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(54) **Electrically photosensitive particles for electrophoretic migration**

(57) Electrically photosensitive particles for electrophoretic migration imaging processes.

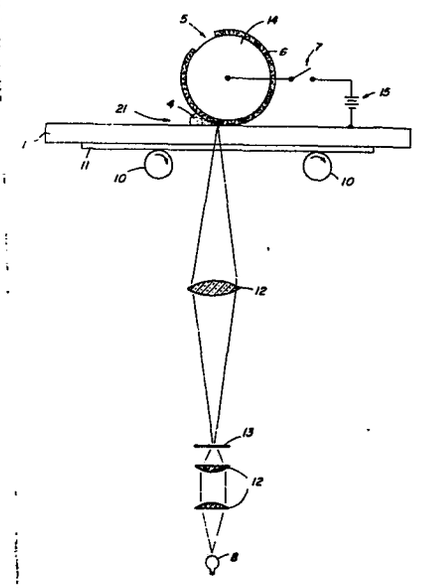
Electrophotosensitive particles (4) for electrophoretic migration imaging processes comprise a compound having the structure

$$A^1 - CL^1 \left(=CL^2-CL^3\right)_m C\begin{matrix}CN\\B^1\end{matrix} \quad \text{or}$$

$$A^2 = CL^4 - CL^5 \left(=CL^6-CL^7\right)_n C\begin{matrix}CN\\B^2\end{matrix}$$

wherein m and n are zero, one or two; L^1 to L^7 are hydrogen, alkyl, cyano aralkyl, aryl or heterocyclyl, and in addition, any two of L^1, L^2 and L^3 and any two of L^4, L^5, L^6 and L^7 may together represent the atoms needed to complete a carbocyclic ring having from 5-10 carbon atoms; A^1 represents an alkyl, aryl group or a heterocyclic nucleus; A^2 represents a basic heterocyclic nucleus; B^1 and B^2 represent cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, acyl, arylcarbonyl, heteroyl, nitro, nitro substituted aryl, sulfonyl, fluorosulfonyl, trifluoromethylsulfonyl, carbamoyl, arylcarbamoyl or alkylcarbamoyl.

The particles (4) can be used in an electrophoretic migration imaging process which consists in placing them between two electrodes (1) and (5) and submitting them to an activating radiation and an electric field for obtaining an image on electrodes (1) and (5).



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ELECTRICALLY PHOTOSENSITIVE PARTICLES FOR ELECTROPHORETIC MIGRATION IMAGING PROCESSES.

This invention relates to electrography and particularly to electrically photosensitive particles for electrophoretic migration imaging processes.

In the past, there has been extensive description in the patent and other technical literature of electrophoretic migration imaging processes. For example, a description of such processes may be found in U.S. Patents 2,758,939, 2,940,847, 3,100,426, 3,140,175, 3,143,508, 3,384,565, 3,384,488, 3,615,558, 3,384,566 and 3,383,993. In addition to the foregoing patent literature directed to conventional photoelectrophoretic migration imaging processes, another type of electrophoretic migration imaging process which advantageously provides for image reversal is described in U.S. Patent 3,976,485. This latter process has been termed photoimmobilized electrophoretic recording or PIER.

In general, each of the foregoing electrophoretic migration imaging processes typically employs a layer of electrostatic charge-bearing photoconductive particles, i.e., electrically photosensitive particles, positioned between two spaced electrodes, one of which may be transparent. To achieve image formation in these processes, the charge-bearing photosensitive particles positioned between the two spaced electrodes, are subjected to the influence of an electric field and exposed to activating radiation. As a result, the charge-bearing electrically photosensitive particles are caused to migrate electrophoretically to the surface of one or the other of the spaced electrodes and one obtains an image pattern on the surface of these electrodes. Typically, a negative image is formed on one electrode and a positive image is formed on the opposite electrode. Image discrimination occurs in the various electrophoretic migration imaging processes as a result of a net change

in charge polarity of either the exposed electrically photosensitive particles (in the case of conventional electrophoretic migration imaging) or the unexposed electrically photosensitive particles (in the case of the electrophoretic migration imaging process described in the above-noted US 3,976,485). Thus the image formed on one electrode surface is composed ideally of electrically photosensitive particles of a negative charge and the image formed on the other electrode surface is composed ideally of electrically photosensitive particles having a positive charge.

In any case, regardless of the particular electrophoretic migration imaging process employed, it is apparent that an essential component of any such process is the electrically photosensitive particles. And, of course, to obtain an easy-to-read, visible image, it is important that these electrically photosensitive particles be colored, as well as electrically photosensitive. Accordingly, as is apparent from the technical literature regarding electrophoretic migration imaging processes, work has been carried on in the past and is continuing to find particles which possess both useful levels of electrical photosensitivity and which exhibit good colorant properties. Thus, for example, various types of electrically photosensitive materials are disclosed for use in electrophoretic migration imaging processes, for example, in U.S. Patents 2,758,939, 2,940,847, 3,384,488 and 3,615,558.

The art has generally selected useful electrically photosensitive or photoconductive particles for electrophoretic migration imaging from known classes of photoconductive materials which may be employed in conventional photoconductive elements, e.g., photoconductive plates, drums, or webs used in electrophotographic office-copier devices, as taught for example in US Patents 2,758,939 and 2,940,847. Also, the phthalocyanine pigments described as a useful electrically photosensitive particles for electrophoretic imaging processes in U.S. Patent 3,615,558 have long been known to exhibit useful photoconductive properties.

The object of the invention is to extend the diversity of particles available as electrically photosensitive particles for use in electrophoretic migration imaging processes by resorting to materials which, to the applicant's knowledge, have not been previously identified as photoconductors.

In accordance with the invention, electrically photosensitive particles for electrophoretic migration imaging processes, comprise a

compound having the following formula :

I. $A^1-CL^1(=CL^2-CL^3\rightarrow_m C(CN)(B^1)$

or

II. $A^2=CL^4-CL^5(=CL^6-CL^7\rightarrow_n C(CN)(B^2)$

wherein :

m and n are zero, one or two ;

L^1, L^2, L^3, L^4, L^5, L^6 and L^7 represent hydrogen, cyano, alkyl, aralkyl, aryl or heterocyclyl, or in addition, any two of L^1, L^2 and L^3 or any two of L^4, L^5, L^6 and L^7 may together represent the atoms needed to complete a carbocyclic ring having from 5-10 carbon atoms ;

A^1 represents an alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic nucleus ;

A^2 represents a basic substituted or unsubstituted heterocyclic nucleus selected from the group consisting of : an imidazole; a 3H-indole; a thiazole; a benzothiazole; a naphthothiazole; a thianaphtheno-7', 6',4,5-thiazole; an oxazole; a benzoxazole, a naphthoxazole; a selenazole; a benzoselenazole; a naphthoselenazole; a thiazoline; a 2-quinoline; a 4-quinoline; a 1-isoquinoline; a benzimidazole; a 2-pyridine; a 4-pyridine; a pyrrolo/1,2-a/pyridine; and a acenaphthothiazole;

B^1 and B^2 represent cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, alkyl sulfonyl, acyl, arylcarbonyl,nitro, nitro substituted aryl, sulfonyl, fluorosulfonyl, trifluoromethylsulfonyl, carbamoyl, aryl carbamoyl, alkyl carbamoyl or heteroyl groups.

In the above mentioned formulae, representatives of substituent ——— A^1 are a substituted or unsubstituted aryl (e.g.,phenyl, naphthyl, anthryl) or a substituted or unsubstituted heterocyclic nucleus such as thiophene, benzo/b/thiophene, naphtho/2,3—b/thiophene, furan, isobenzofuran, chromene , pyran, xanthene, pyrrole, 2H-pyrrole, pyrazole, indolizine, indoline, indole, 3H-indole, indazole, carbazole, pyrimidine, isothiazole, isoxazole, furazan, chroman, isochroman, 1,2,3,4-tetrahydroquinoline ; 4H-pyrrolo /3,2,1-ij/quinoline ; 1,2-dihydro-4H-pyrrolo/3,2,1-ij/quinoline ; 1,2,5,6-tetrahydro-4H-pyrrolo/3,2,1-ij/quinoline; 1H,5H-benzo/ij/quinolizine; 2,3-dihydro-1H,5H-benzo/ij/quinolizine; 2,3,6,7-tetrahydro-1H, 5H-benzo/ij/quinolizine, 10,11-dihydro-9H-benzo/a/xanthen-8-yl; 6,7-dihydro-5H-benzo/b/pyran-7-yl or pyrrolo/2,1-b/benzothiazole.

