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3,730,711

PHOTOCONDUCTIVE MATERIAL FOR ELECTROPHOTOGRAPHY

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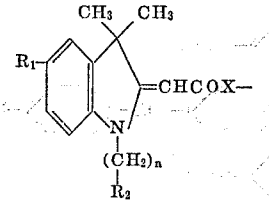
Int. Cl. G03g 5/06
U.S. Cl. 96—1.5 8 Claims

ABSTRACT OF THE DISCLOSURE

A photoconductive material for electrophotography which consists essentially of an indoline derivative having a radical represented by the following Formula I:

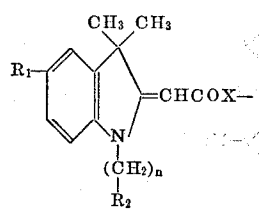


(I)

wherein R_1 represents a hydrogen, a halogen atom, a lower alkyl —NO_2, —OR or —COOR group (R being a lower alkyl group); R_2 represents H, —OR_5, —CN or a phenyl group (R_3 being H or a lower alkyl group); n is an integer having the value of 1–4; X represents either a single bond or —NH— group.

This invention relates to an organic photoconductive material for electrophotography. The photoconductive materials which have been known heretofore as usable for electrophotography include such inorganic substances as selenium and zinc oxide, various organic low-molecular compounds such as anthracene, chrysene, and benzidin and such high-molecular compounds as poly-N-vinyl carbazole, polyvinyl naphthalene, and polyvinyl anthracene.

This invention relates in particular to an organic photoconductive material for electrophotography, made up of 2-substituted-methylene indoline derivative having a radical represented by the following general Formula I:

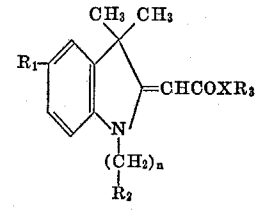


(I)

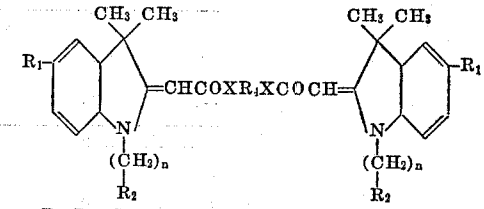
where, R_1 is a hydrogen, a halogen atom, a lower alkyl, —NO_2, —OR or —COOR group (R being a lower alkyl group): R_2 is H, —OR_5, —CN or a phenyl group (R_5 being H or a lower alkyl group): n is an integer having the value of 1–4; X is either a single bond or —NH—.

Of the 2-substituted-methylene indoline derivative in accordance with this invention, compounds represented by the following general Formula II or III are particularly

effective as photoconductive materials for electrophotography:

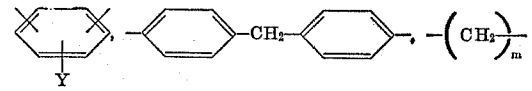


(II)

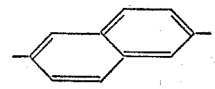


(III)

where, R, R_1, R_2, R_5, n and X have the meanings given in general Formula I, R_3 is an alkyl, an alkenyl, an aryl, or an aralkyl group; and R_4 is a divalent linking radical like:



or



(Y being any substitute and m a positive integer).

The "lower" alkyl group represents an alkyl group having 1–4 carbon atoms.

The foregoing compounds have new structures entirely different from those of the conventionally known organic photoconductive materials for use in electrophotography.

Of the compounds which are represented by the generic Formula II or III, those in which X is —NH— are synthesized by the reaction 2-methylene indoline derivatives with isocyanates (refer to 0. Mumm, Ber 72 2107 (1939)) and further those in which X is a single bond are synthesized by the reaction of 2-methylene indoline derivatives with chlorides of acids (refer to Piccinini; Gazg, chim, ital, 28(i), 187 (1898)).

