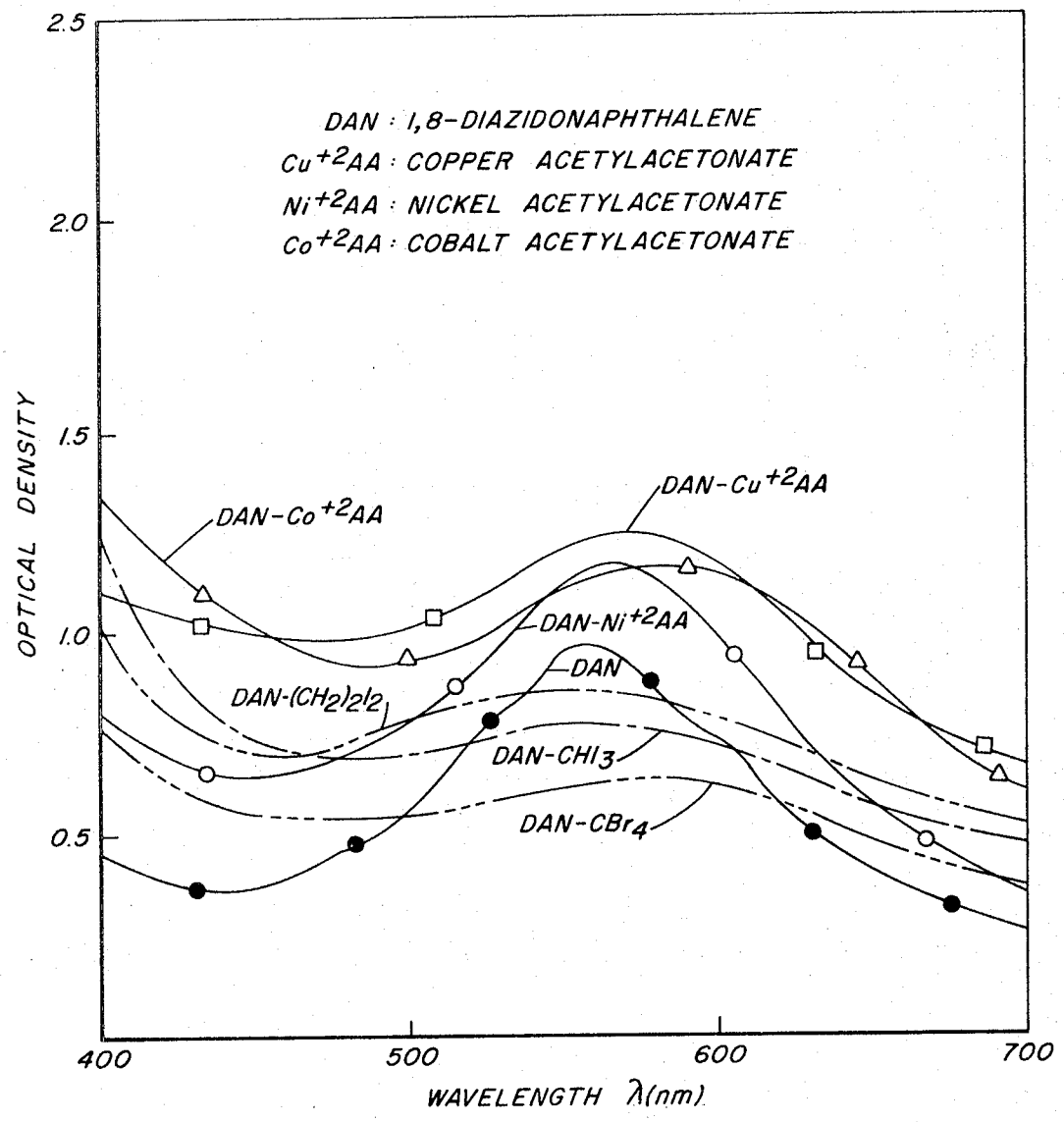
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PHOTOIMAGING PROCESSES AND COMPOSITIONS

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PHOTOIMAGING PROCESSES AND COMPOSITIONS

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Continuation-in-part of abandoned application Ser. No. 147,116, May 26, 1971. This application May 18, 1972, Ser. No. 254,521

Int. Cl. G03c 1/52, 1/72, 5/18

U.S. Cl. 96—49 14 Claims

ABSTRACT OF THE DISCLOSURE

Dry photoimaging processes and compositions employing photosensitive coatings of a volatile peri-substituted aromatic azido compound and a spin-orbital coupling agent in a permeable film-forming plastic are disclosed.

