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3,772,281

MEROCYANINE DYES FOR SENSITIZING ZINC OXIDE PHOTOCONDUCTORS

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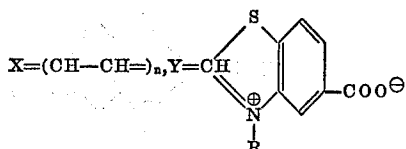
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U.S. Cl. 260-240.1

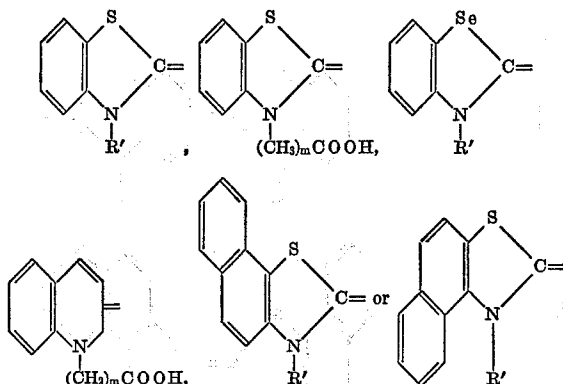
7 Claims

ABSTRACT OF THE DISCLOSURE

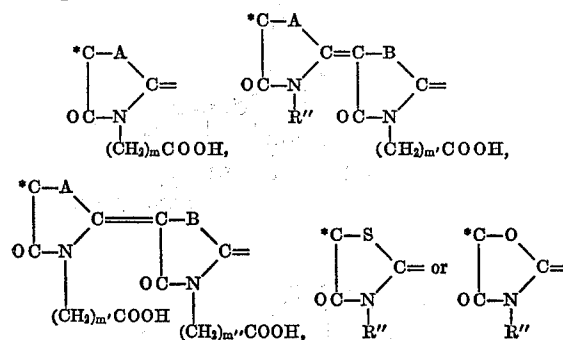
A sensitizer for use in copying materials, which is prepared by the use of water as a medium, for electrophotography, expressed by the following general formula:



wherein X= represents



Y=represents



[provided that R, R' and R'' each represents alkyl radical having carbon atoms in the range of 1-10; n, m, m' and m'' each represents 0 or a natural number in the range of 1-10; A and B each represents oxygen atom or sulfur atom and A may be the same as B; and * indicates the position bonding to (CH-CH=)_n].

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a sensitizer capable of manifesting superb sensitizing effect when applied to the process of preparing a copying material for use in electrophotography carrying a photoconductive layer from a

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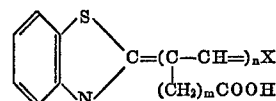
photoconductive layer-formable dispersion in which water is used as the dispersion medium.

DESCRIPTION OF THE PRIOR ART

A copying material for use in electrophotography is generally prepared by forming a photoconductive layer consisting of a photoconductor such as zinc oxide, a resinous binder and a sensitizer on the surface of a support such as metallic plate or paper whose reverse side has been processed for conductivity. The formation of the photoconductive layer is generally effected through the process of dispersing the foregoing components in an organic solvent such as toluene, applying the resulting dispersion onto the support and drying thereafter. This process to use an organic solvent in forming the photoconductive layer, however, is accompanied by various disadvantages such that: the organic solvent is generally so expensive that it is necessary to recover it; it is hazardous due to high inflammability of said solvent; it calls for special cares in respect of the health control of workers concerned; it requires coating devices of special construction and therefore being expensive; because of the use of air knife as a coating head being impossible, high speed coating is infeasible; etc. Therefore, there have hitherto been proposed various processes intended for forming a photoconductive layer from a dispersion prepared by dispersing a photoconductor such as zinc oxide, a resinous binder and a sensitizer in water. With respect to these processes of forming the photoconductive layer by the use of water as the dispersion medium, however, such a sensitizer as capable of manifesting superb efficiency when applied to them has not been disclosed yet. In other words, according to the conventional process of forming a photoconductive layer by the use of an organic solvent as the dispersion medium, such water soluble coloring matters as Rose Bengal, fluoresceine, Eosine, Acridine Yellow, Erythrosine, Methylene Blue, Rhodamine B, etc. have been employed as the sensitizer. But, in case these sensitizers are applied to the process of forming the photoconductive layer by the use of water as the dispersion medium, they scarcely display a remarkable sensitizing effect for the resulting copying materials. On the other hand, as the sensitizer applicable to the process of forming a photoconductive layer by the use of water as the dispersion medium, there has hitherto been employed merocyanine-type coloring matters expressed by the following general formulas:

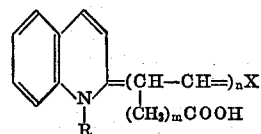
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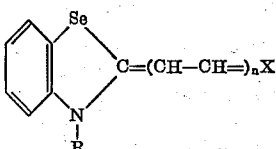
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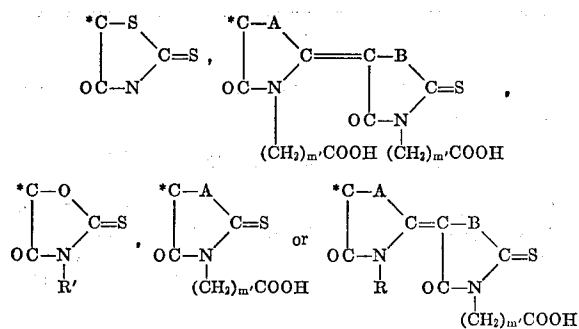


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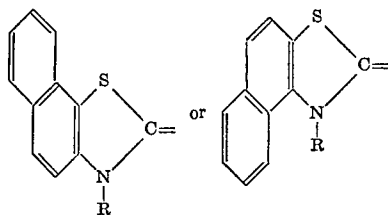
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wherein X respectively represents

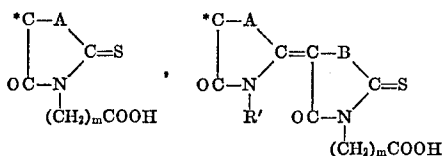


(4) $X = (CH-CH=)_n Y$

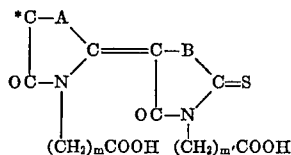
wherein X= represents



Y represents



or



[provided that R and R' each represents alkyl radical having carbon atoms in the range of 1-10; n, m, m' and m'' each represent 0 or a natural number in the range of 1-10; A and B each represents oxygen atom or sulfur atom and A may be the same as B; and * indicates the position bonding to $(CH-CH=)_n$].

These compounds are relatively low in degree of coloring and their wave length range of absorbing light is in the range of visible rays. They can be easily adsorbed to such a photoconductor as zinc oxide and are very effective in sensitizing the photoconductive layer. But, these compounds are defective in that they are apt to fade due to oxidation and bring about bad influences on the copying material for use in electrophotography or post-development copies. For instance, when these compounds are left standing in an aqueous dispersion for use in forming the photoconductive layer, they not only gradually get decolorized due to oxidation by a polymerization initiator present in the dispersion (this initiator is usually a peroxide and remains in the dispersion on the occasion of synthesis of an emulsion of resinous binder), resulting in deterioration of photosensitivity of the copying material, but also fade due to light even in the absence of the polymerization initiator within the copying material thereby to bring on a change in quality of the copy.