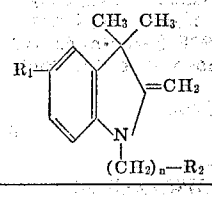
By utilizing the above synthetic method, a number of compounds are synthesized through combination of various 2-methylene indoline derivatives with various isocyanates, diisocyanates, monobasic chlorides of acids, and dibasic chlorides of acids. In this invention, it has been found that many compounds thus prepared are useful as organic photoconductive materials for electrophotography. Now, the method of synthesis is described in further detail. For example, 5 g. of 1,3,3-trimethyl-2-methylene indoline and 3.4 g. of phenyl isocyanate are mixed in toluene and heated at 80° C. for 20 minutes. The reaction solution is concentrated under reduced pressure and the remaining viscous substance is crystallized with addition of petroleum ether. When the crystallization product is recrystallized with a mixed liquid of xylene and ligroin, there is obtained a white crystalline product having a melting point of 137° C. This is a compound of the generic formula wherein R_1 is H, R_2 is H, n is 1, X is —NH— and R_3 is phenyl group.

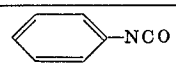
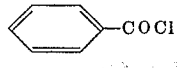
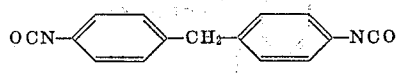
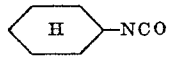
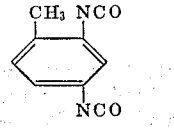
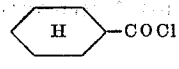
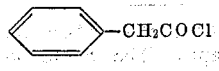
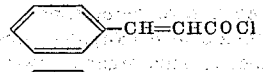
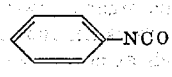
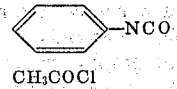
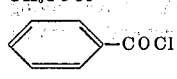
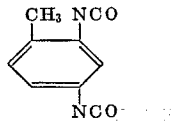
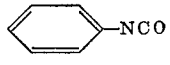
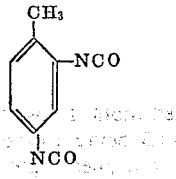
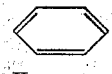
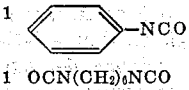
As another example, 3.4 g. of 1,3,3-trimethyl-2-methylene indoline and 2.8 g. of benzoyl chloride are mixed in 30 ml. of toluene and heated at 80° C. for one hour. Thereafter, the reaction mixture is combined with 2 g. of triethylamine and heated at 80° C. for two hours additionally. Hydrochloride triethylamine which elutes in the

form of crystals is separated by filtration and the remaining solution is concentrated under reduced pressure to permit separation of crystals. When the crystalline product is recrystallized with methanol, there is obtained a yellow crystalline product having a melting point of 134° C. This is a compound of the generic formula wherein R_1 is H, R_2 is H, n is 1, X is a single bond, and R_3 is a phenyl group.

By following the same procedure, there were synthesized the compounds which are shown in the table.

TABLE 1



Number	R_1	R_2	n	Isocyanate or acid chloride	Melting point of the reaction product (° C.)
1	H	H	1		137
2	H	H	1		134
3	H	H	1		218
4	H	H	1		189
5	H	H	1		241
6	H	H	1	CH_3COCl	99
7	H	H	1		95
8	H	H	1		104
9	H	H	1		191
10	CH_3	H	1		163
11	Cl	H	1		167
12	OCH_3	H	1	CH_3COCl	131
13	OCH_3	H	1		131
14	$OCOC_2H_5$	H	1		193
15	NO_2	H	1		220
16	H	CN	3		180
17	H		1		190
18	H	H	1	$OCN(CH_2)_6NCO$	190

To put a compound thus preparing to use as a material for electrophotography, the compound is dissolved together with a highly insulative, resinous film-forming binder in an organic solvent capable of dissolving them, and the spreading solution consequently obtained is spread on a base having a relatively high electroconductivity and allowed to dry to form a film and serve as a sensitive layer. Further, the said spreading solution may be combined with a plasitcizer and a sensitizer for the purpose of improving the film behavior and increasing the sensitivity decisively. As resinous film forming binders usable in this case, there may be cited styrene-butadiene copolymer, polystyrene, chlorinated rubber, polyvinyl chloride, vinyl chloride/vinyl acetate copolymer, polyvinylidene chloride, nitrocellulose, polyvinyl acetate, polyvinyl acetal, polyvinyl ether, silicone resin, methacrylic resin, acrylic resin, phenol resin, alkyd resin, urea/aldehyde resin, etc. As electroconductive bases, it is desirable to use metal plate, paper treated so as to acquire electroconductivity, and plastic film. The plasticizers usable include chlorinated biphenyl, chlorinated paraffin, phosphate type plasticizers, and phthalate type plasticizers. As sensitizers, those which are known commonly are useful, including tetracyanoethylene, tetracyanodimethane, chloranil, naphthoquinone, anthraquinone, methylene blue, crystal violet, malachite green, etc.

