PHOTOCONDUCTIVE LAYERS AND PROCESS FOR ELECTROPHOTOGRAPHY

Filed Nov. 2, 1962

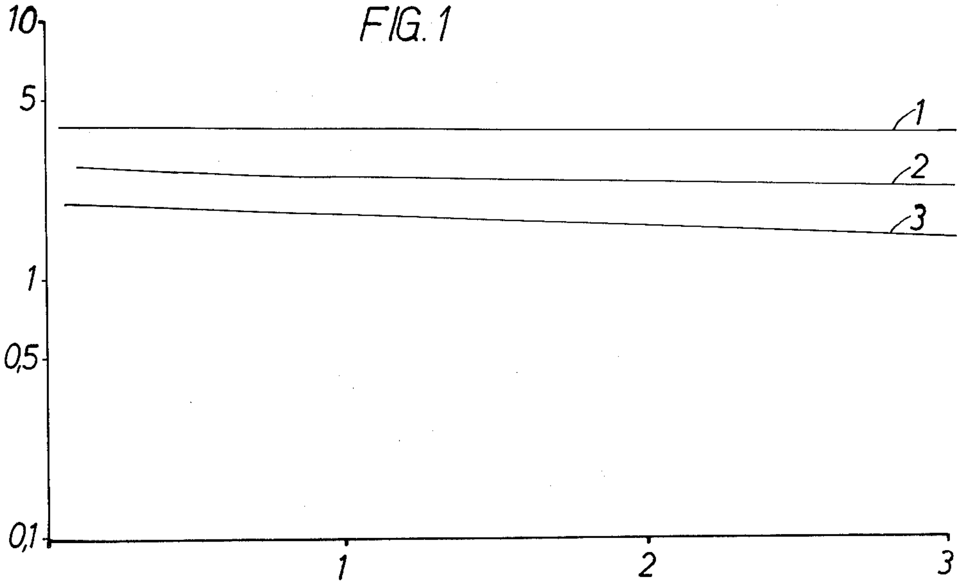

FIG. 1

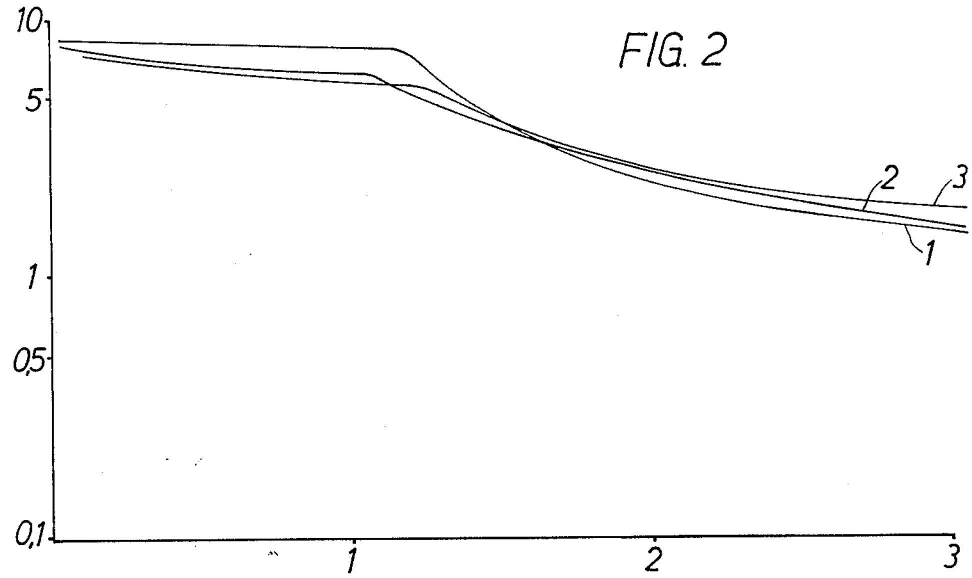

FIG. 2

INVENTORS:
GUSTAV SCHAUM, HILDEGARD HAYDN, ANITA VON KÖNIG,
HEINRICH SEIBERT.
BY
Connolly and Hutz
their ATTORNEYS

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PHOTOCONDUCTIVE LAYERS AND PROCESS FOR ELECTROPHOTOGRAPHY

Gustav Schaum, Hildegard Haydn, Anita von König, and Heinrich Seibert, Leverkusen, Germany, assignors to Agfa Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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15 Claims. (Cl. 96—1)

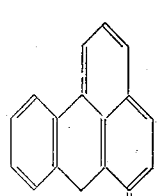
This application is a continuation-in-part of our application Serial No. 696,032, filed November 13, 1957, now abandoned.