SUMMARY OF THE INVENTION

The primary object of the present invention is to provide a sensitizer which, when applied to the process of preparing a copying material for use in electrophotography using a photoconductive layer-forming dispersion in which water is contained as the dispersion medium, is

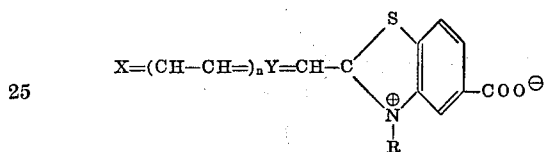
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capable of manifesting superb sensitizing effect with respect to the resulting copying material.

Another object of the present invention is to provide a sensitizer which has such characteristics that it is stable against a polymerization initiator and light, is capable of being sufficiently adsorbed to a photoconductor such as zinc oxide within an aqueous medium for dispersion and is superior in sensitization of the photoconductive layer formed thereby.

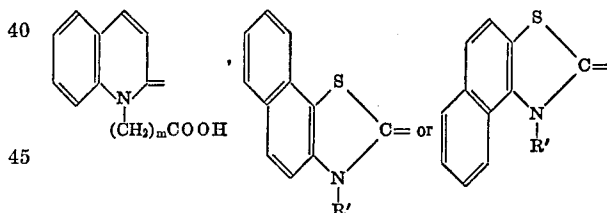
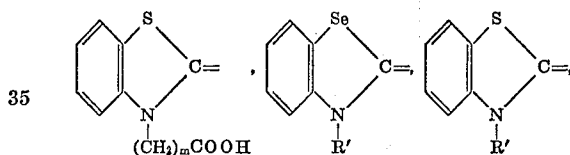
The inventors have conducted a series of studies in search of such a sensitizer as being effective even when a small amount thereof is applied to the process of forming a photoconductive layer by using water as the dispersion medium, and, as a result, they have found that specific merocyanine-type coloring matters are suitable for this purpose. In other words, they have found that the merocyanine-type coloring matters to be expressed by the following general formula are suitable for said purpose.

20 general formula:

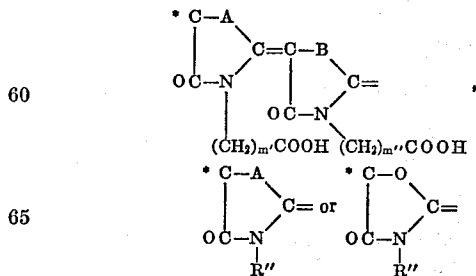
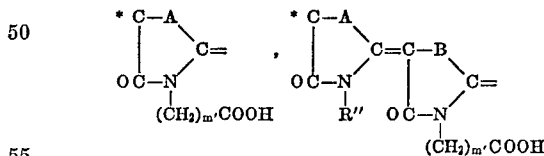


wherein

30 X= represents



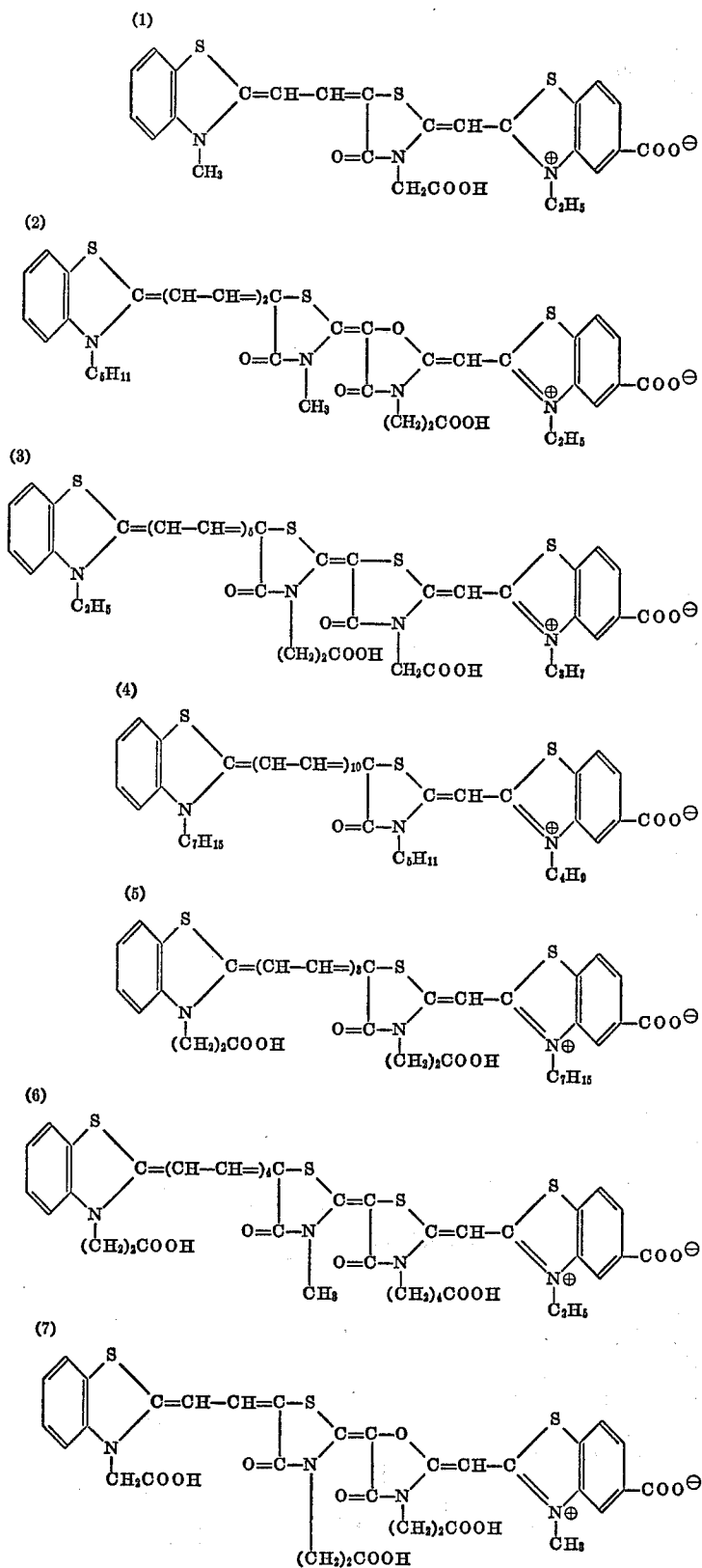
Y= represents



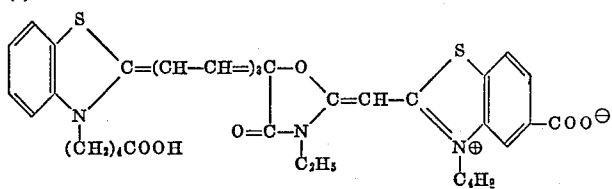
[provided that R represents alkyl radical having carbon atoms in the range of 1-10, and preferably 1-5; n, m, m' and m'' each represents 0 or a natural number in the range of 1-10, and preferably 1-5; A and B each represents oxygen atom or sulfur atom and A may be the same as B; and * indicates the position bonding to $(CH-CH=)_n$].

The merocyanine-type coloring matters expressed by the foregoing general formula are stable against the polymerization initiator and light, and the copying material for electrophotography containing these merocyanine-type coloring matters as the sensitizer in the photoconductive layer thereof shows very little deterioration of sensitivity in spite of a prolonged preservation.

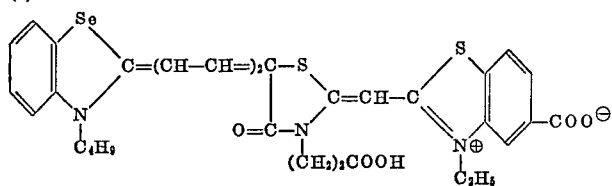
Further, in case a photoconductive layer is formed by using water as the dispersion medium, these merocyanine-type coloring matters have such an advantage that a small amount thereof suffices for enhancement of the sensitivity of photoconductive layer as they can be well adsorbed to such a photoconductor as zinc oxide. Given in the following are some examples of the merocyanine-type coloring matters according to the present invention.