Representatives of substituent A^2 are basic substituted or

unsubstituted heterocyclic nuclei . Representative of such nuclei include :

a) an imidazole nucleus, such as imidazole and 4-phenylimidazole;

b) a 3H-indole nucleus such as 3H-indole, 3,3-dimethyl-3H-indole and 3,3,5-trimethyl-3H-indole ;

c) a thiazole nucleus such as thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole ; 4,5-dimethylthiazole ; 4,5-diphenylthiazole, and 4-(2-thienyl)thiazole ;

d) a benzothiazole nucleus such as benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, and 6-hydroxybenzothiazole ;

e) a naphthothiazole nucleus such as naphtho /1,2-d/-thiazole, naphtho-/2,1-d/thiazole, naphtho/2,3-d/thiazole, 5-methoxynaphtho/2,1-d/-thiazole, 5-ethoxynaphtho/2,1-d/thiazole, 8-methoxynaphtho/1,2-d/-thiazole, and 7-methoxynaphtho /1,2-d/thiazole ;

f) a thianaphtheno-7',6',4,5-thiazole nucleus such as 4'-methoxythianaphtheno-7',6',4,5-thiazole ;

g) an oxazole nucleus such as 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole ; 4-ethyloxazole ; 4,5-dimethyloxazole, and 5-phenyloxazole;

h) a benzoxazole nucleus such as benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole ; 6-methylbenzoxazole, 5,6-dimethylbenzoxazole ; 4,6-dimethylbenzoxazole ; 5-methoxybenzoxazole ; 5-ethoxybenzoxazole ; 5-chlorobenzoxazole; 6-methoxybenzoxazole ; 5-hydroxybenzoxazole, and 6-hydroxybenzoxazole ;

i) a naphthoxazole nucleus such as naphtho /1,2/oxazole and naphtho /2,1/oxazole ;

j) a selenazole nucleus such as 4-methylselenazole and 4-phenylselenazole ;

k) a benzoselenazole nucleus such as benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, and tetrahydrobenzoselenazole ;

l) a naphthoselenazole nucleus such as naphtho/1,2-d/selenazole and

naphtho/2,1-d/selenazole ;

m) a thiazoline nucleus such as thiazoline and 4-methylthiazoline;

n) a 2-quinoline nucleus such as quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, and 8-hydroxyquinoline ;

o) a 4-quinoline nucleus such as quinoline, 6-methoxyquinoline, 7-methylquinoline and 8-methylquinoline ;

p) a 1-isoquinoline nucleus such as isoquinoline and 3,4-dihydroisoquinoline ;

q) a benzimidazole nucleus such as 1,3-diethylbenzimidazole and 1-éthyl-3-phenylbenzimidazole ;

r) a 2-pyridine nucleus such as pyridine and 5-methylpyridine ;

s) a 4-pyridine nucleus ;

t) a pyrrolo/1,2-a/pyridine nucleus ; and

u) an acenaphthothiazole nucleus.

Representatives of substituent B^1 and B^2 are cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, alkylsulfonyl, acyl, arylcarbonyl, nitro, nitro substituted aryl, sulfonyl, fluorosulfonyl, trifluoromethylsulfonyl, carbamoyl, arylcarbamoyl, alkylcarbamoyl, or heteroyl groups such as furoyl or benzofuroyl.

Alkyl refers to aliphatic hydrocarbon groups of generally 1-20 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, heptyl, dodecyl, octadecyl, etc. Aryl refers to aromatic ring groups of generally 6-20 carbons such as phenyl, naphthyl, anthryl or to alkyl or aryl substituted aryl groups such as tolyl, ethylphenyl, biphenylyl, etc. Aralkyl refers to aryl substituted alkyl groups such as benzyl, phenethyl, etc. Carbocyclic ring refers to saturated cycloalkyl groups which may have alkyl, aryl or aralkyl substituents such as cyclopropyl, cyclopentyl, cyclohexyl, 5,5-dimethylcyclohexyl, etc.

The materials of the present invention are relatively insoluble in imaging dispersions but are unexpectedly soluble in certain polymer coated image receiving elements. This solubility in the polymer coatings of image receiving elements results in images having excellent color saturation, density and resolution.

In accordance with the preferred embodiment of the present invention, the electrically photosensitive particles which are useful in electrophoretic migration imaging processes comprise compounds having a structure according to Formula I or II wherein :

L^1, L^2, L^3, L^4, L^5, L^6 and L^7, which may be the same or different represent hydrogen, cyano, methyl, phenyl, benzoyl, 2-thienyl, benzofuryl, 3-dicyanomethylenebutyl, 2-oxo-2H-benzo/b/pyran -3-yl and 2-cyano-2-dicyanomethyleneethyl, or any two of L^1, L^2 and L^3, or L^4, L^5, L^6 and L^7, may represent the atoms needed to complete a nucleus selected from the group consisting of dihydronaphthalene, 1H-indene and cyclohexene ;

A^1 represents an aryl group or a nucleus selected from the group consisting of indole ; 1,2,5,6-tetrahydro-4H-pyrrolo-/3,2,1-ij/quinoline; 2,3,6,7-tetrahydro-1H,5H-benzo/ij/quinolizine and pyrrolo /2,1-b/benzothiazole ;

A^2 represents a substituted and unsubstituted nucleus selected from the group consisting of 3H-indole, naphthothiazole, benzimidazole, 2-pyridine, pyrrolo/1,2-a/pyridine, benzoxazole, benzoselenazole and acenaphthothiazole ; and

B^1 and B^2 represent cyano, ethoxycarbonyl, naphthoyl, benzoyl, benzofuroyl and dihydroxy benzoyl.

In general the particles which comprise compounds of Formulas I and II and which have been found to be electrophotosensitive tend to exhibit a maximum absorption wavelength, λ max, within the range of from about 420 to about 750 nm. A variety of different particles within the class defined by Formulas I and II have been tested and found to exhibit useful levels of electrical photosensitivity in electrophoretic migration imaging processes.

A partial listing of representative such particles are disclosed in Table I. In Table I, Et represents $-C_2H_5$ and Ø represents phenyl. Compounds disclosed herein are also disclosed in, among others, U.S. Patents 2,538,009; 2,721,799 ; 2,860,891 ; 2,860,981 and 2,860,982.

TABLE I

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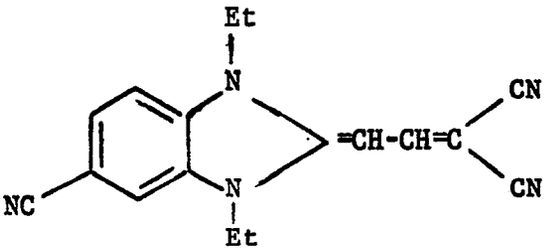
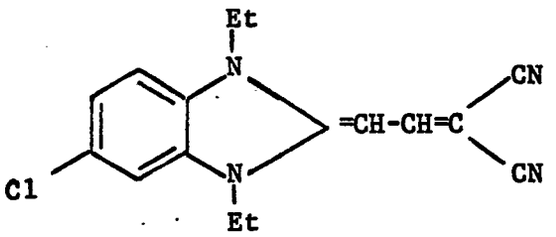
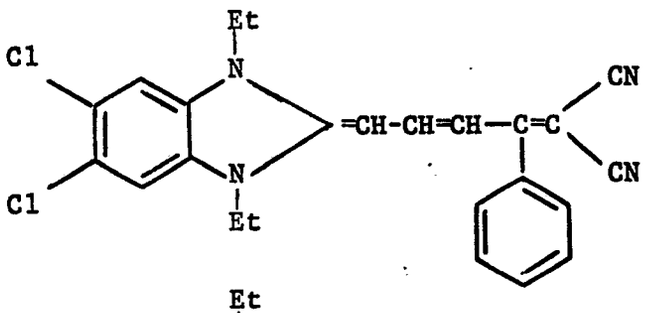
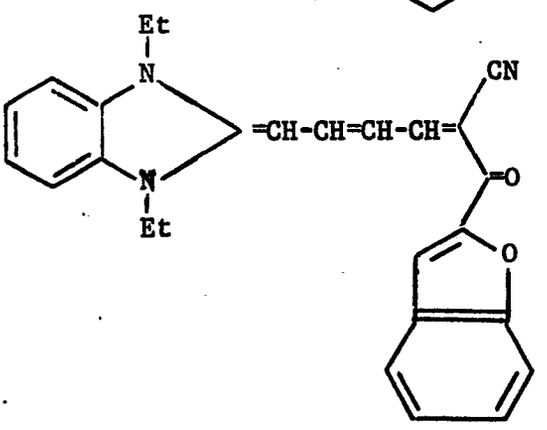
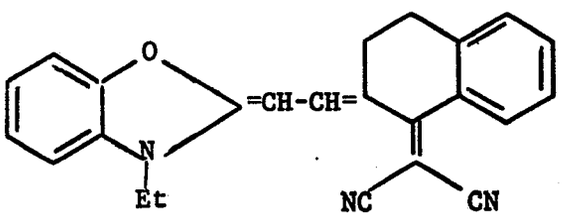
1		Orange
2		Orange
3		Purple
4		Brown
5		Purple