The present invention relates to photoconductive layers for electrophotography.

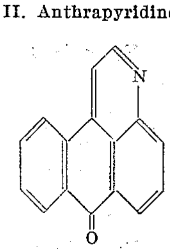
For the production of photoconductive layers for electrophotography it is known to use certain inorganic or organic photoconductive compounds. Examples of such compounds are sulphur, selenium, oxides, sulphides and selenides of zinc, cadmium, mercury, antimony, bismuth, and lead, and also anthracene and anthraquinone. These substances are applied to an electrophotographic plate, especially a plate consisting of metal or another material, for example paper, or to a sheet or foil produced from a film-forming plastic. If necessary, the photoconductive substance can be held dispersed in an electrically isolating, layer-forming binder. Such layers being produced by means of coating solutions in which the binders are either dissolved or dispersed and in which the electro-conductive substances are dispersed. Such photoconductive layers are for instance disclosed in United States Patents Nos. 2,297,691; 2,357,809; 2,727,807; 2,727,808; 2,735,-784; and 2,735,785, and in French Patents Nos. 1,113,-933; 1,122,275; 1,125,235; and 1,136,146.

It has now been found that the electrophotographic layers with very good properties are obtained if organic benzoid compounds containing 4 condensed aromatic rings of the following structures are used in such electrophotographic layers.

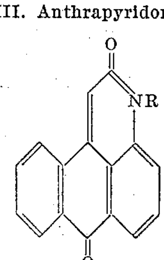
I. Benzanthrone



II. Anthrapyridine



III. Anthrapyridone



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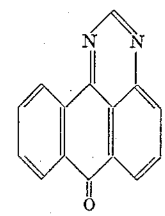
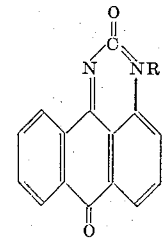
IV. Anthrapyrimidine



V. Anthrapyrimidone



R represents hydrogen, lower alkyl up to 5 carbon atoms or aryl such as phenyl.

The electrophotographic efficacy of the compound of the invention is based on the cyclic structure identified above. The basic compounds such as benzanthrone, anthrapyridine, anthrapyridone, anthrapyrimidine and anthrapyrimidone as well as substitution products thereof are suitable for the instant purpose. In certain cases, substitution products may be advantageous since certain secondary properties such as solubility and the like can be influenced by substituents.

Suitable substituents in particular of the fused benzene rings of the said structures are, for example, cyano, nitro, amino, halogen such as chlorine or bromine, hydroxy- and amino-groups which are substituted with alkyl-, aryl- or acyl-groups.

The following compounds are, for example, suitable:

Group I:
- Benzanthrone
- 3-chlorbenzanthrone
- 3-brombenzanthrone
- 3-cyanobenzanthrone
- 3,9-dichlorbenzanthrone
- 3,9-dibrombenzanthrone
- 3,9-dicyanobenzanthrone
- 3-nitrobenzanthrone
- 2-methylbenzanthrone

Group II:
- Anthrapyridine

Group III:
- Anthrapyridone
- N-methylanthrapyridone
- 6-bromo-N-methylanthrapyridone
- 6-amino-N-methylanthrapyridone
- 6-p-toluidino-N-methylanthrapyridone

Group IV:
- Anthrapyrimidine
- 6-aminoanthrapyrimidine
- 8-aminoanthrapyrimidine

Group V:
- Anthrapyrimidone
- 6-p-toluidino-N-methylanthrapyrimidone
- N-methylanthrapyrimidone

The photoconductive compounds according to the invention are advantageous over prior art because they are more sensitive to longer wavelength. It is furthermore possible to sensitize these substances for still longer wavelengths by suitable compounds as they are for instance disclosed in French Patent No. 1,125,235.

The coating solution which is used for the production of the photoconductive layers comprises at least one of the aforementioned substances and a film-forming binding agent, the electrical specific resistance of which must be higher than that of the photoconductive substance and also higher than that of the layer support. The best results are obtained with binding agents the electrical specific resistance of which amounts to at least 10^{10} ohms per centimeter.