It is desirable that, through combination of these materials, the sensitive layer is deposited to a dry thickness of 2–20μ on the electroconductive base. When the organic photoconductive component accounts for more than 10% by weight all of the film composition, the product is found to exhibit satisfactory properties from the electrophotographic point of view.

The sensitive layer thus obtained is charged uniformly by means of corona discharge, exposed to light projected through a given image, and developed by either cascade developing process or liquid developing process according to the method commonly used for electrophotography. In the case of cascade development, the developed image is fixed by mildly heating the layer or placing it within the vapor of an organic solvent capable of dissolving the resinous component of the toner subsequently to the step of developing.

The invention is now described in further detail by referring to preferred embodiments. This invention is not limited to such embodiments.

EXAMPLE 1

One-half (0.5) g. of Compound No. 1 given in Table 1 and 20 cc. of 10% benzene solution of polystyrene were mixed homogeneously. The resultants solution was spread to a dry film thickness of 5μ on a base of aluminum plate to obtain a sensitive layer. After drying of the solvent, the sensitive layer was positively charged in a dark place. With a film containing a positive image placed thereon, the sensitive layer was exposed through the film to a high-voltage mercury bulb (made by Toshiba, SHL–100) placed at a distance of 30 cm. above for about 8 seconds. When it was developed with a developing agent containing a negatively charged toner (such as developing agent for Xerox 914), there was obtained a positive image. When the layer was placed in the atmosphere of trichloroethylene, the image was fixed to give rise to a clear positive image.

EXAMPLE 2

When Compound No. 2 given in Table 1 was treated in entirely the same manner as in Example 1, there was obtained a clear positive image.

EXAMPLE 3

A clear positive image was obtained by treating Compound No. 3 given in Table 1 in entirely the same manner as in Example 1.

EXAMPLE 4

One-half (0.5) g. of Compound No. 5 given in Table 1 was dissolved in 5 cc. of dimethyl formaldehyde, and the resultant solution was mixed homogeneously with 20 cc. of 10% benzene solution of polystyrene. The final solution was spread to a dry thickness of 5μ on an aluminum plate to form a sensitive layer. On drying of the solvent, the said sensitive layer was charged positively in a dark place. With a positive image film placed on top thereof, the layer was exposed through the film to a high voltage mercury lamp placed at a distance of 30 cm. above for about 3 seconds. Through the steps of developing and fixing, the layer afforded a clear image. In this example, when the spread material was placed in a drier at 90° C. immediately after spreading, the film surface became transparent. When it was maintained at room temperature for some time and then dried, the film was deprived of transparency and there was obtained a sensitive layer having a purely white film surface. In spite of such difference in transparency, electrophotographic properties were the same for both types.

EXAMPLE 5

A clear positive image could be obtained by treating Compound No. 10 given in Table 1 in entirely the same manner as in Example 1.

EXAMPLE 6

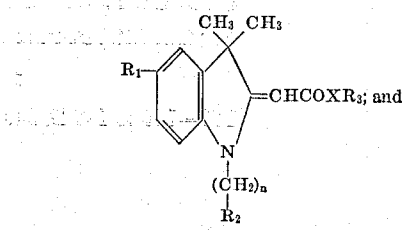
When Compound No. 16 given in Table 1 was treated in entirely the same way as in Example 1, there was obtained a clear positive image.