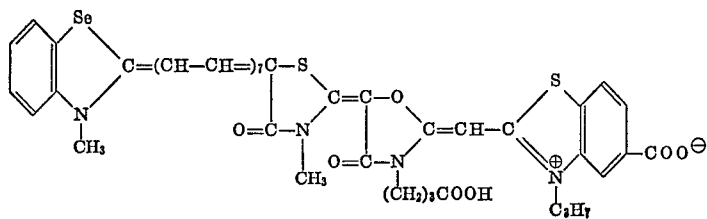
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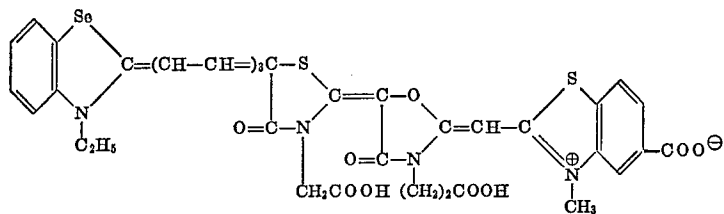
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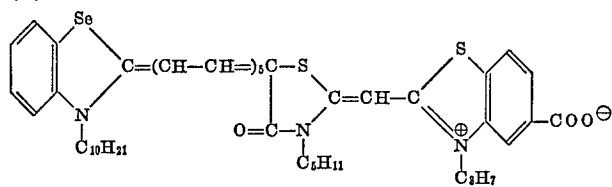
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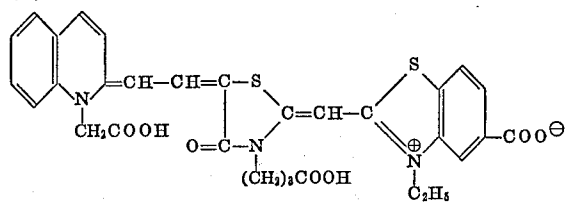
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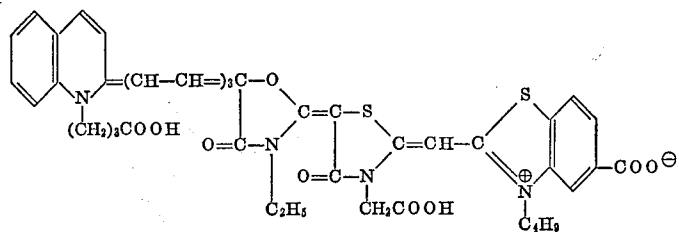
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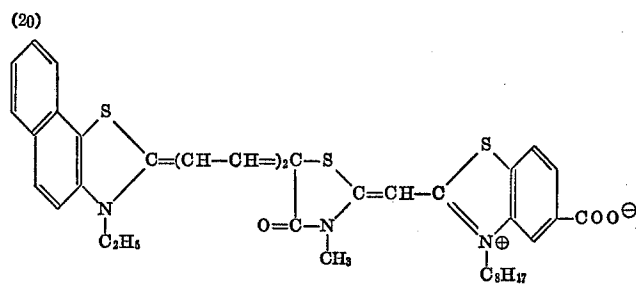
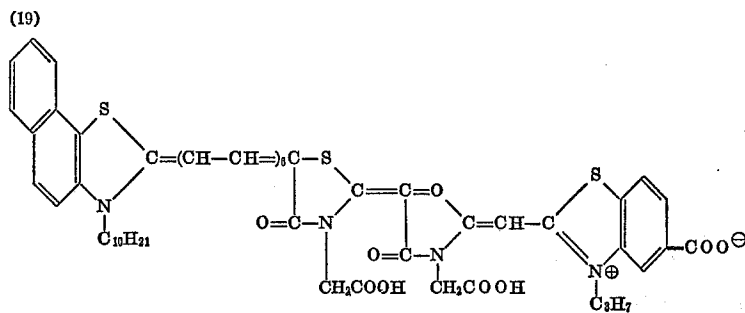
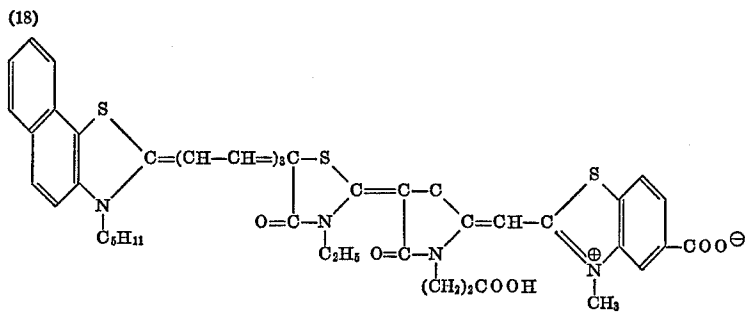
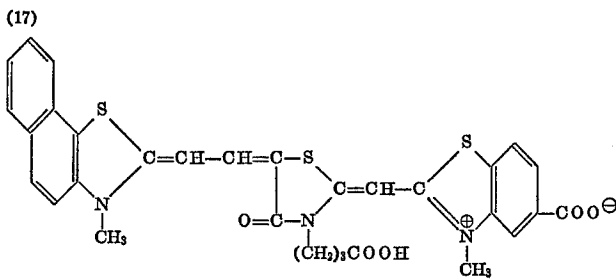
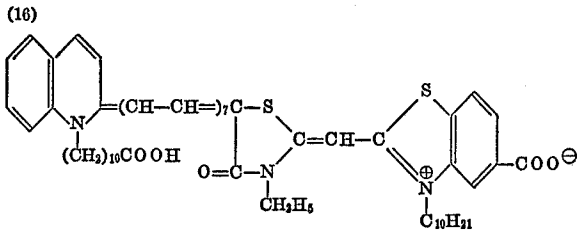
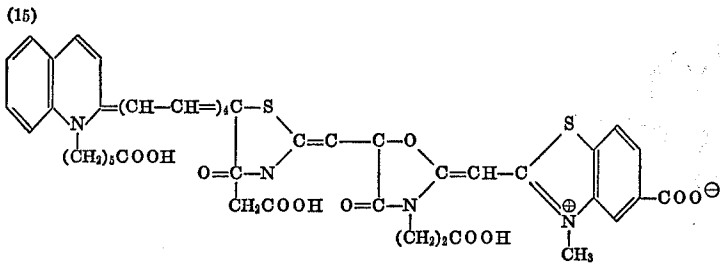


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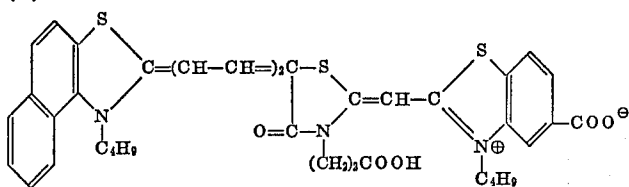


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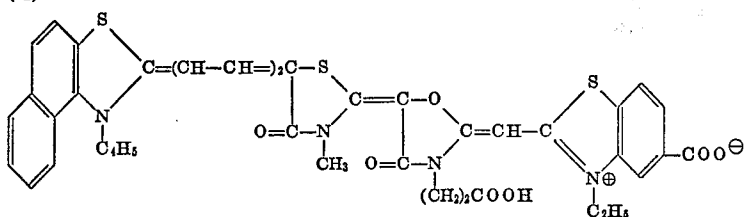