Particularly suitable binding agents are silicone resins such as alkylpolysiloxanes and arylpolysiloxanes, especially pheny and methy polysiloxanes as they are disclosed in German Patents No. 853,351 and 865,975.

Further suitable binding agents are for instance cellulose, cellulose esters, cellulose ethers, polyvinyl chloride, polyurethanes, polyesters, polyamides, polycarbonates with a base of di-(monohydroxyaryl)-alkanes, especially 4,4'-di(monohydroxyaryl)-alkanes according to German Patents Nos. 971,790 and 971,777. Photoconductive compounds can be present in the electrophotographic layers, homogeneously in dissolved form or heterogeneously in a suspended form whereby the particle size of the suspended photoconductor should be as small as possible.

The quantitative ratios between the photoconductive substances and the binding agents may vary within wide limits. It is preferred to use the photoconductive substance in amounts between 1 part for each 0.3 to 2 parts by weight of binding agent which is the equivalent of 0.5 to 3.33 parts by weight of the photoconductive substance to each part by weight of the binding agent, and amounts between about 5 and about 40 grams per square meter of photoconductive layer. The solvent or solvent mixture used for the production of electrophotographic layers containing a photoconductive compound, heterogeneously dispersed therein must be good solvents for the binding agent but non-solvents or poor solvents for the photoconductive compounds. Suitable layers of this type can be produced as follows: An organic solvent is used which dissolves both the photoconductive substance and the binding agent layer former. This solution has added thereto another organic solvent in which the layer former is soluble but the photoconductive substance is insoluble. By this means, the photoconductive compound is deposited in a state of particularly fine distribution, so that layers with a particularly smooth surface are obtained.

As a support for the photoconductive layer there may be used paper or metal plates, such as zinc, aluminium, or brass plates. Furthermore, thin foils of cellulose hydrate, cellulose esters or of polyamide come into question. In processing of the electrophotographic materials said material comprising a support of low electrical resistance and a photoconducting insulating layer, coated thereon, is electrostatically charged in the dark, for instance, by means of a corona discharge device. The charged layer is then exposed with light through a negative photographic film, positive film or mask or otherwise to a light image, to receive a latent electrostatic image. If the electrophotographic material has been properly prepared, the charges leak off rapidly to the support in proportion to the intensity of light to which any given area is exposed. After such exposure, the latent electrostatic image can be developed by any developing process known per se, for example, by dusting a developing powder whereby the powder adheres to the areas where the electrostating charges remain, forming thereby a powder image corresponding to the electrostatic image. Thereafter the powder image can be fixed by melting a developing powder or can be transferred to a sheet of transfer material resulting in a positive or negative print as the case may be.

The such light-conductive layers can also be produced from aqueous dispersions of photoconductive substances and binding agents, for instance by the process disclosed in French Patent No. 1,136,146. If necessary, the cast dispersions or emulsions are subjected to a final condensation or final polymerization by heat treatment at temperatures of about 80–150° C. for about 2 to 30 minutes after being dried. Aqueous dispersions of polymeric substances, such as melamine-formaldehyde or urea-formaldehyde resins, xylene-formaldehyde resins, polymers based on vinyl chloride, vinylidene chloride, vinyl ethers, acrylic esters, methacrylic esters, acrylic amides, such for example as methacrylic amide, aromatic vinyl compounds, such for example as styrene, isoolefins, such for example as isobutylene, copolymers based on the aforementioned compounds, such for example as copolymers of vinyl chloride and butyl acrylate vinylidene chloride and butyl acrylate synthetic elastomers, such for example as copolymers of butadiene and styrene, butadiene and acrylonitrile, and also copolymers of dienes with a preponderant proportion of styrene and/or acrylonitrile or other vinyl compounds, as well as polyamides, polyurethanes, polyesters of polycarboxylic acids and polyhydric alcohols, polycarbonates, cellulose ester, rubber and the like, are for example employed.

Example 1

100 g. of a 30% solution in ethyl acetate of a copolymer of vinyl chloride and acrylic acid ester
100 cc. of ethyl acetate
40 g. of benzanthrone

are mixed and ground for several hours in a ball mill. The mixture is then cast on a support, for example, a paper support and dried. The resulting electrophotographic layer has a very low conductivity in the dark or visible and a high conductivity if exposed to ultraviolet light.