TABLE I

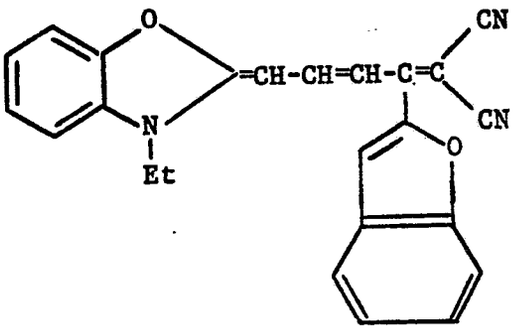
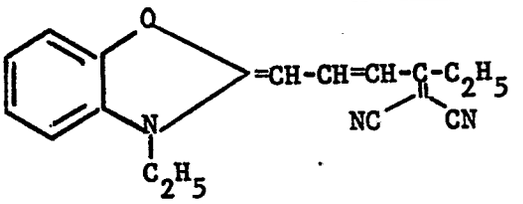
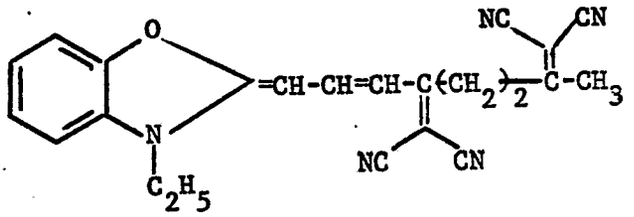
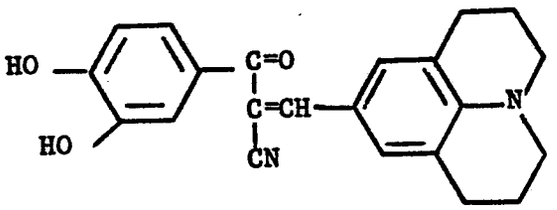
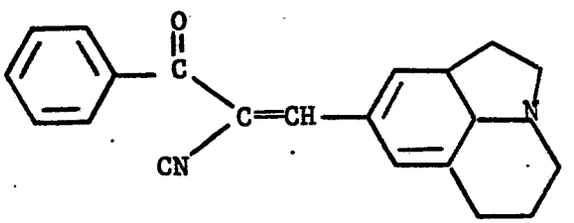
Number	Material	Color
6		Purple
7		Red
8		Magenta
9		Orange
10		Orange

TABLE I

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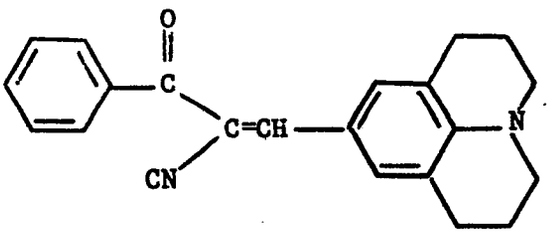
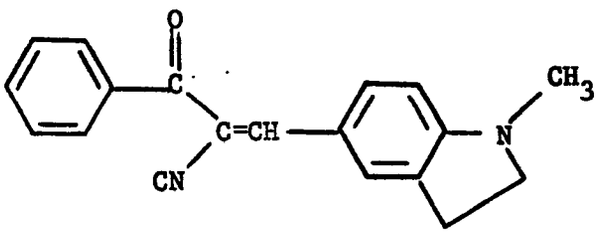
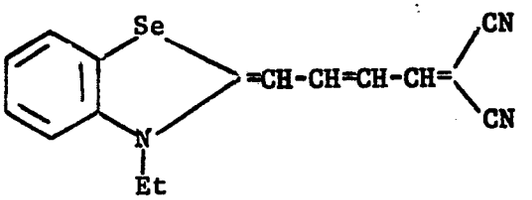
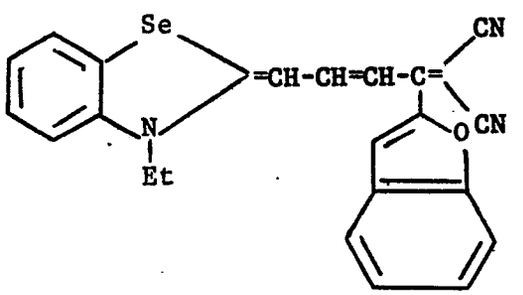
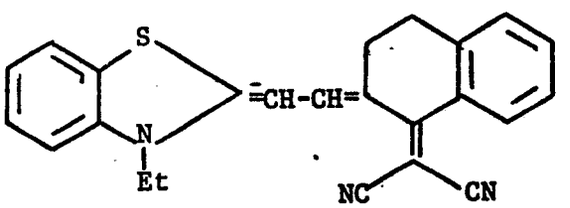
11		Red
12		Orange
13		Purple
14		Purple
15		Blue

TABLE I

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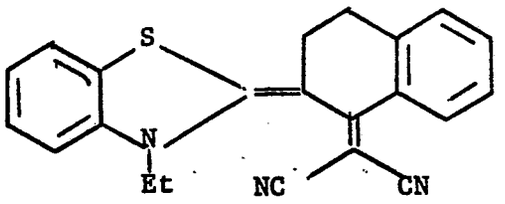
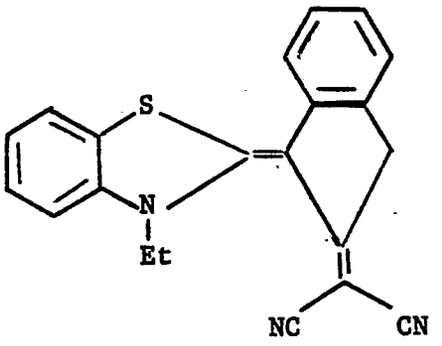
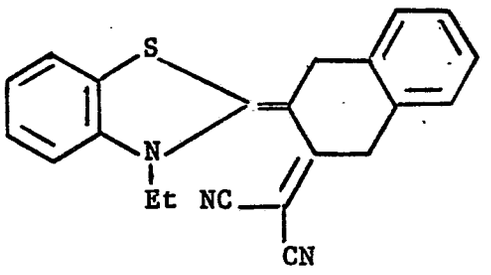
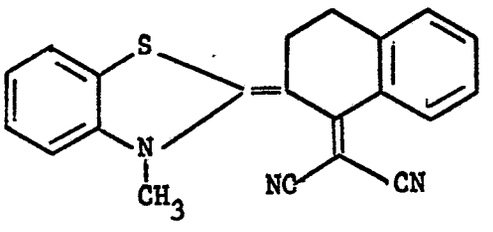
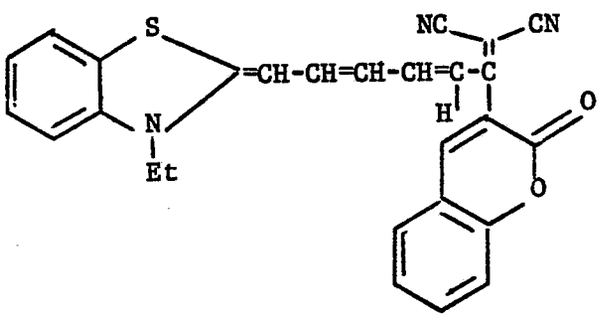
16		Purple
17		Purple
18		Purple
19		Pink
20		Blue

TABLE I

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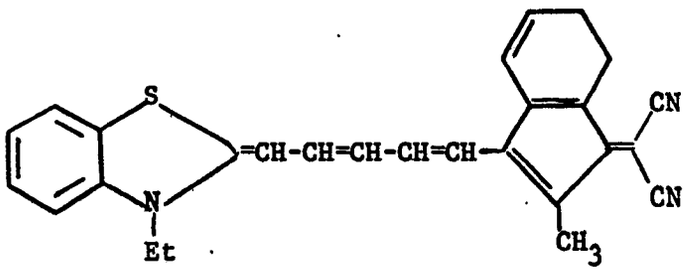
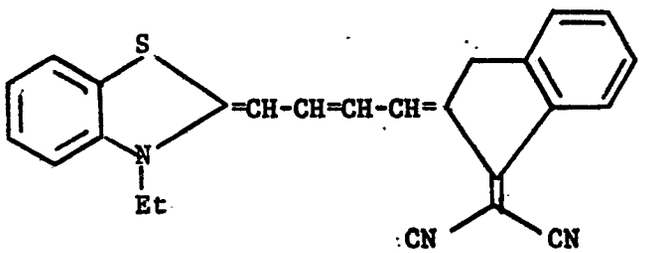
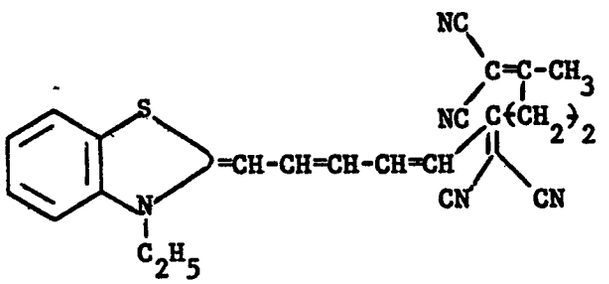
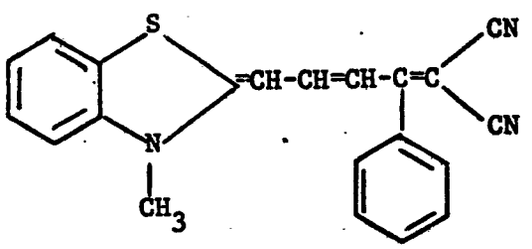
21		Green
22		Blue
23		Blue
24		Purple

