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PHOTOSENSITIVE MATERIAL FOR ELECTROPHOTOGRAPHY INCLUDING INDOLINE DERIVATIVES

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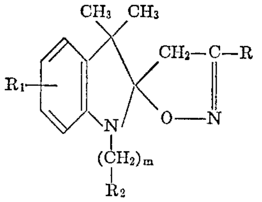
Int. Cl. C07d *85/16*
U.S. Cl. 260—307 F 4 Claims

ABSTRACT OF THE DISCLOSURE

An organic photoconductive material for electrophotography consisting essentially of indoline derivatives represented by the following general formula (A)

(A)

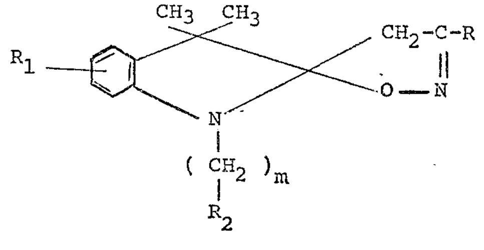


wherein R_1 is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms, alkoxy group having 1 to 4 carbon atoms, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms, nitro group, or alkylene chain having 1 to 3 carbon atoms, R_2 is hydrogen atom, hydroxyl group, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms, cyan or phenyl group, R is substituted phenyl group (where substituted group is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms, or alkoxy group having 1 to 4 carbon atoms), alkylene chain having 1 to 3 carbon atoms or phenylene group, *m* is an integer 1 to 4.

This invention relates to an organic photoconductive material for electrophotography. As photoconductive materials applicable to electrophotography there are known inorganic substances such as selenium and zinc oxide, organic lower molecular compounds such as anthracene, chrysene and benzidine, and higher molecular compounds such as poly-N-vinylcarbazole, polyvinylnaphthalene and polyvinylanthracene.

This invention relates to an organic photoconductive material having a novel structure completely different from known materials, and provides a photosensitive material having as an essential component 2-substituted-methylene-indoline derivatives represented by the following general formula (A):

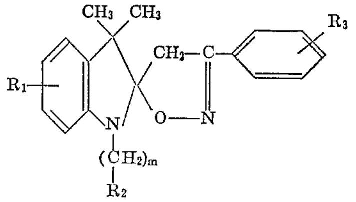
(A)



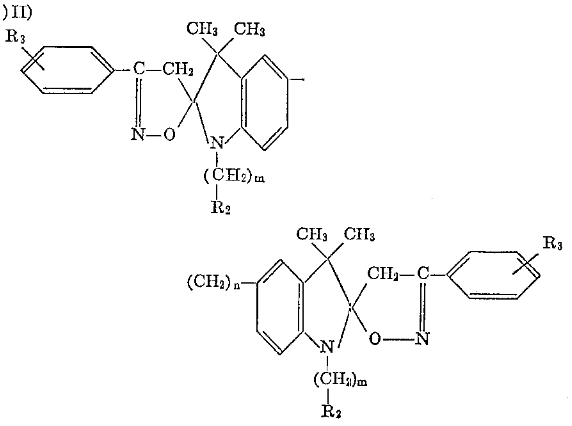
wherein R_1 is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms, alkoxyl group having 1 to 4 carbon atoms, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms, nitro group, or methylene chain having 1 to 3 carbon atoms, R_2 is hydrogen atom, hydroxyl group, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms, cyan or phenyl group, R is substituted phenyl group (wherein substituted group is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms or alkoxyl group having 1 to 4 carbon atoms), methylene chain having 1 to 3 carbon atoms or phenylene group, *m* is an integer from 1 to 4.

The above formula (A) is represented by the following formulae (I) to (IV).