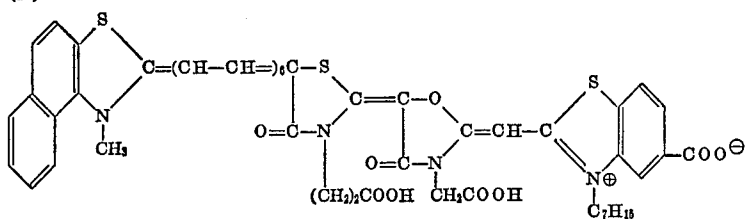
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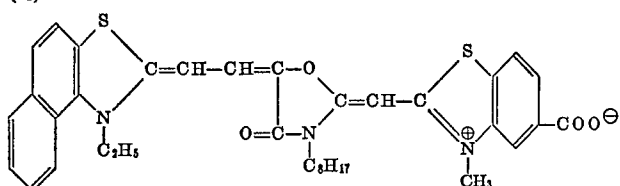
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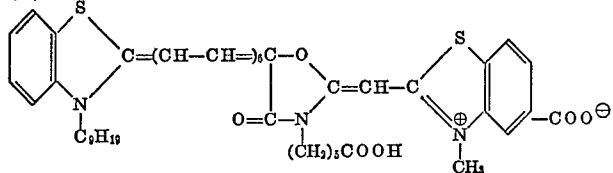
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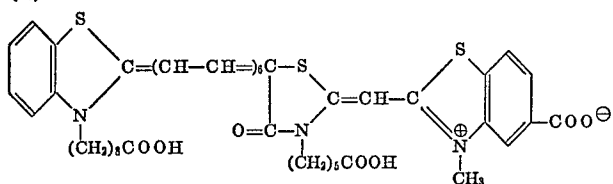
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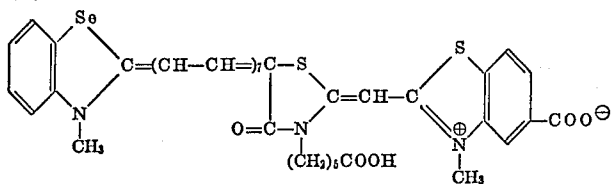
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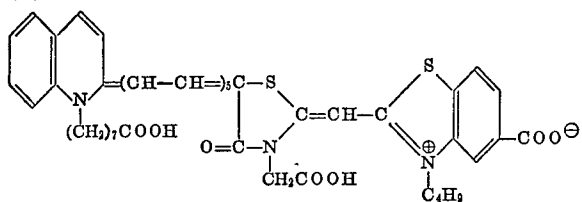
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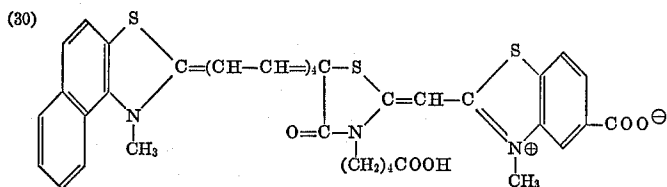
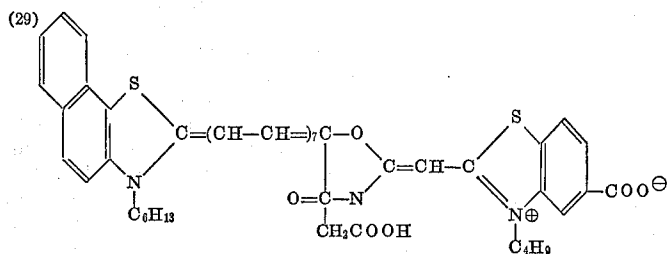


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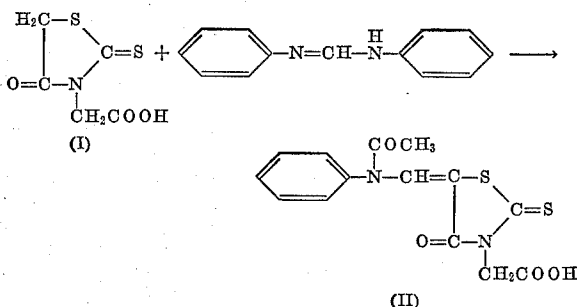


On the occasion of applying the aforementioned merocyanine-type coloring matters as the sensitizer, these compounds are usually dissolved in alcohols such as methanol, ethanol, butanol, etc. to the extent of 0.1-1 wt. percent. In case any of these compounds cannot be easily dissolved in alcohols alone, it is advisable to expedite resolution by adding thereto a small amount of ammonia, amine, pyridine or other base. The sensitizing coloring matter thus dissolved is subsequently mixed with water, a water-soluble or water-dispersible resinous binder and a photoconductor such as zinc oxide to form an uniform dispersion, and thereafter the dispersion is coated onto an appropriate support.

How to synthesize the merocyanine-type coloring matters applicable in the present invention will be exemplified in the following.

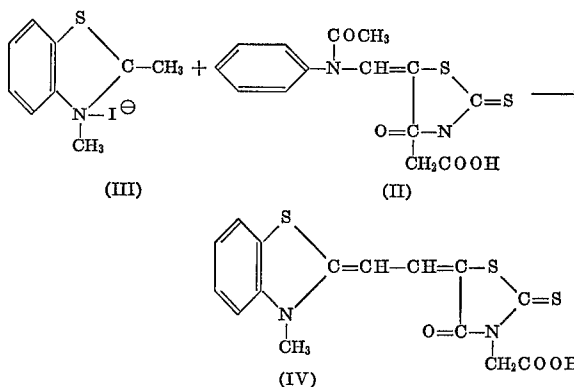
Process for synthesizing merocyanine-type coloring matters expressed by the structural Formula 1 above.

5.1 g. of thiocarboxymethyl rhodanine (as expressed by the following Formula I), 6.4 g. of diphenyl formamidine, 30 cc. of acetic anhydride and 0.8 cc. of triethyl amine are mixed and made to react with one another at 140°-150° C. for about 3 hours. When 75 cc. of ligroin is slowly added to the thus reacted mixture after cooling thereof, there takes place separation of crystals. Upon taking out by a suction filter, cleansing with ether and drying thereafter, these crystals are made to recrystallize by means of methanol, whereby there is obtained 3-carboxymethyl - 5 - (acetanilinomethylene)rhodanine (expressed by the following Formula II) (M.P. 133° C.) as follows: yield 6.2 g.; yield ratio 64%.



Subsequently, 1.7 g. of derivative from benzothiazole expressed by the following structural Formula III, 1.5 g. of the foregoing product expressed by the Formula II, 20 cc. of ethanol and 1.5 cc. of triethyl amine are mixed and subjected to reflux at 78°-80° C. for about 30 minutes. A blue solid separated by cooling the thus treated mixture is taken out by a suction filter and recrystallized by means of methanol, whereby there is obtained 3-carboxymethyl-

dithio-4-keto-5-(N - methyl-benzothiazolydene-1-ethyldene)-tetrahydrothiazole (expressed by the following Formula IV) (M.P. 191°-193° C.) in the form of green crystals: yield 0.72 g.



A mixture consisting of 10 g. of the foregoing product expressed by the Formula IV, 4 g. of 2-methyl-5-carboxy-benzothiazole and 4.5 g. of p-toluene methyl sulfonate is heated at 140° C. for 3.5 hours for reaction. The thus reacted mixture is cooled, mixed with 150 cc. of pyridine, and boiled for 25 minutes. When the mixture treated as above is cooled again, there is obtained precipitate. By subjecting the precipitate to suction filtration, cleansing with a small amount of ethanol as well as ether and recrystallization by means of methanol, there is obtained 3.5 g. of merocyanine-type coloring matter expressed by the aforementioned general Formula 1 (M.P. 224° C.).