This application is a continuation-in-part of application Ser. No. 147,116, filed on May 26, 1971, now abandoned.

This invention relates to photosensitive compositions and processes for the formation of images having broad spectral absorption characteristics. More particularly, it relates to the use of spin-orbital coupling agents to vary the spectral characteristics of the images produced from certain photosensitive peri-substituted aromatic azido compounds.

Photosensitive compounds, compositions and processes play an essential role in photography and the related arts dealing with the formation of images with the aid of some activating influence, such as light, heat, etc. For many applications, as in the case of printing on white paper, it is desirable to maximize the neutrality of the image, in addition to achieving good color stability, speed, acuity, resolution and tonal range as well as the convenient dry imaging process employing relatively inexpensive materials.

Accordingly, it is an object of the present invention to provide photosensitive compositions which are suitable for the formation of images having broad spectral characteristics as well as good image stability, acuity, resolution and tonal range. It is a further object to provide a convenient, dry photoimaging process for the formation of such images. These and other objects of the present invention will become apparent from the description and examples which follow.

In accordance with the present invention, it has been unexpectedly found that images of enhanced neutrality can be conveniently prepared by employing one or more external heavy-atom spin-orbital coupling agents in combination with one or more of certain photosensitive peri-substituted aromatic azido compounds, contained in a permeable film-forming plastic. Suitable spin-orbital coupling agents are available from a variety of commercial sources and described in such publications as M. Kasha, JCP, 20, 71(1952); J. N. Chaughuri et al., Transactions of the Faraday Society, 54, 1605 (1958); S. P. McGlynn, JCP, 37, 1818 (1962); J. N. Chaughuri et al., JCP, 38, 2027 (1963); S. P. McGlynn, JCP, 40, 507 (1964); J. Kosar, Light-Sensitive Systems, Chapter 8, John Wiley & Sons, Inc., New York (1965); R. A. Abromovitch et al., J. Am. Chem. Soc., 91, 7532 (1969); and references cited therein.

Halogen atoms are among the preferred heavy atoms employed in the practice of the present invention for the purpose of spin-orbital coupling. The order of enhancement in image neutrality achieved by introducing one or more halides into the photosensitive composition is generally directly proportional to the atomic number of the halide. Accordingly, while some enhancement can be achieved by the presence of chloride and fluoride atoms, it is generally preferred to employ iodides and bromides.

Other preferred spin-orbital coupling agents for use in the practice of the present invention are one or more paramagnetic metal ions. Among the suitable paramagnetic ions, one may mention Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Mn^{+3} and Fe^{+3}.

Mixtures of spin-orbital coupling agents, such as, two or more halides or two or more paramagnetic ions or mixtures of halides and paramagnetic ions can also be employed.

Close physical proximity of the coupling agent and the photosensitive azido compound is required for the establishment of uniform enhancement of the image neutrality. Accordingly, it is preferred to establish a uniform solution of both the azido compounds and the coupling agents within the film-forming plastic. This may be conveniently achieved by selecting forms of the paramagnetic metals or other heavy atoms which are soluble in the film of choice. Chelates of the previously mentioned metal ions and organic ligands are commonly soluble in a variety of conventional film-forming plastics and are, accordingly, among the preferred spin-orbital coupling agents.