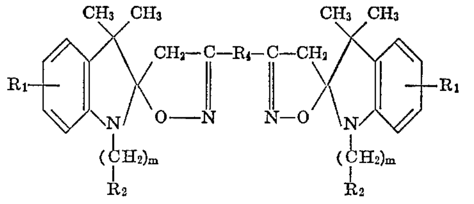
(I)



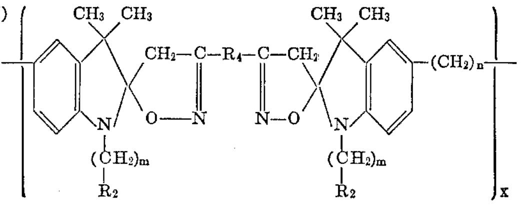
)II)



(III)



(IV)



wherein R_1 is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms, alkoxyl group having 1 to 4 carbon atoms, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms or nitro group, R_2 is hydrogen atom, hydroxyl group, alkoxycarbonyl group having alkyl group having 1 to 4 carbon atoms, cyan or phenyl group, R_3 is hydrogen atom, halogen atom, alkyl group having 1 to 4 carbon atoms, or alkoxyl group having 1 to 4 carbon atoms, R_4 is direct bond of carbon atoms, methylene chain having 1 to 3 carbon atoms or phenylene group, *m* is an integer from 1 to 4, *n* is zero, an integer 1 or an integer 2, *x* is degree of polymerization.

Compounds represented by the above formulae are novel compounds prepared by addition reactions of 2-methylene-indoline derivatives with nitrile oxides. Nitrile oxides are active intermediates produced by reacting hydroxamic acid halides with bases and provide ring compounds by

1,3-dipolar cyclo-addition to multiple bonds such as acetylene, nitrile, carbonyl, olefin and the like. Mechanism of these reactions is known as dipole ring formation reaction, and concerning it R. Huisgen wrote general considerations in Angewandte Chemie, *75,* 604 (1963). Recently synthesis of polymers containing heterocycles utilizing the 1,3-dipolar cycloaddition reaction were reported, for instance, see Iwakura, Shiraishi et al. Bulletin of the Chemical Society of Japan, *38,* 335 (1965); ibid., *38,* 513 (1965); and Polymer Letters, *4,* 305 (1966) etc.

With reference to these reports, many addition products were obtained by reacting various 2-methyleneindolines with various hydroxamic acid halides in the presence of a base. It was proved that the structure of these addition products is a spiro (indoline-2,5′-isoxazoline) structure from the results of elemental analysis and measurements of infrared absorption spectrum, ultraviolet absorption spectrum, visible ray absorption spectrum, NMR spectrum, etc. For instance 1,3,3-trimethyl-2-methylene-5-chloroindoline and benzhydroxamic acid chloride were dissolved in ether. To the solution was added dropwise, 1N sodium hydroxide solution and the mixture was stirred at room temperature for 30 minutes. Then the ether layer was dried and concentrated, in reduced pressure and crystals were obtained.

Thus isolated compound was colorless, needle-like and had a melting point of 167 to 168° C. and had the following results of elemental analysis: carbon 69.49%, hydrogen 5.86%, nitrogen 8.36%. The results were in good agreement with theoretical value of 1,3,3-trimethyl-5-chloro-3′-phenyl-spiro (indoline-2,5′-isoxazoline)

$$(C_{19}H_{19}N_2OCl)$$

carbon 69.59%, hydrogen 5.86%, nitrogen 8.57%. Meanwhile, the agreement was supported by the fact that the parent peak (M^+) of mass spectrum was 326, and the compound had the absorption in infrared absorption spectrum at 1560 cm.$^{-1}$ which agreed with $\nu C{=}N$, and had a maximum absorption in ultraviolet absorption spectrum at 262 mμ ($\epsilon = 2.58 \times 10^4$). On the basis of these absorptions it was concluded that the compound had an indoline type structure altered from the methylene-indoline type structure starting material. Moreover, in NMR spectrum (tetramethylsilane dissolved in deuterated chloroform solution, internal reference) the compound had peaks at δ value (as p.p.m.) 1.25 (S, 3H), 1.34 (S, 3H), 2.61 (S, 3H), 3.03, 3.33, 3.38, 3.39 (AB type 2H $|J| = 18.0$ c.p.s.) and ring protons (8H) were observed.

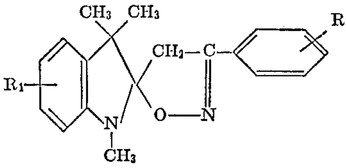
On the basis of above-mentioned data it is obvious that the compound of this invention has spiro (indoline-2,5′-isoxazoline) structure.