Those merocyanine-type coloring matters which are expressed by the foregoing Formulas 1-30 can also be prepared through similar processes.

The merocyanine-type coloring matters prepared as above are applicable to (A): the photoconductive layer-formable dispersion consisting mainly of water, a water-soluble resinous binder and such photoconductor as zinc oxide and (B): the photoconductive layer-formable dispersion consisting mainly of water, a water-dispersible binder and such photoconductor as zinc oxide, as described hereunder.

(A) Type photoconductive layer-formable dispersion:
(a) A dispersion which is prepared by dissolving in water a water-soluble copolymer obtained by treating a copolymer with ammonia or an organic amine, said copolymer being obtained by copolymerizing vinyl acetate with at least one vinyl monomer such as styrene, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate and butyl methacrylate, and at least one unsaturated carboxylic acid such as methacrylic acid,

crotonic acid, maleic acid and itaconic acid and dispersing in the resulting solution such photoconductor as zinc oxide.

- (b) A dispersion which is prepared by dissolving in water a water-soluble copolymer obtained by treating the partially saponified product of vinyl acetate-unsaturated carboxylic acid copolymer such as the partially saponified product of vinyl acetate-crotonic acid copolymer, the partially saponified product of vinyl acetate-itaconic acid copolymer, etc. with ammonia or an organic amine and dispersing in the resulting solution such photoconductor as zinc oxide.

(B) Type photoconductive layer-formable dispersion:

- (a) A dispersion which is prepared through the steps: dissolving such resin as enumerated in the following (1) in a small amount of organic solvent; dispersing the thus dissolved resin in water by the use of such acidic compound as enumerated in the following (2) together with such volatile basic compound as enumerated in the following (3); and dispersing such photoconductor as zinc oxide in the foregoing dispersion.

(1) Resins:

colophony (rosin), modified colophony, dammar resin, ethyl cellulose acetate, hydroxyethyl cellulose acetate, cellulose acetate, and ethylcellulose stearate—poly-N-vinylcarbazole, N-vinylcarbazole-ethylacrylate copolymer
polyvinylchloride, vinylchloride-vinylisobutyl ether copolymer, vinylchloride-vinylacetate-vinylalcohol copolymer, vinylchloride-vinylacetatemaleic anhydride copolymer, polyalkylmethacrylate vinylacetate resin, vinylacetate-crotonic acid copolymer, vinylacetate-vinylstearate copolymer, polyvinylstearate, vinylacetate-maleic acid copolymer—polyvinyl butyral, vinyl butyral-vinylacetate copolymer polystyrene, styrene-methacrylic acid copolymer, styrene-butadiene copolymer, styrene-dimethyl itaconate copolymer polymethacrylic ester, polyalkylmethacrylate, polymethylmethacrylate styrenated alkyd resin, alkyd-modified rosin resin, alkyd-modified phenol resin, epoxy ester resin, pentaerythritol phthalate resin, polycarbonate, poly indene, poly cyclopentadiene, silicone resin, ketone resin, rubber chloride; resins obtained by copolymerizing at least one member selected from the vinyl monomer group consisting of glycidyl acrylate, glycidyl methacrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, 5-hydroxypentylvinyl ether



with at least one member selected from the monomer group consisting of styrene, alkyl acrylate, alkyl methacrylate, acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, and fumaric acid; resins obtained by copolymerizing at least one ester selected from the group consisting of alkylacrylate and alkylmethacrylate, at least one monomer selected from the group consisting of crotonic acid, itaconic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, and at least one vinyl monomer selected from the group consisting of acrylonitrile, methacrylonitrile, styrene, dichlorostyrene, vinyl acetate, vinyl chloride and vinylidene chloride.

(2) Acidic compounds:

aliphatic saturated monocarboxylic acid such as caproic acid, heptanoic acid, caprylic acid, pelargonic acid, capric acid, n-undecylenic acid, lauric acid, n-tridecylenic acid, myristic acid, n-pentadecylenic acid, palmitic acid, margaric acid, stearic acid, n-nonadecylenic acid, arachidic acid, n-heneicosanoic acid, behenic acid, n-tricosanoic acid.
aliphatic unsaturated monocarboxylic acid such as

2-hexenoic acid, 3-hexenoic acid, 4-hexenoic acid, 5-hexenoic acid, 2-methyl-2-pentenoic acid, 3-methyl-2-pentenoic acid, 4-methyl-2-pentenoic acid, 4-methylpentenoic acid, α -ethylcrotonic acid, 2,2-dimethyl-3-butenic acid.

aliphatic diolefin carboxylic acid such as

2,4-hexadienoic acid, diallylacetic acid, geranium acid, 2,4-decadienoic acid, 2,4-dodecadienoic acid.

aliphatic higher unsaturated monocarboxylic acid such as hexadecatrienoic acid, linoleic acid, linolenic acid, 6,9,12-octadecatrienoic acid, eicosadienoic acid, eicosatrienoic acid, docosadienoic acid, docosatrienoic acid.

aliphatic saturated dicarboxylic acid such as

adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane dicarboxylic acid, dodecane dicarboxylic acid, brassylic acid, and tetradecane dicarboxylic acid.

aromatic monocarboxylic acid such as

benzoic acid, o-toluylic acid, m-toluylic acid, p-toluylic acid, dimethyl benzoic acid, o-ethylbenzoic acid, m-ethylbenzoic acid, p-ethylbenzoic acid, 2,3,4-trimethylbenzoic acid, 2,3,5-trimethylbenzoic acid, 2,3,6-trimethylbenzoic acid, 2,4,5-trimethylbenzoic acid, 2,4,6-trimethylbenzoic acid.

aromatic dicarboxylic acid such as

phthalic acid, isophthalic acid, terephthalic acid, 3-chlorophthalic acid, 4-chlorophthalic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, tetrabromophthalic acid.

aromatic tricarboxylic acid such as

1,2,3-hemimellitic acid and 1,2,4-trimellitic acid.

alicyclic carboxylic acid such as

abietic acid, bisnorbornic acid, β -boswellic acid, chenodesoxycholic acid, quinic acid, cholic acid, cholic acid, dehydrocholic acid, dioxycolic acid, doisanolic acid, erythrocholic acid, etiocholic acid, glycocholic acid, glycyrrhetic acid, oleanolic acid, helvolic acid, hiodesoxycoalic acid, risocoalic acid, naphthenic acid.

natural resins containing a resin acid such as

elemi, Gurjun balsam, jalap, scammonium, amber, bdellium, sagapenum, Euphorbium, myrrhe, Opopanax, benak, dead dammar, melanty, chan, yan panoun, papuan dammar, shellac, acaroid, dragon brad, mustic, styrax, canada balsam, mecca balsam, copaiba balsam, kauri kopal, soft manila kopal, hard manila kopal, congo kopal, benguela kopal.

vinyl copolymers having carboxyl radical such as

styrene-maleic acid-methacrylic acid copolymer, acrylic ester-acrylic acid copolymer, vinyl acetate-crotonic acid copolymer and styrene-vinylacetate-maleic acid copolymer.

(3) Volatile basic compounds such as:

ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, butylamine, hexylamine, ethylenediamine, aniline, morpholine, piperidine and hydrazine.

(b) A dispersion which is prepared through the steps: dispersing such polymeric monomer as enumerated in the following (1) in water by the use of such acidic compound as enumerated in the following (2) together with a small amount of surface active agent; effecting emulsion polymerization of said monomer by adding a reaction initiator; and dispersing such photoconductor as zinc oxide in the thus polymerized monomer.