Example 2

64 g. of a 60% solution in toluene of a silicone resin as disclosed in Example 1 of German Patent No. 853,351,
97 cc. of toluene and
40 g. of 3,9-dibrom benzanthrone

are mixed and thoroughly ground for several hours in a ball mill. The mixture is further treated as described in Example 1.

Example 3

64 g. of a toluene solution of a silicone resin as described in Example 2,
97 cc. of toluene and
20 g. of anthrapyridone

are mixed and thoroughly ground in a ball mill. The mixture is cast on a paper support and dried. An excellent smooth layer, which is only very slightly yellow colored is obtained. The layer is sensitive to the visible range of the spectrum.

By usual processing which comprises charging by corona discharge exposing and developing the resulting electrostatic latent image, a developing powder image is obtained having excellent detail and quality.

Example 4

An electrophotographic material is produced as described in Example 3 with the exception that anthrapyridone is replaced with 22 g. of 8-aminoanthrapyridine. The resulting layers show a very low conductivity in the dark and a high conductivity if exposed to ultraviolet and blue light of the spectrum.

Example 5

An electrophotographic material is produced as described in Example 3 with the exception that anthrapyridone is replaced by anthrapyrimidine. The resulting layer is very smooth, only slightly yellow colored and sensitive to the visible range of the spectrum. Similar results are obtained if anthrapyrimidine is replaced with equivalent amounts of anthrapyrimidone, anthrapyridine, N-methylanthrapyrimidone, 4-brom-N-methylanthrapyridone, 4-amino-N-methylanthrapyridone or 4-p-toluidino-N-methylanthrapyridone.

Example 6

100 g. of a 30% solution in ethyl acetate of a copolymer of phenyl chloride and acrylic acid methyl ester,
100 cc. of ethyl acetate and
40 g. of 6-aminoanthrapyrimidine

are mixed and further treated as described in Example 1.

The resulting photographic layer has excellent electrophotographic properties.

Example 7

100 cc. of a 2.5% solution of a 2.5% solution in acetone of cellulose acetate,
100 cc. of acetone and
22 g. of 6-p-toluidino-N-methylanthrapyridone

are heated while stirring up to a temperature of about 50° C., whereby the photoconductive compound is partially dissolved. The hot mixture is cast on a paper support and slowly dried.

The resulting electrophotographic layer has good properties and can be processed in the usual manner.

Example 8

30 g. of 3-nitrobenzanthrone are added to a mixture of 100 cc. of a 30% aqueous dispersion of a heat-hardenable melamine-formaldehyde condensation product and 80 cc. of water.

The mixture is treated for 2 hours in a ball mill and thereafter coated on a paper support. After drying at room temperature the material is heated to 80° C. for 15 minutes.

By usual processing which comprises charging by corona discharge exposing and developing the resulting electrostatic latent image, a developing powder image is obtained having excellent detail and quality.

Example 9

In this example the electrophotographic properties of several compounds according to the invention are compared with known photoconductive compounds.

The sensitivity of an electrophotographic material depends essentially on the difference between the photoconductivity and the dark-conductivity. The more electrostatic charge drains off by a given exposure the higher shall be the contrast respectively the quality of the resulting image. The graphs attached thereto present the draining off of the charge by exposure as a function of time. The steeper is the slope of the curve the more suitable is the compound for electrophotographic purposes. The axis of abscissa shows the relative charge per unit area in logarhythmic scale in arbitrary units and the axis of ordinate the time in arbitrary units.

The electrophotographic material to be tested where prepared according to Example 2 by mixing each 40 g. of photoconductive compounds with 64 g. of a solvent of the silicone resin described in that example. With each compound the processing, charging and exposure used identical technic.

The curves in FIGURES 1 and 2 represent the following photoconductive compounds:

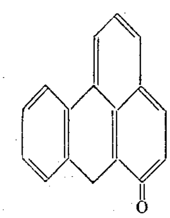
FIGURE 1: Known photoconductive compounds.
Curve 1: Anthracene.
Curve 2: p-Terphenyl.
Curve 3: Anthraquinone.