TABLE I

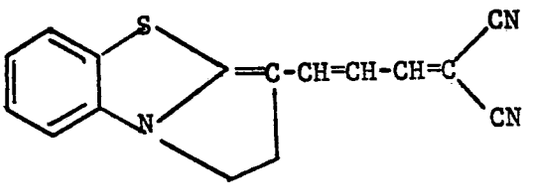
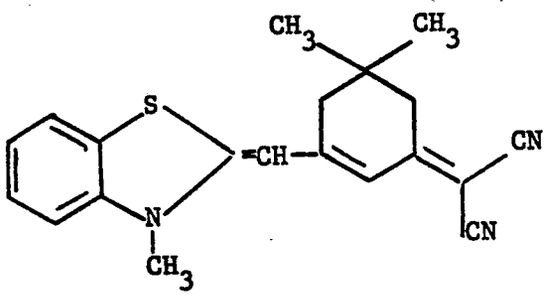
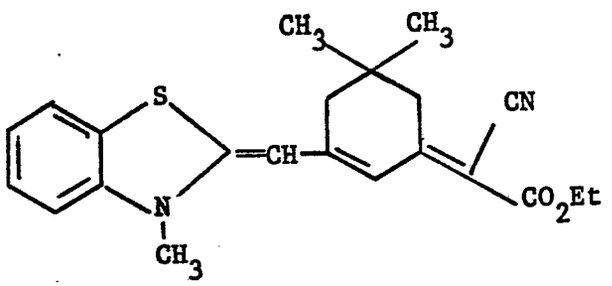
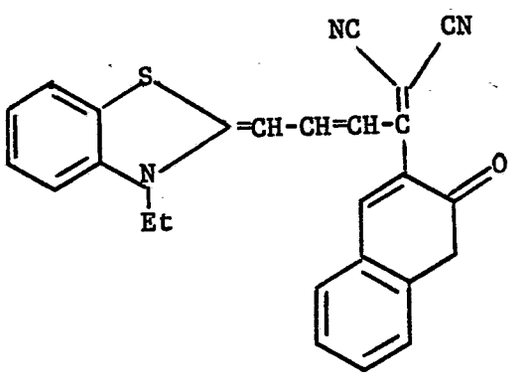
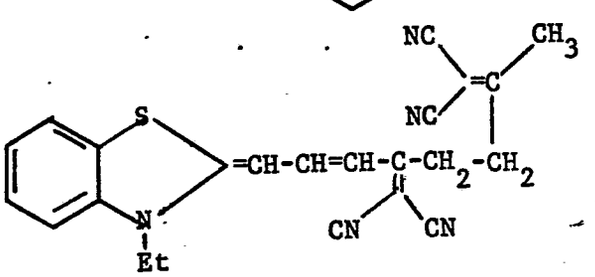
Number	Material	Color
25		Brown
26		Purple
27		Purple
28		Blue
29		Blue

TABLE I

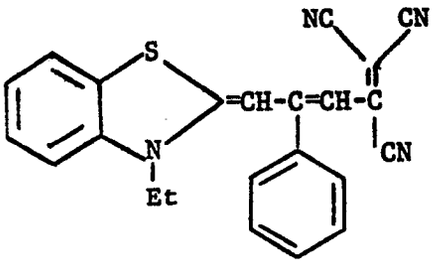
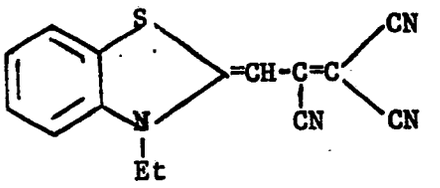
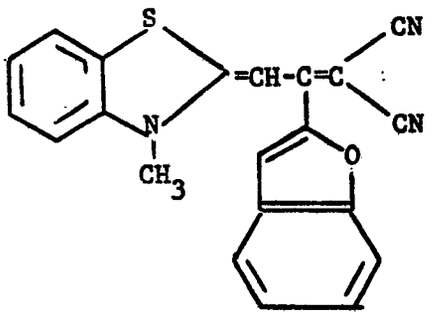
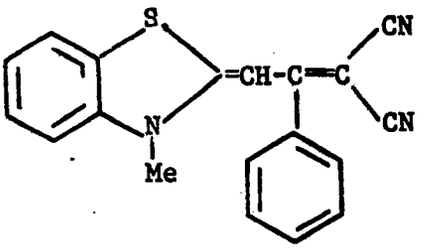
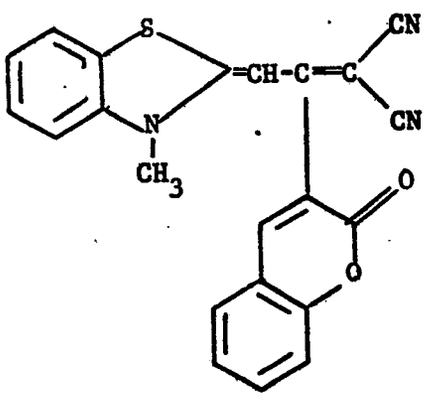
Number	Material	Color
30		Blue
31		Pink
32		Orange
33		Yellow
34		Yellow

TABLE I

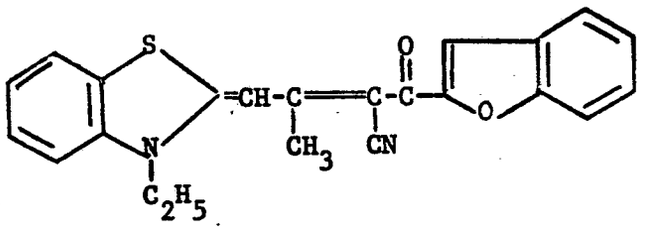
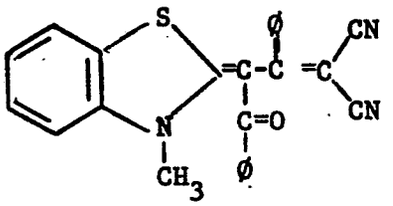
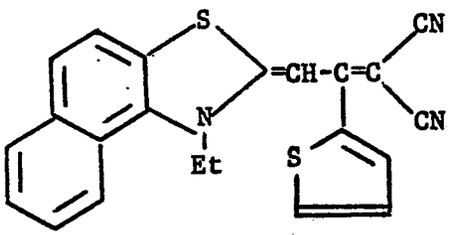
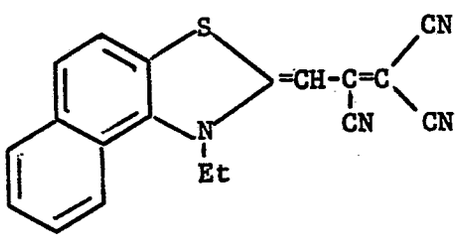
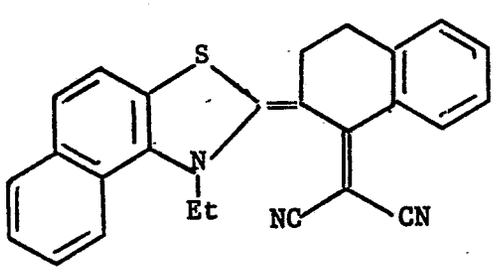
Number	Material	Color
35		Orange
36		Orange
37		Orange
38		Purple
39		Purple