(1) Polymeric monomers:

vinyl acetate, vinyl chloride, styrene, vinyl propionate, vinylidene chloride, crotonic acid, itaconic acid, maleic acid, fumaric acid, vinylstearate, vinyl isobutylether, vinyl alcohol, methacrylic acid, acrylic acid, butadiene, dimethyl itaconate, acrylonitrile, glycidyl methacrylate,

glycidyl acrylate, hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, hydroxypropylmethacrylate, hydroxypropyl acrylate, 5-hydroxypentyl vinyl ether, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate and cyclohexyl methacrylate, α -methylstyrene, p -methylstyrene, p -methoxystyrene, vinyl toluene, vinyl xylene, isopropyl styrene, ethyl vinylbenzene and divinylbenzene, acrylonitrile, methacrylonitrile, vinylidene cyanide, acrylamide, methacrylamide, N- and N'-dimethylacrylamide, N- and N'-dipropylmethacrylamide, N-phenylacrylamide, N-methylolacrylamide and N-vinylpyrrolidone, 2-vinylpyridine, 3-vinylpyridine, vinyl bromide, vinyl fluoride, vinylidene fluoride.

(2) Acidic compounds:

The same as the foregoing (B)-(a)-(2).

Further, the surface active agent applicable in the dispersion (B) includes alkylbenzene sulfonic acid-triethanolamine, sodium benzenesulfonate, sodium lauryl sulfate, dialkylsulfosuccinate, sodium dodecylbenzenesulfonate, etc.

In case of the dispersion coming under (B)-(a) above, the appropriate amount of said acidic compound to be applied is in the range of 1-10 wt. percent or thereabout against said resin, and the appropriate amount of said volatile basic compound to be applied is in the range of 1-10 wt. percent or thereabout against the resin.

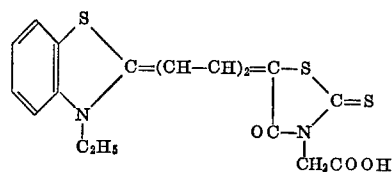
In case of the dispersion coming under (B)-(b) above, the appropriate amount of said acidic compound to be

Primal AC-61 (the trade name of an acrylic resin emulsion manufactured by Nippon Acryl Kagaku K.K.; solid content: 40%): 50 g.

zinc oxide (a manufacture of SAKAI KAGAKU K.K.; trade name: Sazex 1000): 100 g.

A mixture according to the foregoing prescription was stirred by a homomixer for 10 minutes for the sake of dispersion. The dispersion thus prepared was applied to the reverse side of a paper support whose surface had been processed for conductivity and was dried for 10 minutes at 100° C., whereby there was obtained a copying material for electrophotography provided with a photoconductive layer having a thickness of about 20 μ .

On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter applied in the foregoing prescription, a comparative copying material was prepared.



These two copying materials were made to adapt to the atmosphere of a dark place of 20° C. and 65% RH for 24 hours and thereafter were subjected to electrification, exposure and development through conventional processes, thereby forming copied images. When the clearness, the sensitivity and the rate of light-fading in the copy were tested, the result was as shown in the following Table 1.

TABLE 1

Copying material	Saturation potential (v.)	Sensitivity (lux. sec.) ¹	Clearness of image	Light-fading (800 lux ² 4 hrs.) percent
Copying material under the present invention.....	520	310	Excellent...	80 → 80.5
Comparative copying material.....	500	928	Good.....	80 → 86.2

¹ The quantity of light required for reducing by half the electrical potential charged on the photoconductive layer immediately before light-exposure.

² The photovolt reflection factor in case the copying material is left standing for 4 hours while being exposed to 800-lux fluorescent light (when a green filter is employed). In this connection, the photovolt employed herein was a manufacture of Photovolt Co., U.S.A.

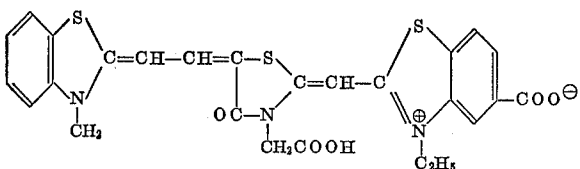
applied is in the range of 1-10 wt. percent or thereabout against said polymeric monomer, and the appropriate amount of said surface active agent is in the range of 0.05-3 wt. percent or thereabout against the polymeric monomer. Further, in the dispersion coming under the foregoing (A)-(a), (A)-(b), (B)-(a) and (B)-(b), the appropriate amount of said photoconductor such as zinc oxide to be applied is in the range of 1-10 parts by weight or thereabout against said copolymer, resin and polymeric monomer of 1 part by weight, respectively, and the appropriate amount of the sensitizer according to the present invention is in the range of 0.001-0.1 wt. percent or thereabout against zinc oxide.

Hereunder will be given a further elucidation of the present invention with reference to practical embodiments thereof.

PREFERRED EMBODIMENTS OF THE INVENTION

Example 1

1% methanol solution of a compound expressed by the formula:

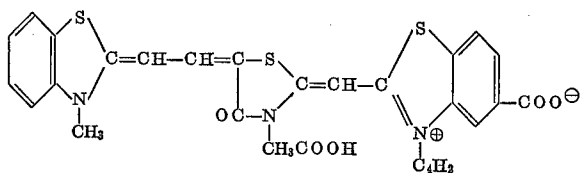


water: 100 g.

This proves that the copying material prepared by using merocyanine-type coloring matters according to the present invention is more sensitive than the comparative copying material, and, accordingly, it brings about excellently clear image and minimizes the light-fading of the resulting copies.

Example 2

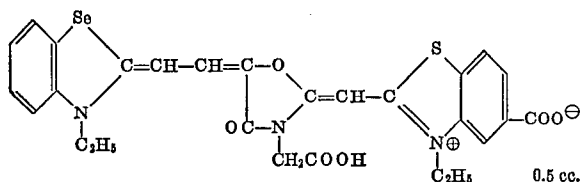
By applying the same process as in Example 1 above except for substituting a compound expressed by the following formula for the coloring matter applied therein, a copying material was prepared.



This copying material was made to adapt to the atmosphere of a dark place of 20° C. and 65% RH for 24 hours, and thereafter was made to form copied images. When the clearness of image, the sensitivity and the rate of light-fading in the copy were tested, the result was similar to that in Example 1 above.

Example 3

1% methanol solution (containing 0.001% of triethyl amine added thereto) of a compound expressed by the formula:



Water: 100 g.

Goselan (the trade name of a vinyl acetate-crotonic acid copolymer manufactured by Nippon Gosei, K.K.: water soluble; solid content 20%): 100 g.

Zinc oxide (Sazex 3000): 100 g.

A mixture according to the foregoing prescription was stirred by a homomixer for 10 minutes for the sake of dispersion. A dispersion thus prepared was applied to the reverse side of an art paper whose surface had been processed for conductivity and was dried, whereby there was obtained a copying material for electrophotography provided with a photoconductive layer having a thickness of about 20 μ .

On the other hand, by applying the same condition as above except for equivalently substituting 1% methanol solution (not containing triethyl amine) of tetrabromophenol blue, a comparative copying material was prepared.

When these two copying materials were treated in the same way as in Example 1 above and made to form copied images to compare their efficiency, the result was as shown in the following Table 2.

TABLE 2

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image
Copying material under the present invention.	500	300	Excellent.
Comparative copying material.	50	1,020	Poor.

This proves that the copying material according to the present invention is superior to the comparative copying material both in sensitivity and clearness of image.