Suitable compounds within this preferred group include, for example, the acetylacetonates of the six previously mentioned paramagnetic metal ions. Other ligands which may be employed for the formation of the metal chelates in lieu of the acetylacetone include, for example,

1,3-bis(p-methoxyphenyl)-1,3-propanedione,
2-chloro-5-cyano-3,6-dihydroxy-p-benzoquinone disodium salt,
5-(p-dimethylaminobenzylidene)-3-propylrhodanine,
2,6-dimethyl-3,5-heptanedione,
2,9-dimethyl-1,10-phenanthroline,
1,5-diphenyl-1,3,5-pentanetrione,
4,7-diphenyl-1,10-phenanthroline,
(ethanediylidenetetrathio) tetraacetic acid,
1-formyl-3-thiosemicarbazide,
4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione,
3,5-heptanedione,
1,1,1,5,5,5-hexafluoro-2,4-pentanedione,
hexamethylphosphorus triamide,
4,4'-methylenedianiline,
6-methyl-2,4-heptanedione,
N-(p-nitrophenyl) glycine,
4,6-nonanedione,
salicylaldehyde hydrazone,
N-salicylideneanthranilic acid,
stearohydroxamic acid,
2,2,5,5-tetramethyl-1,3-cyclohexanedione,
1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione,
1,1,1-trifluoro-2,4-hexanedione,
1,1,1-trifluoro-6-methyl-2,4-heptanedione,
1,1,1-trifluoro-5-methyl-2,4-hexanedione,
4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione,
1,1,1-trifluoro-2,4-pentanedione, and the like.

Ligands such as acetylacetone, 2,6-dimethylheptanedione, 4,6-nonanedione, etc. are preferred because these result in low background color.

The heavy-atom, spin-orbital coupling agents employing halogen atoms as the heavy atom are preferably selected from the group consisting of alkyl and aryl halides. This is due to the fact that the organic portion thereof facilitate solubility in the polymeric binder.

Alkyl halides in the range of C_1–C_{12} provide a preferred source of reagents; however, higher molecular weight compounds such as iodinated and brominated waxes, C_{20}–C_{40}, may also be advantageously employed. The alkyl halide may contain one or more halogen atoms, e.g.

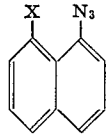
$CH_2ICH_2CH_2I$,

$CH_2I(CH_2)_3CH_2I$, CBr_4, $HCBr_3$ CHI_3, CH_2Br_2, $CHBr_3$, $BrCH_2$—CH_2—Br, CBr_3—CBr_3, and the like.

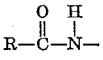
Phenyl and naphthyl halides provide a convenient source of the suitable aromatic halides, however, heterocycles such as halofurans or halopyridines and the like may also be advantageously employed.

Spectral broadening of the images produced in the practice of the present invention is favored by maximizing the ratio of the halo atoms to the carbon atoms in the heavy-atom reagent as well as selecting halides of higher atomic numbers. Accordingly, among the suitable halo compounds, one may mention 2,4,6-triiodobenzoic acid, 2,3,4,5-tetraiodobenzoic acid, 4,4'-diiodobiphenyl, 1,2-diiodobenzene, 1,4-diiodobenzene, 1,4-diiodobenzene, 2,4,6-triiodophenol, 2,4,6-triiodoanisole, and the like.

The photosensitive azido compounds employed in combination with the spin-coupling agent are peri-substituted aromatic azido compounds having the formula:



wherein X is selected from the group consisting of: azido, hydroxy, trifluoroacetamido, amino and



wherein R is lower alkyl, C_{1-6}. The 2 through 7 positions of the compounds are substituted with hydrogens or other substituents which are inert in the context of the process of the present invention.

Preferred compounds include, for example, 1,8-diazidonaphthalene, 1-acetamido-8-azidonaphthalene, 1-amino-8-azido-naphthalene, 1 - azido-8-trifluoroacetamidonaphthalene and 1-azido-8-hydroxynaphthalene.

The photosensitive compositions of the present invention are prepared by uniformly distributing a layer of the sensitized polymer dope over the surface of a conventional photographic substrate.

Suitable substrates include, for example, such materials as paper, plastic, wood, metal and glass.

Among the suitable conventional polymeric binders one may mention, for example, polyvinyl chloride, polyethylene, polymethylmethacrylate, polyvinyl acetate, cellulose acetate, copolymers of the corresponding monomers, and mixtures of the above polymers. Polyvinyl chloride is especially preferred. The polymer dopes can be applied to the substrates by way of a variety of standard coating methods.