TABLE I

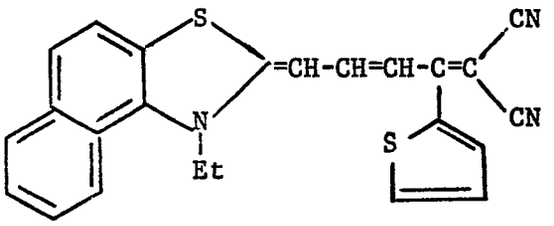
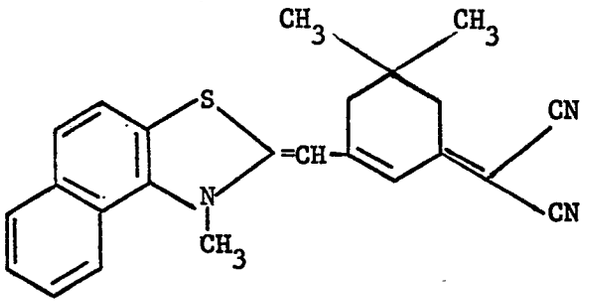
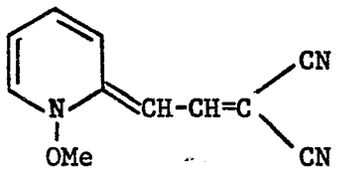
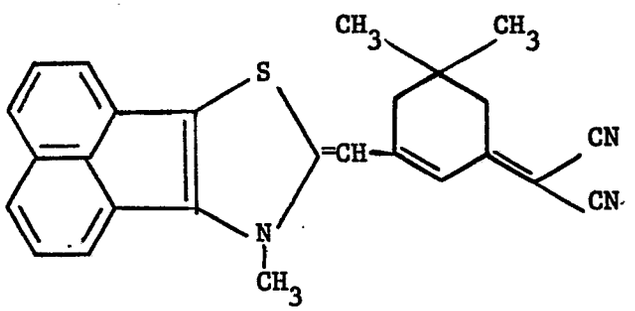
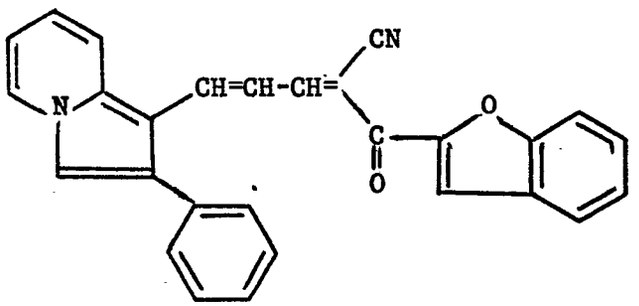
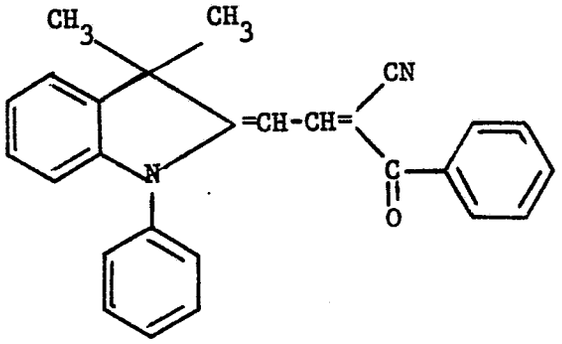
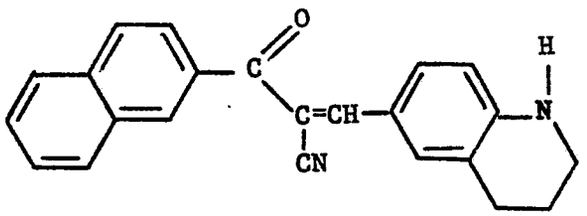
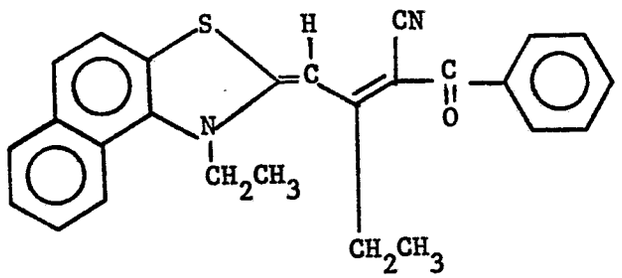
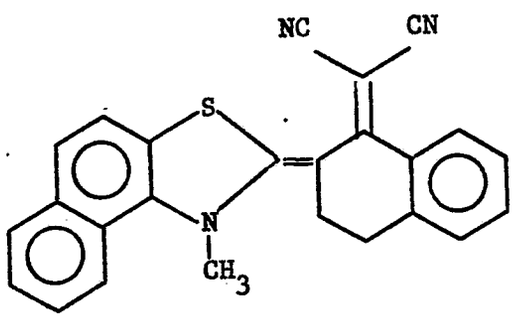
Number	Material	Color
40		Purple
41		Purple
42		Orange
43		Purple
44		Purple

TABLE I

Number	Material	Color
45		Yellow
46		Orange
47		Red
48		Magenta

In general, electrically photosensitive particles useful in electrophoretic migration imaging processes have an average particle size within the range of from about 0.01 micron to about 20 microns, preferably from about 0.01 to about 5 microns. Typically, these particles are colorants. These electrically photosensitive particles may also contain various nonphotosensitive materials such as electrically insulating polymers, charge control agents, various organic and inorganic fillers, as well as various additional dyes or pigments to change or enhance various colorant and physical properties of the electrically photosensitive particles. In addition, such electrically photosensitive particles may contain other photosensitive materials such as various sensitizing dyes and/or chemical sensitizers to alter or enhance their response characteristics to activating radiation.

When used in an electrophoretic migration imaging process described in the present invention, the electrically photosensitive particles mentioned in Table I are positioned between two or more spaced electrodes, one or both of which typically being transparent to radiation to which the electrically photosensitive particles are light sensitive i.e., activating radiation. The electrically photosensitive particles may be dispersed simply as a dry powder between two spaced electrodes and then subjected to a typical electrophoretic migration imaging operation such as that described in U.S. Patent 2,758,939. It is more typical to disperse the electrically photosensitive particles in an electrically insulating carrier, such as an electrically insulating liquid or an electrically insulating, liquefiable matrix, such as a heat- and/or solvent-softenable polymer or a thixotropic polymer. Typically, when one employs such a dispersion of electrically photosensitive particles and electrically insulating carrier between the spaced electrodes of an electrophoretic migration imaging system, it is conventional to employ from about 0.05 part to about 2.0 parts of electrically photosensitive particles for each 10 parts by weight of electrically insulating carrier.

The carrier can comprise an elec-

trically insulating liquid such as decane, paraffin, "Sohio Oderless Solvent 3440" (a kerosene fraction marketed by the Standard Oil Company, Ohio), various isoparaffinic hydrocarbon liquids such as those sold under the trademark "Isopar G" by Exxon Corporation and having a boiling point in the range of 145°C to 186°C, various halogenated hydrocarbons such as carbon tetrachloride, trichloromonofluoromethane, and the like, various alkylated aromatic hydrocarbon liquids such as the alkylated benzenes, for example, xylenes, and other alkylated aromatic hydrocarbons such as are described in U.S. Patent 2,899,335. An example of one such useful alkylated aromatic hydrocarbon liquid which is commercially available is "Solvesso 100" made by Exxon Corporation. "Solvesso 100" has a boiling point in the range of about 157°C to about 177°C and is composed of 9 percent xylene, 16 percent other monoalkyl benzenes, 34 percent dialkyl benzenes, 37 percent trialkyl benzenes, and 4 percent aliphatics. Typically, whether solid or liquid at normal room temperatures, i.e., about 22°C, the electrically insulating carrier material used in the present invention is a material having a resistivity greater than about 10^9 ohm-cm, preferably greater than about 10^{12} ohm-cm.

When the electrically photosensitive particles of the present invention are incorporated in a carrier, such as one of the above-described electrically insulating liquids, various other addenda may be incorporated in the resultant imaging suspension. For example, various charge control agents may be incorporated in such a suspension to improve the uniformity of charge polarity of the electrically photosensitive particles dispersed in the liquid suspension. Such charge control agents are well known in the field of liquid electrographic developers where they are employed for purposes substantially similar to that described herein. Thus, extensive discussion of the charge control agents herein is deemed unnecessary. These charge control agents are typically polymers incorporated by admixture thereof into the liquid carrier of the suspension. In addition, charge control agents often provide more stable suspensions, i.e., suspensions which exhibit substantially less settling out of the dispersed photosensitive particles.

Useful polymeric charge control agents comprise a copolymer having at least two different repeating units,

(a) one of said units being present in an amount of at least about $0,5 \times 10^{-4}$ moles/gram of said copolymer and being derived from monomers selected from the group consisting of metal salts of sulfo

acrylates and methacrylates and metal salts of acrylic and methacrylic acids, and

(b) one of said repeating units being derived from monomers soluble in said carrier vehicle and being present in an amount sufficient to render said copolymer dispersible in said carrier.

Examples of such copolymer charge control agents are poly-(vinyltoluene-co-lauryl methacrylate-co-lithium methacrylate-co-methacrylic acid), poly(styrene-co-lauryl methacrylate-co-lithium sulfoethyl methacrylate), poly(vinyltoluene-co-lauryl methacrylate-co-lithium methacrylate),poly(styrene-co-lauryl methacrylate-co-lithium methacrylate), poly(t-butylstyrene-co-lauryl methacrylate-co-lithium methacrylate), and poly(t-butylstyrene-co-lithium methacrylate).

In addition to the foregoing charge control agents , various polymeric binders such as various natural, semi-synthetic resins, may be dispersed or dissolved in the electrically insulating carrier to fix the final photosensitive particle image formed on one of the spaced electrodes used in electrophoretic migration imaging systems. The use of such fixing addenda is conventional and well known in the closely related art of liquid electrographic developers so that extended discussion thereof is unnecessary herein.

The accompanying drawing illustrates a typical apparatus which employs an electrophoretic migration imaging process in which electrically photosensitive particles of the invention can be used.

The drawing shows a transparent electrode 1 supported by two rubber drive rollers 10 capable of imparting a translating motion to electrode 1 in the direction of the arrow. Electrode 1 may be composed of a layer of optically transparent material, such as glass or an electrically insulating, transparent polymeric support such as polyethylene terephthalate, this layer or support being covered

with a thin, optically transparent, conductive layer such as tin oxide, indium oxide, nickel, and the like. Optionally, depending upon the particular type of electrophoretic migration imaging process desired, the surface of electrode 1 may bear a "dark charge exchange" material, such as a solid solution of an electrically insulating polymer and 2,4,7,trinitro-9-fluorenone as described in the above-described Groner U.S. Patent 3,976,485 issued August 24, 1976.

Spaced opposite electrode 1 and in pressure contact therewith is a second electrode 5, an idler roller which serves as a counter electrode to electrode 1 for producing the electric field used in the electrophoretic migration imaging process. Typically, electrode 5 has on the surface thereof a thin, electrically insulating layer 6. Electrode 5 is connected to one side of the power source 15 by switch 7. The opposite side of the power source 15 is connected to electrode 1 so that as an exposure takes place, switch 7 is closed and an electric field is applied to the electrically photosensitive particles 4 which are positioned between electrodes 1 and 5. Typically electrically photosensitive particles 4 are dispersed in an electrically insulating carrier such as described hereinabove.