Meanwhile, a high polymer compound obtained by the reaction of 5,5′-methylenebis-(1,3,3-trimethyl-2-methylene-indoline) with dichloroglyoxime had a maximum absorption in ultraviolet absorption spectrum at 262 mμ, and in NMR spectrum the high molecular compound had peaks at δ value 1.24 (S), 137 (S), 2.66 (S), 3.01, 3.34, 3.67 (Transition type to A_2 type from AB type) and multiplate ring protons (8H). The intensity ratio of these peaks was 6:6:4:2:6, and infrared absorption spectrum also agreed nearly with spectrum of the above mentioned mono-spiro-compound. From these data it is obvious that the high molecular compound of this invention has a structure containing spiro-(indoline - 2,5′ - isoxazoline) as repetition unit.

In this invention, it was found that the many compounds which were prepared and which had structures which were confirmed as stated above are useful as organic photoconductive materials for electrophotography. These compounds are listed in Table 1 to Table 4.

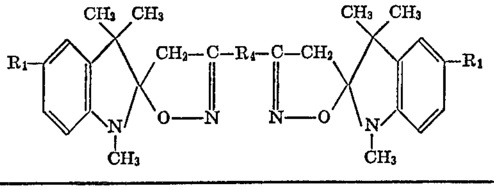
The high molecular compounds of this invention are soluble in various organic solvents such as chloroform, tetrahydrofuran, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and the like, and are so highly polymerized that they give a strong film by applying a solution of the polymer in a lower boiling solvent such as tetrahydrofuran to a metallic plate and drying, and their reduced viscosity value ($\eta_{sp./c.}$) was about from 0.03 to 0.6.

TABLE 1



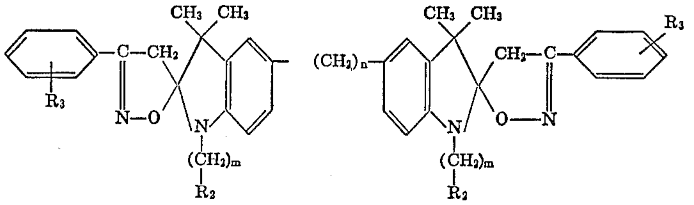
Compound number	R₁	R₃	M.P. (° C.)	CHCl₃ λ max.	(Mμ)₁ (ε)
1	—H	—H	118	260	(1.95×10^4)
2	—Cl	—H	167–168	262	(2.58×10^4)
3	—H	—Cl	170–171	268	(2.18×10^4)
4	C_2H_5OCO—	—H	123–124	304	(3.07×10^4)
5	—NO_2	—Cl	184–185	265 372	(2.16×10^4) (2.04×10^4)
6	—NO_2	—H	210.5–211.5	260 373	(1.83×10^4) (2.13×10^4)
7	CH_3O—	—H	155	259	(1.94×10^4)
8	—H	—CH_3	140	260	(2.05×10^4)

TABLE 2



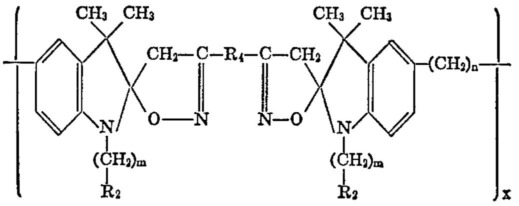
Compound number	R₁	R₄	M.P. (° C.)	CHCl₃ λ max.	(Mμ)₁ (ε)
9	—H	Direct bond of carbon atoms	231	259	(3.06×10^4)
10	—Cl	do	154	262	(4.06×10^4)
11	C_2H_5OCO—	do	242	305	(4.64×10^4)
12	—H	—CH_2—	200	259	(3.30×10^4)
13	—H	(—CH_2—)$_3$	185	259	(3.21×10^4)
14	—H		273	299	(3.30×10^4)

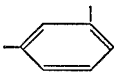
TABLE 3



Compound number	n	m	R_2	R_3	M.P. (° C.)	$\lambda^{CHCl_3}_{max}$	(ε)
16	0	2	$-COOC_2H_5$	—H	210	265	$(5.78\times10_4)$
17	1	1	—H	—H	196	264	$(4.32\times10_4)$
18	1	1	—H	P-Cl—	250	274	$(3.97\times10_4)$

TABLE 4



Compound number	n	m	R_2	R_4	Reaction time (hr.)	Yield, (percent	M.P. (° C.)	$\eta_{sp./c.}$ solvent
19	0	1	—H	Direct bond of carbon atoms	1	80	273–275	0.15 (THF).
20	1	1	—H	do	20/60	90	>300	0.49(THF).
21	1	1	—H	do	3	90	230–240	0.11(THF).
22	1	2	$-CO_2C_2H_5$	do	20/60	70	174–185	0.06(THF).
23	1	1	—H		1	90	300	0.27(NMP).
24	0	1	—H		20/60	[1]	>300	Impossible to measure.
25	1	1	—H		1	80	>300	0.15(NMP).
26	0	3	—CN	Direct bond of carbon atoms	1	90	>300	0.11(THF).
27	2	2	—OH	do	1	50	250–270	0.07(THF).