The sensitized polymer dopes are prepared by incorporating the aromatic azide, the spin-coupling agent and, optionally, an infrared or ultraviolet sensitizer into the polymeric binder selected. It is generally preferred to tailor the photosensitive composition to achieve uniform distributions of the added ingredients as well as solubility thereof within the binder dope. This can be conveniently achieved through the use of an organic solvent, such as tetrahydrofuran, in which the azide, spin-coupling agent and sensitizer are dissolved prior to the addition of the polymeric binder. After blending the solution with the binder, the composition may be coated onto the substrate to produce a uniform, photosensitive layer thereon. Prior to imaging the solvent is removed from the sensitized dope composition by evaporation.

Of the suitable methods of applying the sensitized dope to the substrate, the Fixed Blade Method, the Imbibing Method and the Meyer Rod Method are among the preferred techniques.

In the Fixed Blade Method, the base material is positioned under a fixed blade and an excess of the coating material is placed on the base. The base is then passed under the blade to produce a uniform coating having a thickness determined by the distance between the mounted blade and the base material.

In the Imbibing Method, a base stock having a plastic surface is coated with the active compound by passing it under a roller, touching a solution of the azido compound. The excess coating is removed from the surface by an air knife. By way of illustration, one may mention passing paper coated with polyvinyl chloride, polyvinyl acetate or polymethylmethacrylate through a solution of 1,8-diazidonaphthalene in a solvent such as tetrahydrofuran, methyl ethyl ketone, acetone or toluene or mixtures thereof.

In the Meyer Rod Method, the coating composition is placed at one end of the base material and a metal rod wound with fine wire is passed through the liquid causing it to be spread over the surface of the base material. The thickness of the coating produced by this method is determined by the size of the wire used in the winding.

The concentrations of azido compound and spin-orbit coupling agent advantageously employed in the coating compositions and the thickness of the layer applied to the base may be varied to tailor the photosensitive system to achieve the desired degree of image intensity, speed, length of fixing period, etc. Optimum concentration and thicknesses will, of course, vary depending on the particular photosensitive compound and coupling agent employed, the binder material and thickness of the binder layer used, fixing time and temperature, among other factors. In general, satisfactory photoimages can be produced using binder compositions having from about 10% to about 15% by weight of the azido compound and from about 0.1% to about 10% by weight of the coupling agent with coatings of from about 0.05 to about 1.00 mils in thickness. Preferred concentrations and thicknesses are about 15% and 0.3 mils, respectively.

Background colorup is generally minimized by selecting azido compounds of maximum thermal stability and volatility and binders of maximum permeability to azido compounds, applied in minimum thicknesses and by selecting a spin-orbit coupling agent of low color in the visible

Generally, background colorup and diffusion time increase exponentially with film thickness. However, they are relatively unaffected by increases in the concentration of the azido compounds.

The aromatic azido compounds are themselves generally sensitive to radiation containing wavelengths within the ultraviolet region. By means of the addition of a sensitizing agent to the polymer binder, the sensitivity can be extended into the range of from 360 mμ to 470 mμ or greater. The energy transfer of such system is surprisingly efficient in view of the typically high viscosity of the binder polymer systems being sensitized.

Several advantages are provided by the use of sensitized systems. They permit the use of apparatus equipped with inexpensive and convenient light sources, such as incandescent lamps, and allow projection printing through various optical systems with normal optical glass. They also permit the simultaneous use of both direct and indirect excitation of azido compounds through simultaneous exposure of the photosensitive compounds to both visible and ultraviolet light. Alternatively, enhanced absorption can be achieved by using an ultraviolet absorbing sensitizer in combination with the azido composition.

Suitable sensitizers include, for example, fluoranthene, thioxanthrone, fluorenone, perylene, benzanthrone, benzophenone, phenazine and thioacridone.

Sensitizers which absorb light in the visible spectrum are of necessity colored compounds. Many of the suitable coupling agents are also colored. Where the colors caused thereby are found to be objectionable, one may employ a colorless spin coupling agent, such as in combination with the azido compounds in an unsensitized polymer dope or one containing a colorless, ultraviolet absorbing sensitizer or a member of a class of volatile, colored sensitizers such as fluorenone or benzanthrone which diffuse out of the binder composition during the process of the present invention.