The electrically photosensitive particles 4 may be positioned between electrodes 1 and 5 by applying the particles 4 to either or both of the surfaces of electrodes 1 and 5 prior to the imaging process or by injecting the electrically photosensitive particles 4 between electrodes 1 and 5 during the electrophoretic migration imaging process.

As shown in the drawing, exposure of electrically photosensitive particles 4 takes place by use of an exposure system consisting of light source 8, an original image 11 to be reproduced, such as a photographic transparency, a lens system 12, and any necessary or desirable radiation filters 13, such as color filters, whereby electrically photosensitive particles 4 are irradiated with a pattern of activating

radiation corresponding to original image 11. Although the electrophoretic migration imaging system represented in the drawing shows electrode 1 to be transparent to activating radiation from light source 8, it is possible to irradiate electrically photosensitive particles 4 in the nip 21 between electrodes 1 and 5 without either of electrodes 1 or 5 being transparent. In such a system, although not shown in the drawing, the exposure source 8 and lens system 12 is arranged so that particles 4 are exposed in the nip or gap 21 between electrodes 1 and 5.

As shown in the drawing, electrode 5 is a roller electrode having a conductive core 14 connected to power source 15. The core is in turn covered with a layer of insulating material 6, for example, baryta paper. Insulating material 6 serves to prevent or at least substantially reduce the capability of electrically photosensitive particles 4 to undergo a radiation induced charge alteration upon interaction with electrode 5. Hence, the term "blocking electrode" may be used, as is conventional in the art of electrophoretic migration imaging, to refer to electrode 5.

Although electrode 5 is shown as a roller electrode and electrode 1 is shown as essentially a flat plate electrode in the drawing, either or both of these electrodes may assume a variety of different shapes such as a web electrode, rotating drum electrode, plate electrode, and the like as is well known in the field of electrophoretic migration imaging. In general, during a typical electrophoretic migration imaging process wherein electrically photosensitive particles 4 are dispersed in an electrically insulating, liquid carrier, electrodes 1 and 5 are spaced such that they are in pressure contact or very close to one another during the electrophoretic migration imaging process, e.g., less than 50 microns apart. However, where electrically photosensitive particles 4 are dispersed simply in an air gap between electrodes 1 and 5

or in a carrier such as a layer of heat-softenable or other liquefiable material coated as a separate layer on electrode 1 and/or 5, these electrodes may be spaced more than 50 microns apart during the imaging process.

The strength of the electric field applied between electrodes 1 and 5 during the electrophoretic migration imaging process of the present invention may vary considerably; however, it has generally been found that optimum image density and resolution are obtained by increasing the field strength to as high a level as possible without causing electrical breakdown of the carrier in the gap between the electrodes. For example, when electrically insulating liquids such as isoparaffinic hydrocarbons are used as the carrier in the imaging apparatus of the drawing, the applied voltage across electrodes 1 and 5 typically is within the range of from about 100 volts to about 4 kilovolts or higher.

As explained hereinabove, an image is formed in electrophoretic migration imaging processes as the result of the combined action of activating radiation and electric field on the electrically photosensitive particles 4 disposed between electrodes 1 and 5 in the attached drawing. Typically, for best results, field application and exposure to activating radiation occur concurrently. However, as would be expected, by appropriate selection of various process parameters such as field strength, activating radiation intensity, incorporation of suitable light sensitive addenda in or together with the electrically photosensitive particles by incorporation of a persistent photoconductive material, and the like, it is possible to alter the timing of the exposure and field application so that one may use sequential exposure and field application rather than concurrent field application and exposure.

When disposed between electrodes 1 and 5 of the drawing, electrically photosensitive particles 4 exhibit an electrostatic charge polarity, either as a

result of triboelectric interaction of the particles or as a result of the particles interacting with the carrier in which they are dispersed, for example, an electrically insulating liquid, such as occurs in conventional liquid electrographic developers composed of toner particles which acquire a charge upon being dispersed in an electrically insulating carrier liquid.

Image discrimination occurs in the electrophoretic migration imaging process of the present invention as a result of the combined application of electric field and activating radiation on the electrically photosensitive particles dispersed between electrodes 1 and 5 of the apparatus shown in the drawing. That is, in a typical imaging operation, upon application of an electric field between electrodes 1 and 5, the electrically photosensitive particles 4 are attracted in the dark to either electrodes 1 or 5, depending upon which of these electrodes has a polarity opposite to that of the original charge polarity acquired by the electrically photosensitive particles. And, upon exposing particles 4 to activating radiation, it is theorized that there occurs neutralization or reversal of the charge polarity associated with either the exposed or unexposed particles. In typical electrophoretic migration imaging processes wherein electrode 1 bears a conductive surface, the exposed, electrically photosensitive particles 4, upon coming into electrical contact with such conductive surface, undergo an alteration (usually a reversal) of their original charge polarity as a result of the combined application of electric field and activating radiation. Alternatively, in the case of photoimmobilized electrophoretic recording (PIER), wherein the surface of electrode 1 bears a dark charge exchange material as described by Groner in aforementioned U.S. Patent 3,976,485, one obtains reversal of the charge polarity of the unexposed particles, while maintaining the original charge polarity of the exposed electrically photosensitive particles, as these particles come into electrical contact with the dark charge

exchange surface of electrode 1. In any case, upon the application of electric field and activating radiation to electrically photosensitive particles 4 disposed between electrodes 1 and 5 of the apparatus shown in the drawing, one can effectively obtain image discrimination so that an image is formed by the electrically photosensitive particles which corresponds to the original pattern of activating radiation. Typically, using the apparatus shown in the drawing, one obtains a visible image on the surface of electrode 1 and a complementary image on the surface of electrode 5.

Subsequent to the application of the electric field and exposure to activating radiation, the images which are formed on the surface of electrodes 1 and 5 of the apparatus shown in the drawing may be temporarily or permanently fixed to these electrodes or may be transferred to a final image receiving element. Fixing of the final particle image can be effected by various techniques, for example, by applying a resinous coating over the surface of the image bearing substrate. For example, if electrically photosensitive particles 4 are dispersed in a liquid carrier between electrodes 1 and 5, one may fix the image or images formed on the surface of electrodes 1 and 5 by incorporating a polymeric binder in the carrier liquid. Many such binders (which are well known for use in liquid electrophotographic liquid developers) are known to acquire a change polarity upon being admixed in a carrier liquid and therefore will, themselves, electrophoretically migrate to the surface of one or the other of the electrodes. Alternatively, a coating of a resinous binder (which has been admixed in the carrier liquid), may be formed on the surfaces of electrodes 1 and 5 upon evaporation of the liquid carrier.

The electrically photosensitive particles comprising compounds of Formulas I & II may be used to form monochrome images, or the particles may be admixed with other electrically photosensitive particles of proper color and photosensitivity and used to form polychrome images. Said electrically photosensitive

particles of the present invention also may be used as a sensitizer for other electrically photosensitive materials in the formation of monochrome images. When admixed with other electrically photosensitive particles, selectively the electrically photosensitive particles of the present invention may act as a sensitizer and/or as an electrically photosensitive particle. Many of the electrically photosensitive particles comprising compounds having Formulas I or II have especially useful hues which make them particularly suited for use in polychrome electrophoretic migration imaging processes which employ a mixture of two or more differently colored electrically photosensitive particles. When such a mixture of multicolored electrically photosensitve particles is formed, for example, in an electrically insulating carrier liquid, this liquid mixture of particles exhibits a black coloration. Preferably, the specific cyan, magenta, and yellow particles selected for use in such a polychrome electrophoretic migration imaging process are chosen so that their spectral response curves do not appreciably overlap whereby color separation and subtractive multicolor image reproduction can be achieved.

The following examples illustrate the utility of electrically photosensitive particles comprising the compounds of Formulas I and II in electrophoretic migration imaging processes.

Examples 1-48

Imaging Apparatus

An imaging apparatus was used in each of the following examples to carry out the electrophoretic migration imaging process described herein. This apparatus was a device of the type illustrated in the drawing. In this apparatus, a film base having a conductive coating of 0.1 optical density cermet (Cr SiO) served as electrode 1 and was in pressure contact with a 10 centimeter diameter aluminum roller 14 covered with dielectric paper coated with poly(vinyl butyral) resin

which served as electrode 5. Electrode 1 was supported by two 2.8 cm. diameter rubber drive rollers 10 positioned beneath electrode 1 such that a 2.5 cm. opening, symmetric with the axis of the aluminum roller 14, existed to allow exposure of electrically photosensitive particles 4 to activating radiation. The original transparency 11 to be reproduced was taped to the back side of electrode 1.