Example 4

	G.
Vinyl acetate monomer	80.0
Crotonic acid	4.3
Styrene	2.0
Sodium dihydrogen phosphate	1.2
Sodium dodecyl sulfate	1.1
2,2'-azobisisobutyronitrile	1.5
Distilled water	300.0

The above prescribed components were put in a three-necked flask having a capacity of 3 l. and equipped with a condenser as well as a nitrogen feeding tube. After replacing air within the flask with nitrogen, these components were made to react for polymerization by stirring for about 15 hours at 50° C. The copolymer resulting from the reaction was separated from the aqueous layer, washed in water several times and dried.

Subsequently, a solution of binder according to the following prescription was prepared.

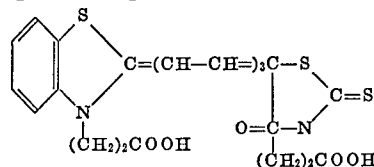
	G.
Dry copolymer obtained as above	20
Triethyl amine	1
Methanol	10
Distilled water	89

To this solution was added a dispersion containing photoconductive substance, which dispersion was prepared according to the following prescription, and mixed therewith thoroughly, whereby there was prepared a photoconductive layer-formable solution.

Zinc oxide	g. 100
1% methanol solution (containing 1% of ammonia) expressed by the aforementioned Formula 5	cc. 1
Distilled water	g. 120

The photoconductive layer-formable solution prepared as above was applied to the surface of an art paper whose reverse side had been processed for conductivity, to the extent of 30 g./m.² in terms of dry weight of the coating. The art paper thus coated was dried at 130° C. for 10 minutes and subsequently was subjected to humidity adjustment for 12 hours in a dark place with a humidity of 65% (RH), whereby a copying material for electrophotography was prepared.

On the other hand, by applying the same process as above except for substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



When these two copying materials were subjected to the same comparative test as in Example 1 above, the result was as shown in the following Table 3.

TABLE 3

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.	508	324	Good	79.6 → 80.6
Comparative copying material.	498	695	Indistinct	78 → 84.5

Example 5

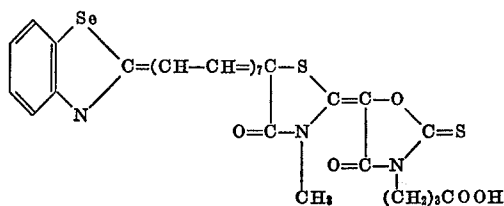
While stirring a mixture consisting of 100 g. of Styresol 4440 (a 50% mineral turpentine solution of styrenated alkyl resin, manufactured by Dainihon Ink Kagaku Kogyo K.K.) and 3 g. of naphthenic acid by a homomixer, a solution consisting of 100 g. of water and 3 g. of morpholine was slowly added to said mixture, thereby effecting emulsification.

On the other hand, 100 g. of photoconductive zinc oxide was added to 100 g. of water and dispersed therein by means of a homomixer. Subsequently, 1 cc. of 1% methanol solution (containing 1% of pyridine) expressed by the aforementioned Formula 10 was added to the dispersion and mixed by stirring.

80 g. of the dispersion thus treated was added to 80 g. of the foregoing emulsion and mixed by stirring, whereby a photoconductive layer-formable dispersion was obtained. This dispersion was coated onto the surface of an art paper, whose reverse side had been processed for conductivity, to the extent of 25 g./m.² in terms of dry weight of the coating. Then, by drying the thus coated art paper, a copying material for electrophotography was obtained.

Meanwhile, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.

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When these two copying materials were subjected to the same comparative test as in the foregoing Example 1, the result was as shown in the following Table 4.

TABLE 4

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	425	308	Good.....	76.1 → 79.2
Comparative copying material.....	430	684	Indistinct...	78.4 → 85.2

Example 6

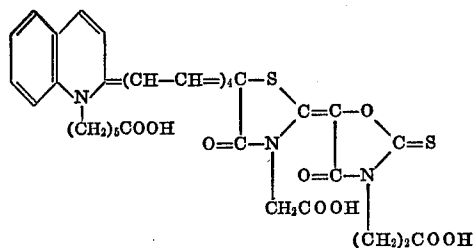
A mixture consisting of 70 g. of KR 211 (a 70% xylene solution of silicon resin, manufactured by Shinetsu Kagaku Kogyo K.K.) and 3 g. of Stebelite resin (a manufacture of Hercules Co., U.S.A.) was dissolved by heating at 70° C. Subsequently, while stirring the resulting solution by a homomixer, another solution prepared by dissolving 3 g. of triethyl amine in 100 g. of water was slowly added, thereby effecting emulsification.

On the other hand, a liquid was prepared by adding 100 g. of photoconductive zinc oxide to 100 g. of water and dispersing by a homomixer. This liquid was then mixed with 80 g. of the foregoing emulsion by stirring.

Further, 1 cc. of 1% methanol solution (containing 0.5% of triethyl amine) expressed by the aforementioned Formula 15 was added to said liquid and mixed by stirring.

A photoconductive layer-formable dispersion prepared as above was coated on the surface of an art paper, whose reverse side had been processed for conductivity, to the extent of 25 g./m.² in terms of dry weight of the coating. Then, by drying the thus coated art paper, a copying material for electrophotography was obtained.

Meanwhile, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



When these two copying materials were subjected to the same comparative test as in the foregoing Example 1, the result was as shown in the following Table 5.

TABLE 5

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	412	414	Good.....	75.9 → 78.0
Comparative copying material.....	360	838	Poor.....	76.5 → 84.9

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EXAMPLE 7

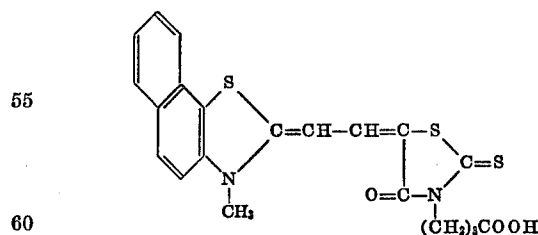
600 g. of toluene, 270 g. of styrene, 200 g. of butyl methacrylate, 60 g. of γ -hydroxy propyl methacrylate, 20 g. of itaconic acid and 12 g. of azobisisobutyronitrile were put in a three-nozzle flask, and, upon replacing air within the flask with nitrogen, were made to react for polymerization for 5 hours by heating at 100° C., whereby a copolymer resin for use in preparing a binder (hereinafter called "copolymer A" for short) was obtained.

While stirring a mixture of 100 g. of this copolymer A and 3 g. of naphthenic acid by a homomixer, 100 g. of

3% aqueous solution of triethyl amine was slowly added to emulsify said copolymer A, whereby a binder was prepared.

80 g. of this emulsified binder, 100 g. of photoconductive zinc oxide, 100 g. of water and 1 g. of tartaric acid were mixed together by using a homomixer for 10 minutes, and then 1 cc. of 1% methanol solution (containing 1% of ammonia) expressed by the aforementioned Formula 17 was added and mixed by stirring, whereby a photoconductive layer-formable dispersion was obtained. This dispersion was coated onto the surface of an art paper, whose reverse side had been processed for conductivity, to the extent of 30 g./m.² in terms of dry weight of the coating. Then, by drying the thus coated art paper at 120° C. for 10 minutes and subsequently hanging it in the atmosphere of a dark place of 20° C. having a humidity of 65% (RH) for 24 hours for adjustment of humidity, whereby a copying material for electrophotography was prepared.

On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



When these two copying materials were subjected to the same comparative test as in Example 1 above, the result was as shown in the following Table 6.

