring. After allowing to stand at room temperature for about two hours, the preparation was washed with ligroin to give a yield of 10 grams.

The pyrylium salt used in the above preparation was prepared by mixing 8.3 grams (0.018 mole) of the crude 1,5-bis(4-ethylphenyl)-3-(4-n-amyloxyphenyl)pentan-1,5-dione with 10 ml. of boron fluoride ethyl ether and allowing the preparation to stand one hour at room temperature followed by warming for one hour on a steam bath. After cooling to room temperature, the preparation was dissolved in 75 ml. of ethyl alcohol containing 2 ml. of 70 percent perchloric acid. The preparation was then filtered, washed with ether and dried to give a yield of about 5.0 grams.

In another method of preparation, 2,4-diphenyl-6(3,4-diethoxystyryl)pyrylium perchlorate cited in a previous example can be prepared by condensing 2,4-diphenyl-6-methyl pyrylium perchlorate with 3,4-diethoxybenzaldehyde.

The sensitizer compound of Example 1, 4-anisyl-2,6-diphenylthiapyrylium perchlorate, was prepared by mixing 14 grams of anisaldehyde, 25 grams of acetophenone and 35 ml. of phosphoryl chloride and warming to 50° C. in a constant temperature bath for two hours. The excess phosphoryl chloride was removed by evaporation and the residue dissolved in 500 ml. of warm alcohol. Some insoluble material was removed by filtration and 10 ml. of perchloric acid (72 percent) was added to the filtrate. The mixture was allowed to stand two hours and the solid was collected, dried and recrystallized from acetonitrile to yield about 13 grams of product. The product was then added to a solution of about 8 grams in about 320 ml. of acetone containing 8 grams of sodium sulfide dissolved in 80 ml. of water. The resulting solution was allowed to stand at room temperature for 0.5 hour and then 80 ml. of 20 percent perchloric acid diluted with 320 ml. of water was added. After standing for two hours, the final thiapyrylium product of the example was collected, dried and recrystallized from acetic anhydride.

Many pyrylium and thiapyrylium salts suitable for use in the present invention and methods of preparation have been described in our copending application VanAllan et al., entitled "Light-Sensitive Layers Containing Pyrylium and Thiapyrylium Salts," Serial No. 146,743, filed October 23, 1961.

The invention has been described in detail with particular reference to 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.

We claim:

1. A photoconductive composition consisting essentially of (a) an aryl amine selected from the group consisting of diaryl amines and triaryl amines and a sensitizing amount of (b) a member selected from the group consisting of pyrylium, thiapyrylium and selenapyrylium salts.

2. The photoconductive composition of claim 1 wherein said sensitizing compound is 2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium perchlorate.

3. The photoconductive composition of claim 1 wherein said sensitizing compound is 2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium fluoborate.

4. The photoconductive composition of claim 1 wherein said sensitizing compound is 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate.

5. The photoconductive composition of claim 1 wherein said sensitizing compound is 2,6-bis(4-methoxyphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate.

6. The photoconductive composition of claim 1 wherein said sensitizing compound is 2,4,6-tri(4-methoxyphenyl)thiapyrylium perchlorate.

7. A photoconductive composition consisting essentially of (a) an aryl amine selected from the group consisting of diaryl amines and triaryl amines which are not also pyrylium, thiapyrylium, and selenapyrylium salts and a sensitizing amount of (b) a member selected from the group consisting of pyrylium, thiapyrylium, and selenapyrylium salts.

8. The photoconductive composition of claim 1 wherein said aryl amine is triphenyl amine.

9. The photoconductive composition of claim 1 wherein said sensitizing amount of component (b) is in the range of from about 0.1 to about 2 mols per 100 mols of nitrogen present in component (a).

10. An electrophotographic element comprising a sheet of support material and coated thereon a photoconductive insulating layer comprising the photoconductive composition defined in claim 1.

11. An electrophotographic element comprising a sheet of support material and coated thereon a photoconduc-

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tive, electrically insulating layer consisting essentially of the photoconductive composition defined in claim 1 dispersed in an electrically insulating resin binder.

12. An electrophotographic element comprising a sheet of support material and coated thereon a photoconductive electrically insulating layer comprising a photocon-

ductive composition as defined in claim 7 dispersed in an insulating resin binder.

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