The original transparency to be reproduced consisted of adjacent strips of clear (WO), red (W29), green (W61) and blue (W47B) Wratten filters. The light source consisted of a projector with a 1000 watt Xenon Lamp. The light was modulated with an eleven step 0.3 neutral density step tablet. The residence time in exposure zone was 10 milliseconds. The log of the light intensity (Log I) was as follows:

Filters		Log I erg/cm^2/sec.
WO	Clear	5.34
W29	Red	4.18
W61	Green	4.17
W47B	Blue	4.15

The voltage between the electrodes 1 and 5 was about 2 kV. Electrode 1 was negative polarity in the case where electrically photosensitive particles 4 carried a positive electrostatic charge, and electrode 1 was positive in the case where electrically photosensitive particles 4 were negatively charged. The translational speed of electrode 1 was about 25 cm. per second. In the following examples, an image was formed on the surfaces of electrodes 1 and 5 after simultaneous application of light exposure and electric field to electrically photosensitive particles 4 admixed with a liquid carrier as described below to form a liquid imaging dispersion and which dispersion had been placed in nip 21 between the electrodes 1 and 5. If the

compounds being evaluated for use as particles 4 possessed a useful level of electrical photosensitivity, one obtained a negative-appearing image reproduction of original 11 on electrode 5 and a complementary image on electrode 1.

Imaging Dispersion Preparation

Imaging dispersions were prepared to evaluate each of the compounds in Table I as electrically photosensitive particles. The dispersions were prepared by first making a stock solution of the following components. The stock solution was prepared simply by combining the components.

"Isopar G"	2.2 g
"Solvesso 100"	1.3 g
"Piccotex 100"**	1.4 g
"PVT"*	0.1 g

* Poly(vinyltoluene-co-lauryl methacrylate-co-lithium methacrylate-co-methacrylic acid)(56/40/3.6/0.4)

** Polyvinyltoluene-styrene copolymer

A 5 g aliquot of the stock solution was combined in a closed container with 0.045 g of the Table I compound to be tested and 12 g of stainless steel balls. The preparation was then milled for three hours on a paint shaker.

Each of the 48 compounds described in Table I was tested according to the just outlined procedures. Each of the compounds was found to be electrophotosensitive as evidenced by obtaining a negative appearing image of the original on one electrode and a complementary image on the other electrode. Image quality was determined visually having regard to minimum and maximum densities, speed and color saturation.

Examples 49-65 :

Imaging dispersions containing the Table I compounds listed in Table II were prepared as in the previous Examples 1-48. Imaging was also carried out as in the previous examples except the polymeric coating on the paper covering aluminum roller 14 was either Polymer A and Polymer B as indicated in Table II.

A portion of the imaged polymer coated paper for each Table II compound was heated at 170°C for 15 seconds. The sample generally changed to a brighter hue when heated in the polymer coating. Reflection spectra were taken of both the unheated and heated samples using diffuse illumination. Results are reported in Table II.

TABLE II

Table I Compound	λ max*	% Density Change **	λ max Polymer A or B***
3	575	51	544(A)
25	450	117	560(A)
39	566	59	536(A)
43	635	67	585(A)
47	536	105	509(A)
33	456	234	456(A)
24	552	37	554(A)
5	588	238	563(A)
26	590	888	553(A)
41	554	618	550(B)
27	541	361	537(A)
15	666	42	613(A)
48	549	66	524(A)
40	620	5	589(B)
18	560	14	565(B)
7	510	533	515(B)
23	658	10	652(B)
8	560	38	561(B)

* Wavelength of maximum absorption for unheated crystalline dyes.

** Percent increase in optical density (color reflection measured through appropriate filters) between heated and unheated images.

*** Wavelength of maximum absorption for heated dye in polymer A or Polymer B. Polymer A is a poly(vinylbutyral) resin under the tradename Butvar B76 from Shawinigan Products Corp. Polymer B is ethyleneglycol/cyclohexane dimethanol/terephthalic acid copolyester (70:30).

Claims

1. Electrically photosensitive particles for electrophoretic migration imaging processes characterized in that they comprise a compound having the following formula :

I. $A^1-CL^1(=CL^2-CL^3)_m=C<^{CN}_{B^1}$

or

II. $A^2=CL^4-CL^5(=CL^6-CL^7)_n=C<^{CN}_{B^2}$

wherein:

m and n are zero, one or two ;

L^1, L^2, L^3, L^4, L^5, L^6 and L^7 represent hydrogen, cyano, alkyl, aralkyl, aryl or heterocyclyl, or in addition, any two of L^1, L^2 and L^3 or any two of L^4, L^5, L^6 and L^7 may together represent the atoms needed to complete a carbocyclic ring having from 5-10 carbon atoms ;

A^1 represents an alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic nucleus ;

A^2 represents a basic substituted or unsubstituted heterocyclic nucleus selected from the group consisting of : an imidazole; a 3H-indole; a thiazole ; a benzothiazole ; a naphthothiazole ; a thianaphtheno-7',6'-4,5-thiazole ; an oxazole ; a benzoxazole ; a naphthoxazole ; a selenazole ; a benzoselenazole ; a naphthoselenazole ; a thiazoline, a 2-quinoline ; a 4-quinoline ; a 1-isoquinoline ;a benzimidazole; a 2-pyridine ; a 4-pyridine ; a pyrrolo/1,2-a/pyridine ; and a acenaphthothiazole ;

B^1 and B^2 represent cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, alkyl sulfonyl, acyl, arylcarbonyl, nitro substituted aryl, sulfonyl, fluorosulfonyl, trifluoromethylsulfonyl, carbamoyl, aryl carbamoyl, alkyl carbamoyl or heteroyl groups.

2. Particles according to Claim 1 wherein A^1 is a nucleus selected from the group consisting of thiophene, benzo/b/thiophene, naphtho/2,3-b/thiophene, furan, isobenzofuran, chromene, pyran, xanthene, pyrrole, 2H-pyrrole, pyrazole, indolizine, indoline, indole, 3H-indole, indazole, carbazole, pyrimidine, isothiazole, isoxazole, furazan, chroman, isochroman, 1,2,3,4-tétrahydroquinoline, 4H-pyrrolo/3,2,1-ij/-quinoline, 1,2-dihydro-4H-pyrrolo/3,2,1-ij/quinoline ; 1,2,5,6-tetrahydro-4H-pyrrolo/3,2,1-ij/quinoline ;1H,5H-benzo/ij/quinolizine ; 2,3-dihydro-1H,5H-benzo/ij/quinolizine ; and 2,3,6,7-tetrahydro-1H,5H-

benzo/ij/quinolizine, 10,11-dihydro-9H-benzo/a/xanthen-8-yl ; 6,7-dihydro-5H-benzo/b/pyran-7-yl and pyrrolo/2,1-b/ benzothiazole.

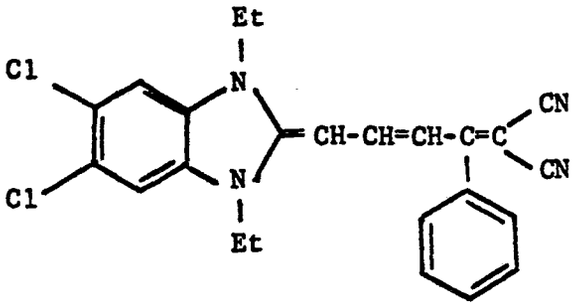
3. Particles according to Claim 1 wherein : A^1 represents a substituted or unsubstituted nucleus selected from the group consisting of indole ; 1,2,5,6-tetrahydro-4H-pyrrolo /3,2,1-ij/quinoline ; 2,3,6,7-tetrahydro-1H,5H-benzo/ij/quinolizine, and pyrrolo/2,1-b/benzothiazole;

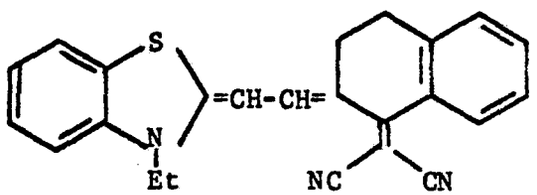
A^2 represents a substituted and unsubstituted nucleus selected from the group consisting of 3H-indole ; naphthothiazole ; benzimidazole ; 2-pyridine ; pyrrolo/1,2-a/pyridine ; benzoxazole ; benzoselenazole ; and acenaphthothiazole ;

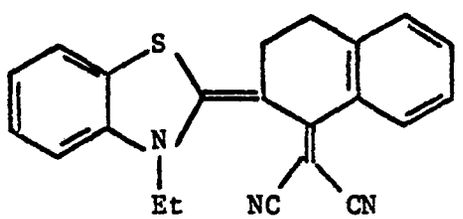
L^1,L^2,L^3,L^4,L^5,L^6 and L^7 are the same or different and represent hydrogen, cyano,methyl,phenyl, benzoyl, 2-thienyl, benzofuryl, 3-dicyanomethylenebutyl, 2-oxo-2H-benzo/b/pyran-3-yl and 2-cyano-2-dicyanomethyleneethyl,or any two of L^1, L^2 and L^3, or L^4, L^5, L^6 and L^7 represent the atoms needed to complete a nucleus selected from the group consisting of dihydronaphthalene, iH-indene and cyclohexene ; and

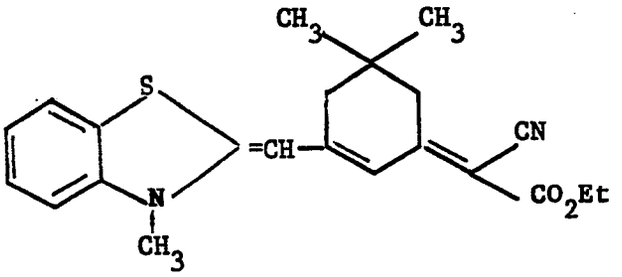
B^1 and B^2 represent cyano, ethoxy carbonyl, naphthoyl, benzoyl, furyol, benzofuroyl, or dihydroxy benzoyl.