[1] Quantitative.

For utilizing lower molecular compounds which were above-mentioned for use as materials for electrophotography, coatings as light-sensitive layer are made by dissolving the compounds in organic solvents with highly insulating coating-forming resinous binders, applying the solutions to comparatively electroconductive supports and drying, if desired. It is also possible to add plasticizers and sensitizers thereby to improve the characters of coatings and to increase greatly the sensitivity. In the case of high molecular compounds listed in Table 4, coatings for use as a light-sensitive layer are made by dissolving the high molecular compounds in organic solvents without highly insulating coating-forming resinous binder, applying the solution to comparatively electroconductive supports and drying, if desired. It is also possible to add plasticizers and sensitizers thereby to improve the characteristics of the coatings and to increase greatly the sensitivity.

As coating-forming resinous binders, styrene-butadiene copolymers, polystyrenes, chlorinated rubbers, polyvinyl chlorides, vinyl chloride/vinyl acetate copolymers, polyvinylidene chloride, nitrocelluloses, polyvinyl acetates, polyvinylacetals, polyvinyl ethers, silicon resins, methacrylic resins, acrylic resins, phenol resins, alkyd resins, urea/aldehyde resins, etc. may be used, and as electroconductive supports, metallic plates, electroconductive papers, electroconductive plastic films, etc. may be used, and as plasticizers chlorinated biphenyls, chlorinated paraffins, phosphate plasticizers, phthalate plasticizers, etc. may be used, and as sensitizers, conventional sensitizers such as tetracyanoethylene, tetracyanoquinodimethane, chloranil, naphthoquinone, anthraquinone, Methylene Blue, Crystal Violet and Malachite Green, etc. may be used.

It is preferred to suitably combine these materials and apply them on an electroconductive support to provide a dried coat of 2 to 20 microns in thickness. When organo-photoconductive component is more than 25 percent of the total components of the coating, electrophotographically excellent characteristics are obtained.

The light-sensitive layer obtained by above-mentioned process is uniformly charged by corona discharge according to the conventional method of electrophotography, and after image-exposure is developed by cascade development, liquid development, etc. In the case of cascade development it may be fixed by weakly heating after development or by standing in solvent-vapor capable of dissolving the resin of toner.

This invention is further illustrated by the following examples. However, this invention shall not be limited to the following examples.

EXAMPLE 1

Half a gram of compound No. 1 in Table 1 and 20 ml. of 10% polystyrene solution in tetrahydrofuran were blended uniformly, the resulting solution was applied to an aluminum plate support to provide a dried coating of 0.5 micron in thickness.

After drying it was charged with positive electricity in a dark place, and a positive picture film was placed upon it, then they were exposed with a high-pressure mercury lamp (Toshiba, SHL–100) from 30 cm. in height for about 5 seconds. Then it was developed with toner charged with negative electricity (for instance developer for Xerox 914), whereby a positive picture was developed, and allowed to stand in an atmosphere of trichloroethylene for fixation, whereby a clear positive image was obtained.

EXAMPLE 2

Compound No. 2 in Table 1 was applied and dried as described in Example 1. After exposure for 2 seconds similar treatments were repeated and a clear positive image was obtained.

EXAMPLE 3

By treating compound No. 9 in the exactly similar manner of Example 1 a clear positive image was obtained.

EXAMPLE 4

Compounds No. 15 in Table 3 was applied and dried as described in Example 1. After exposure for about 1 second similar treatments were repeated and a clear positive image was obtained.

EXAMPLE 5

Half a gram of compound No. 21 in Table 4 was dissolved in 3 ml. of tetrahydrofuran, then the solution was applied to an aluminum plate to provide a dried coating of 5 microns in thickness. This test plate was exposed for about 1 second as described in Example, and by treating as in Example 1 a clear positive image was obtained.