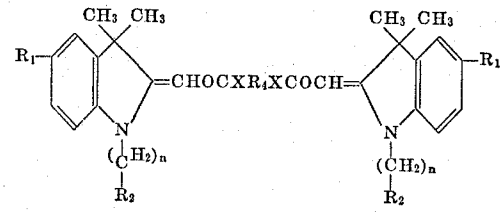
EXAMPLE 7

One-half (0.5) g. of Compound No. 18 given in Table 1 and 0.005 g. of chloranil were dissolved in 20 cc. of acetone. The resultant solution was mixed homogeneously with 20 cc. of 10% benzene solution of polystyrene. The final solution was spread to a dry film thickness of 5μ on an aluminum plate to form a sensitive layer. After drying of the solvent, the said sensitive layer was charged positively in a dark place. With a positive image film placed on top thereof, the sensitive layer was exposed through the film to a high-voltage mercury bulb placed at a distance of 30 cm. above for a second. Through the steps of developing and fixing, there was obtained a clear positive image.

What is claimed is:

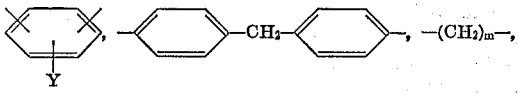
1. A photoconductive element for electrophotography comprising an indoline derivative selected from the group consisting of



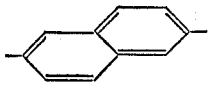


where, R_1 is a hydrogen, a halogen atom, a lower alkyl, —NO_2, —OR or —COOR group (R being a lower alkyl group); R_2 is H, —OR_5, —CN or a phenyl group (R_5 being H or a lower alkyl group); n is an integer having the value of 1–4; X is either a single bond or —NH—; R_3 is an alkyl, an alkenyl, an aryl, or an aralkyl group;

and R_4 is a divalent linking radical selected from the group consisting of:



and

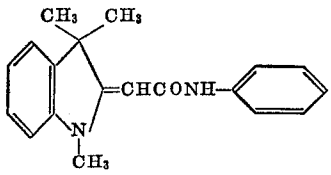


where Y is an alkyl and *m* a positive integer; said indoline derivative being mixed with an electrically insulating resinous, film-forming binder applied as a layer to an electrically conductive base and containing said indoline derivative by more than 10 percent by weight of said layer.

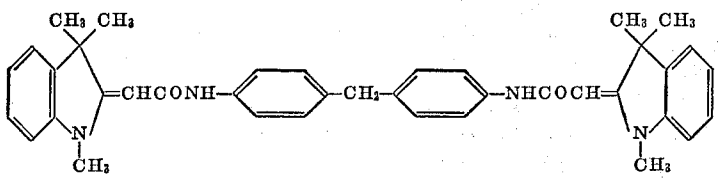
2. A photoconductive element as in claim **1** where said layer has a thickness of 2 to 20 microns on said electrically conductive base.

3. A photoconductive element as in claim **1** where said mixture contains a sensitizer and a plasticizer.

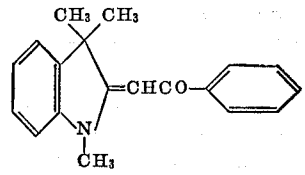
4. The photoconductive material as claimed in claim **1** where the indoline derivative is



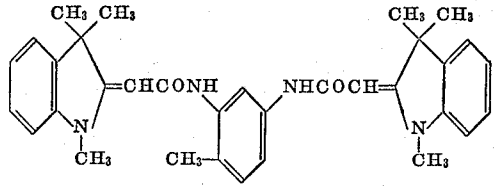
5. The photoconductive material as claimed in claim **1** where the indoline derivative is:



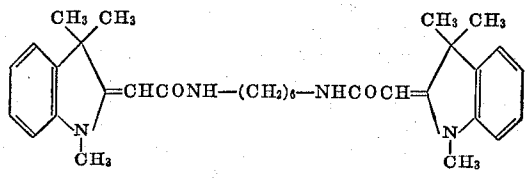
6. The photoconductive material as claimed in claim **1** wherein the indoline derivative is:



7. The photoconductive material as claimed in claim **1** where the indoline derivative is:



8. The photoconductive material as claimed in claim **1** where the indoline derivative is:



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Piccinini: Gazg, chim, ital, 28 (i), 189–196 (1898).

GEORGE F. LESMES, Primary Examiner

R. MILLER, Assistant Examiner

U.S. Cl. X.R.

260—240 R, 240 D, 240.8, 326.11; 96—1.6