TABLE 6

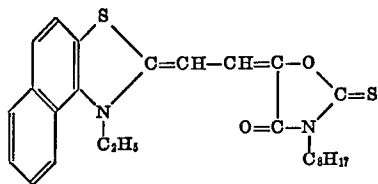
Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	468	408	Good.....	78.1 → 78.2
Comparative copying material.....	448	920	Poor.....	78.0 → 85.4

Example 8

As the material, 60 parts of methyl ester acrylate, 20 parts of ethyl ester acrylate, 15 parts of glycidyl methacrylate, 5 parts of acrylic acid, 4 parts of dammar, 0.1 part of triethanol amine salt of dodecylbenzene sulfonic acid, 0.3 part of ammonium persulfate and 150 parts of water were employed. A 2-l. glass flask equipped with a stirrer, reflux condenser, inlet for introducing the material and thermometer was steeped in a hot bath, and the foregoing monomer, dammar, dodecylbenzene sulfonate and water (excluding its portion required for dissolving said ammonium persulfate) were laid in this flask. Then, upon replacing the air within the flask by sending nitrogen gas therein, the temperature of the hot bath was raised slowly until the temperature inside the flask came up to 65°–70° C. In order to control the reaction temperature, said ammonium persulfate was divided into three batches and each batch was fed at intervals of 1 hour. Thus, the stock in the flask was further vigorously stirred for a spell, and, through polymerization for 6 hours in all, a resin emulsion with 39.7% of solid matter and pH 2.8 was obtained.

50 g. of said resin emulsion, 100 g. of zinc oxide, 100 g. of water and 1 cc. of 1% methanol solution (containing 1% of ammonia) expressed by the aforementioned Formula 24 were mixed by stirring, whereby a photoconductive layer-formable dispersion was prepared. This dispersion was coated onto the surface of an art paper, whose reverse side had been processed for conductivity, to the extent of 25 g./m.² in terms of dry weight of the coating. Then, by drying the thus coated art paper, a copying material for electrophotography according to the present invention was prepared.

On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



When these two copying materials were subjected to the same comparative test as in Example 1 above, the result was as shown in the following Table 7.

TABLE 7

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	424	304	Good.....	80.1 → 80.3
Comparative copying material.....	415	685	Poor.....	80.0 → 86.1

Example 9

Preparation of resin emulsion:

A 2-l. glass flask equipped with a stirrer, reflux condenser, inlet for introducing the material and thermometer was steeped in a hot bath, and the material according to the following composition (a) was stocked in said flask. Upon replacing the air within the flask by nitrogen, the stock was polymerized for 6 hours by heating at 60° C., whereby an O/W-type resin emulsion with about 40% of solid matter was obtained.

Composition (a)

	G.
25 Vinyl acetate	70
Styrene	15
Crotonic acid	2
Abietic acid	13
Sodium dodecylbenzene sulfonate	0.08
30 Ammonium persulfate	0.3
Water	150

Further, another material according to the following composition (b) was stirred by a homomixer for 10–15 minutes, whereby a photoconductive layer-formable dispersion was prepared.

Composition (b)

Zinc oxide	g-- 100
Resin emulsion prepared as above	g-- 50
40 1% methanol solution (containing 1% of trimethyl amine) expressed by the aforementioned Formula 2	cc-- 1
Water	g-- 60

45 This dispersion was coated onto the surface of an art paper, whose reverse side had been processed for conductivity, to the extent of 25 g./m.² in terms of dry weight of the coating. Then, by drying the thus coated art paper at 130° C. for 2 minutes, a copying material for electrophotography was prepared.

50 On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.

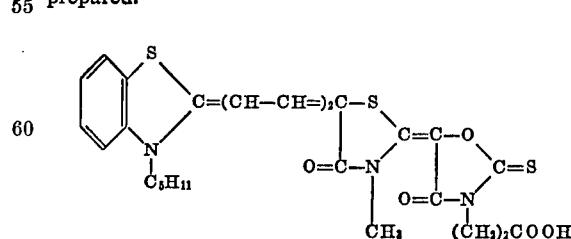


TABLE 10

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	443	326	Good.....	78.2 → 79.4
Comparative copying material.....	450	723	Poor.....	78.2 → 84.1

Example 12

By applying the same process as in Example 8 except for substituting the following Composition (g) for said Composition (a) and the following Composition (h) for said Composition (b), a copying material for electrophotography was prepared.

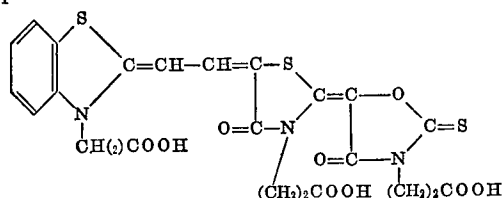
Composition (g)

	G.
Ethyl acrylate	45
Acrylonitrile	30
Styrene	22
Acrylic acid	3
Oleic acid	4
Triethanol amine salt of dodecylbenzene sulfonic acid	0.1
Ammonium persulfate	0.3
Water	150

Composition (h)

	G.
Zinc oxide	100
Resin emulsion prepared as above	50
1% methanol solution (containing 1% of triethanol amine) expressed by the aforementioned Formula 7	1
Water	60

On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



When these two copying materials were subjected to the same comparative test as in Example 1, the result was as shown in the following Table 11.

TABLE 11

Copying material	Saturation potential (v.)	Sensitivity (lux sec.)	Clearness of image	Light-fading (800 lux, 4 hrs.), percent
Copying material under the present invention.....	466	314	Good.....	79.1 → 79.1
Comparative copying material.....	468	624	Poor.....	79.3 → 83.9

EXAMPLE 13

By applying the same process as in Example 8 except for substituting the following Composition (i) for said Composition (a) and the following Composition (j) for said Composition (b), a copying material for electrophotography according to the present invention was prepared.

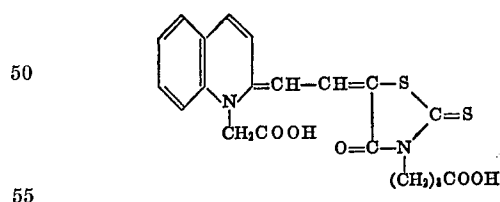
Composition (i)

	G.
Ethyl acrylate	40
Styrene	55
Acrylic acid	5
Phthalic anhydride	4.5
Sodium lauryl sulfate	0.08
Ammonium persulfate	0.3
Water	150

Composition (j)

	G.
Zinc oxide	100
Resin emulsion prepared as above	50
1% methanol solution (containing 1% of diethyl amine) expressed by the aforementioned formula 13	1
Water	60

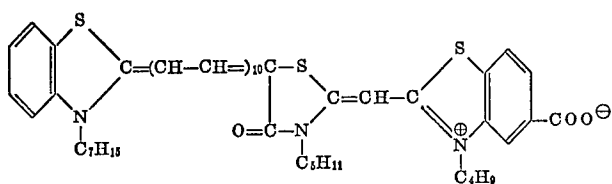
On the other hand, by applying the same process as above except for equivalently substituting a compound expressed by the following formula for the coloring matter used therein, a comparative copying material was prepared.



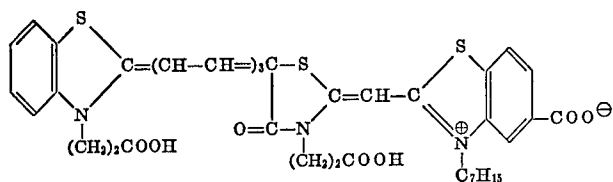
When these two copying materials were subjected to the same comparative tests as in Example 1, the result was as shown in the following Table 12.

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6. A sensitizer as in claim 1 represented by the formula:



7. A sensitizer as in claim 1 represented by the formula:



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GEORGE F. LESMES, Primary Examiner

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U.S. Cl. X.R.

96—1.6, 1.7, 130, 141; 260—240.65