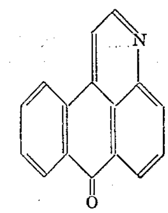
FIGURE 2: Photoconducters according to the invention.
Curve 1: 3,9-dibromobenzanthrone.
Curve 2: 6-aminoanthrapyrimidine.
Curve 3: Anthrapyrimidone.

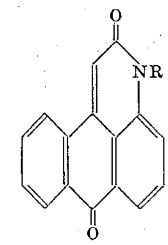
We claim:

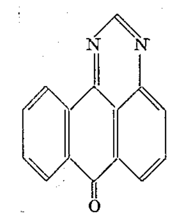
1. An electrophotographic material comprising a photoconducting insulating layer carried on a support, said photoconducting layer being composed of a dielectric film forming organic resin and a photoconductive organic compound dispersed therein, said photoconductive organic

compound containing 4 condensed aromatic rings selected from those having the following structure:

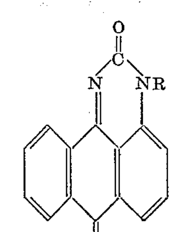








and



wherein R stands for a radical selected from the group consisting of hydrogen, lower alkyl having up to 5 carbon atoms and phenyl, said photoconductive organic compound being employed in an amount of 1 part per 0.3–2 parts by weight of film forming organic resin and in an amount of 5 to 40 g./sq. meter of surface, the film forming organic resin having an electrical specific resistance of at least 10^{10} ohms per centimeter which specific resistance is higher than the specific resistance of the support.

2. An electrophotographic material according to claim **1**, wherein said photoconducting insulating layer contains as a photoconductive compound benzanthrone.

3. An electrophotographic material according to claim **1**, wherein said photoconducting insulating layer contains as a photoconductive compound 3.9-dibrombenzanthrone.

4. An electrophotographic material according to claim **1**, wherein said photoconducting insulating layer contains as a photoconductive compound anthrapyridone.

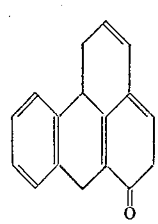
5. An electrophotographic material according to claim **1**, wherein said photoconducting insulating layer contains as a photoconductive compound 8-aminoanthrapyrimidine.

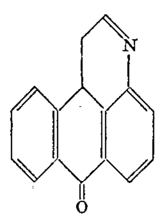
6. An electrophotographic material according to claim

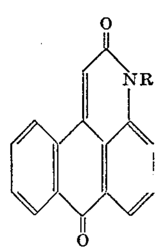
1, wherein said photoconducting insulating layer contains as a photoconductive compound anthrapyrimidine.

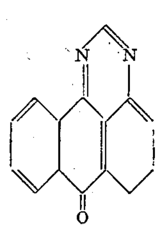
7. An electrophotographic material according to claim 1, wherein said photoconducting insulating layer contains as a photoconductive compound 6-aminoanthrapyrimidine.

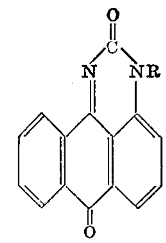
8. An electrophotographic reproduction process which comprises exposing an electrostatically charged supported photoconductive insulating layer to light under a master to discharge the layer in proportion to the intensity of light to which any given area is exposed and developing the resulting latent electrostatic image with an electrophotographic developer, the said photoconductive layer comprising as a photoconductive compound an organic benzonoid compound containing 4 condensed aromatic rings selected from those having the following structures:











the said photoconductor being employed in an amount of 1 part per 0.3–2 parts by weight of binding agent, and in an amount of 5 to 40 g./sq. meter of surface.

9. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound benzanthrone.

10. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound 3.9-dibrombenzanthrone.

11. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound anthrapyridone.

12. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound 8-aminoanthrapyrimidine.

13. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound anthrapyrimidine.

14. A process according to claim **8**, wherein said photoconductive layer contains as a photoconductive compound 6-aminoanthrapyrimidine.

15. A photoconductive sheet material for electrophotography consisting of a photoconductive substance comprising a silicone resin binding agent having dispersed therein as a photoconductive insulating substance anthrapyrimidone, the photoconductive layer being cast upon an electrically conductive support, the anthrapyrimidone being employed in an amount of 1 part per 0.3–2 parts by weight of silicone resin, and in an amount of 5 to 40 g./sq. meter of photoconductive layer.

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