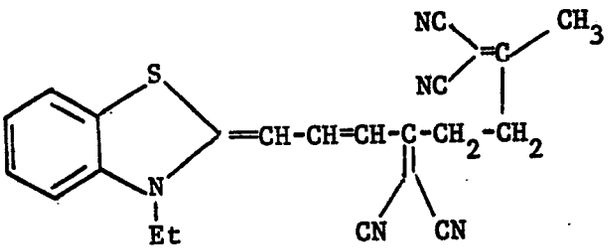
4. Particles according to Claim 1 wherein said material has a formula selected from the following group :

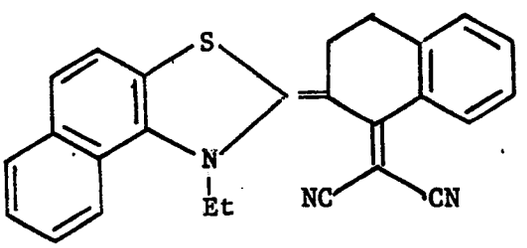


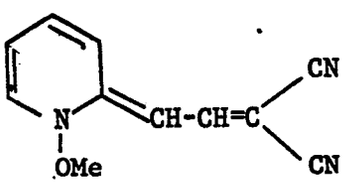


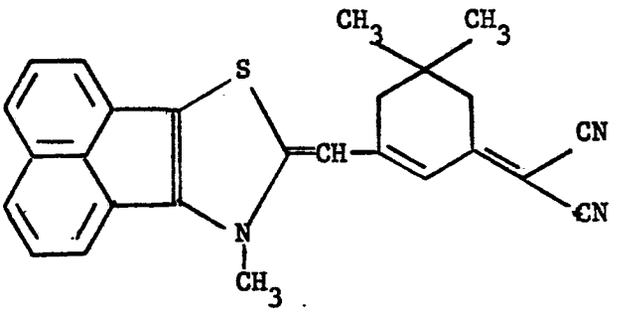


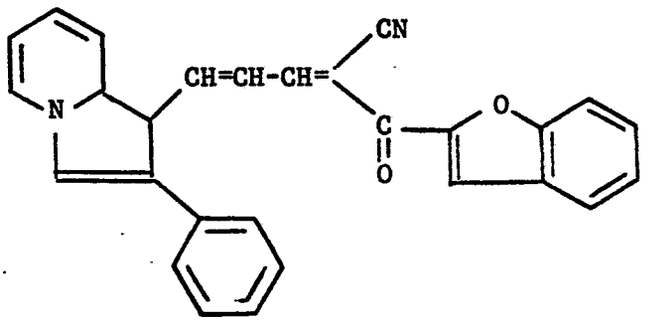












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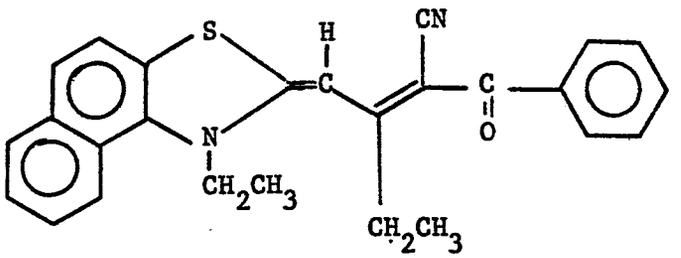

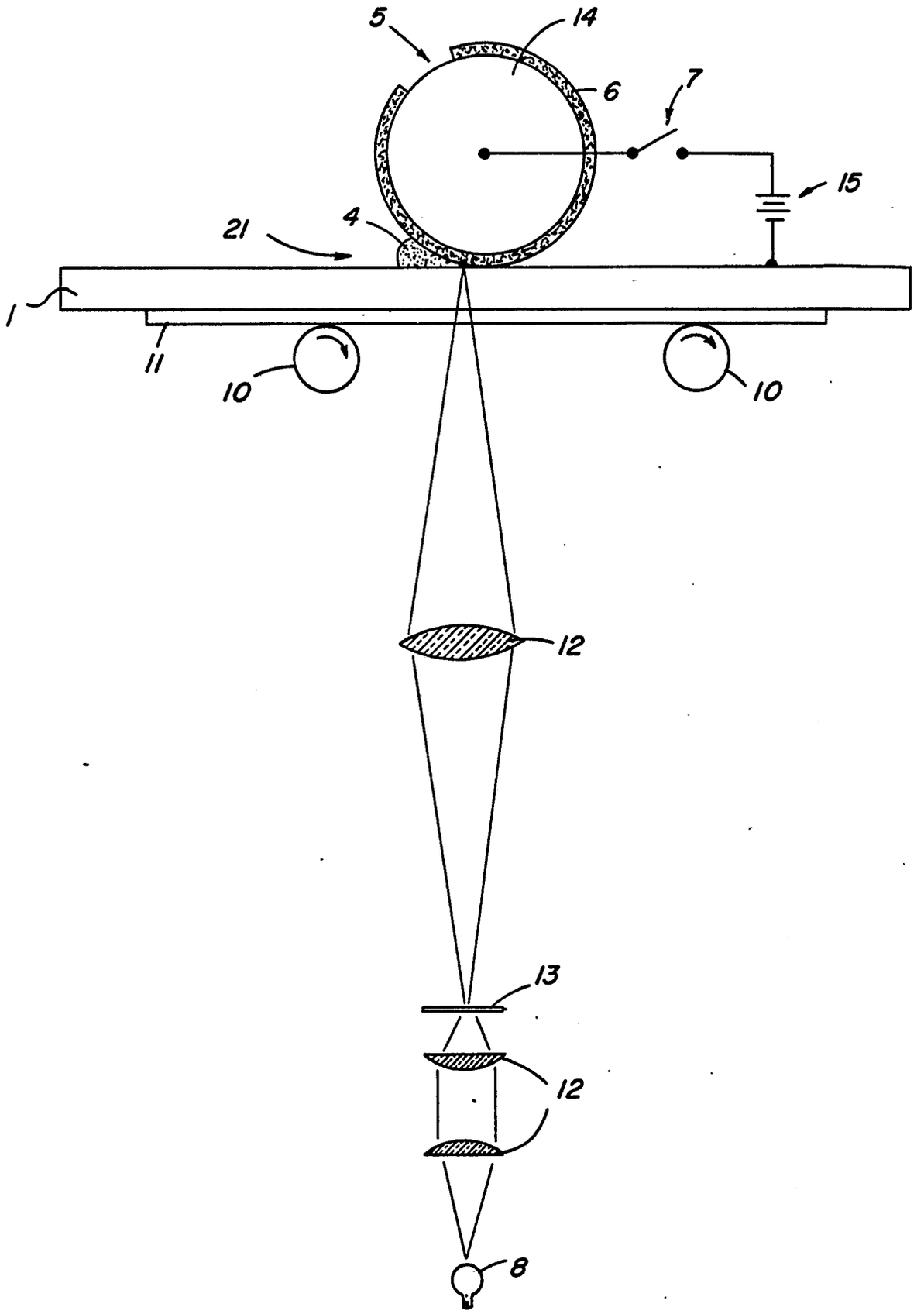
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European Patent Office

EUROPEAN SEARCH REPORT

0000599

Application number

EP 78 20 0084

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	FR - A - 2 185 814 (CIBA-GEIGY) * The claims; the figures; page 1, lines 33-35; page 3, formula F-12; example 2 *	1	G 03 G 17/04 C 09 B 23/00
	DE - A - 2 532 306 (FUJI) * The claims; the figures; page 12, paragraph 3; page 15, paragraph 2; page 17, formula IV *	1	
A	RESEARCH DISCLOSURE, no. 154, February 1977, art. 15437. Hampshire U.K. M.S.BLOOM et al: "Solubilized dark exchange materials for photoimmobilized electrophoretic recording", pages 32-36. * Page 32, column 1, paragraph 1 to page 33; column 2, paragraph 6; page 33, formula 2,5,7,15,16, 18 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.³) G 03 G 17/04
DA	US - A - 3 976 485 (C.F.GRONER) * The claims; the abstract; the figures *	1	
A	RESEARCH DISCLOSURE, no. 150, October 1976, art. 15029 Hampshire U.K. H.E.WRIGHT et al. "Electrophoretic migration imaging process", pages 51-56. * Page 51, column 2, last paragraph to page 52, column 1, ./.	1	

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: conflicting application
- D: document cited in the application
- L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	12-10-1978	VANHECKE

EPO Form 1503.1 06.78

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	paragraph 3; page 54, column 2, paragraph 4 to page 55, column 2, paragraph 1; the figure 1 *		
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P	RESEARCH DISCLOSURE, no. 162, October 1977, art. 16257 Hampshire U.K. L.G.WEBSTER et al "Electrophotosensitive material for migration imaging processes", pages 75-77: * Page 75, column 1, last paragraph to page 77, column 1, paragraph 3 *	1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.²)