EXAMPLE 6

A similar test plate as in Example 5 was charged with positive electricity in a dark place, and a positive image film was placed upon it; then they were exposed with 100 w. tungsten lamp (Toshiba lamp) from 30 cm. in height and then by treating as described in Example 1 a clear positive image was obtained.

EXAMPLE 7

Half a gram of Compound 23 in Table 4 was dissolved in 4 ml. of tetrahydrofuran. After separation of a small amount of insoluble substances, the solution was applied as described in Example 5 and the test plate was exposed for about 3 seconds as in Example 6. Further treatments as described in Example 1 gave a clear image.

EXAMPLE 8

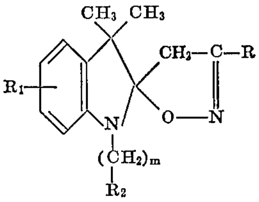
A test plate of Example 7 was charged with electricity in a dark place and overlaid with a positive image film, then they were exposed with a diazotype duplicator (for instance Recopy-standard) at full reproduction speed (for instance in the case of Recopy-standard, the dial was set at 20). Recopy-standard is a diazo-type wet copying machine equipped with a mercury lamp and manufactured by Ricoh Kabushiki Kaisha, Japan. Further treatments as described in Example 1 gave a clear image.

EXAMPLE 9

To the solution of Example 7 was added 0.001 g. of chloranil, and similarly in Example 7 the solution was applied and the test plate was exposed, developed and fixed. When the exposure time was less than even 1 second, a clear image was obtained.

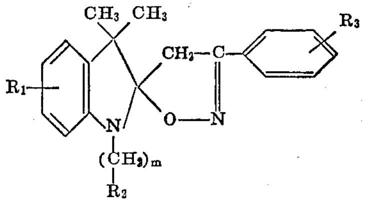
What is claimed is:

1. A compound of the formula



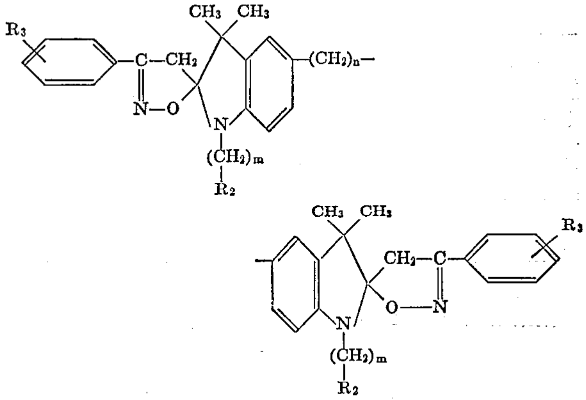
wherein R_1 is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms, nitro, R_2 is hydrogen atom, hydroxyl, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms, cyan or phenyl, R is substituted phenyl (where the substituent is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms, or alkoxy having 1 to 4 carbon atoms), *m* is an integer from 1 to 4.

2. A compound of the formula



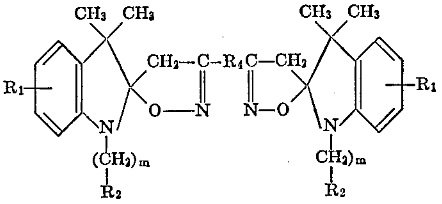
wherein R_1 is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms or nitro, R_2 is hydrogen atom, hydroxyl, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms, cyan or phenyl, R_3 is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms, or alkoxy having 1 to 4 carbon atoms, *m* is an integer from 1 to 4.

3. A compound of the formula



wherein R_2 is hydrogen atom, hydroxyl, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms, cyan or phenyl, R_3 is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms or alkoxy having 1 to 4 carbon atoms, *m* is an integer from 1 to 4, *n* is zero, an integer 1 or an integer 2.

4. A compound of the formula



wherein R_1 is hydrogen atom, halogen atom, alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms or nitro, R_2 is hydrogen atom, hydroxyl, alkoxycarbonyl having alkyl having 1 to 4 carbon atoms, cyan or phenyl, R_4 is direct bond of carbon atoms, alkylene chain having 1 to 3 carbon atoms or phenylene, and *m* is an integer from 1 to 4.

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RAYMOND V. RUSH, Primary Examiner

U.S. Cl. X.R.

96—1.5, 1.6