Optimum relative concentrations of the sensitizer and azido compound will, of course, vary with the particular system being employed. Generally, energy transfer is favored by high concentrations of the azido compound. It is preferred to employ the sensitizer in a sufficient concentration to absorb the incident light. However, excessively high concentrations of the sensitizer will cause complete absorption of the incident light at the surface of the plastic matrix and may thereby reduce the efficiency of the system.

Imaging is achieved by exposing the photosensitive compositions to patterned activating radiation, namely, an information containing beam of visible or ultraviolet light.

A convenient source of ultraviolet radiation is provided by lamps which emit a wide range of ultraviolet frequencies. A light table equipped with a film transparency (positive or negative) and a bank of ultraviolet-rich blacklight fluorescent lamps, such as, 15 Watt Black Light, No. F15T8–BL by General Electric and Rayonet Photochemical Reactor Lamps, No. RPR 3000A by The Southern New England Ultraviolet Company provides a convenient source of activating radiation. Conventional azo printing machines, equipped with high pressure mercury vapor lamps may also be employed. Since they emit both visible and ultra-violet light, they are especially well adapted for use with those compositions having sensitizers to visible light.

Absorption of incident light can be maximized by matching the frequencies of the incident light with the absorption frequencies of the aromatic azido compound or the sensitizer.

Patterning of the activating radiation can generally be achieved by any of the conventional methods. Suitable methods include passing the light through a film transparency or a template, use of a cathode ray tube containing an ultraviolet phosphor, such as a Litton Industries' Cathode Ray Tube, Ser. No. 4188, which contains a P16 phosphor; and using an ultraviolet pen light, such as Ultraviolet Products, Inc. Pen-Light, or Ultraviolet laser, such as might be used in spatial frequency modulation.

Optimum periods of irradiation will vary widely, depending upon the particular photosensitive composition, opacity of transparency, and light source employed. Exposure for a few seconds in a conventional azo printer is generally adequate while periods of two minutes or more may be required for a source such as the above-mentioned light table.

In the formation of neutral images from the azido compounds without the use of a spin coupling agent, one generally employs a high temperature step in which the fixed image is heated for about 3 to about 4 minutes at temperatures of from about 190° C. to about 200° C. Alternatively, one can employ a second exposure to ultraviolet light, such as that produced by a high pressure mercury lamp. In the practice of the present invention, neutral images are achieved without the necessity of these intervening steps.

Fixing of the image produced by the practice of the present invention can be achieved by volatilizing the unreacted azido compound from the polymer binder by merely heating the photographic substrate. The optimum temperature and heating period will vary with the particular system employed and the heating means used. In the case of 1,8-diazidonaphthalene and polyvinyl chloride, permanent fixing can generally be achieved by heating the exposed composition at 135° C. for a period of from about 1 to about 5 minutes or less.

Thermal fixing of the images can be achieved merely by placing the exposed film or paper in an oven; however, any other conventional means of heating the substrate may suitably be employed. For example, the exposed substrates may be passed under a bank of heating lamps or where a base such as Mylar® is employed, through a bath of hot fluid such as silicon oil. It is preferred, however, to employ a dry fixing process, maximizing the speed of the fixing step. A preferred means for fixing an exposed film or paper is to pass it over a heated platen while directing a stream of hot air on the film surface from above. In addition to heating both surfaces of the exposed film or paper, this method has the added advantage of facilitating the volatilization of the unreacted azido compound from the background, thereby greatly reducing the required fixing time.

The processes and compositions of the present invention are further illustrated by the following examples which are not to be taken as limitative thereof. All parts specified therein are by weight unless otherwise indicated.

EXAMPLES 1–10

A stock binder solution was prepared by dissolving 20 grams of polyvinyl chloride powder (Geon 101, d.=1.4, by the B.F. Goodrich Chemical Co.) in 200 ml. of well-stirred tetrahydrofuran. The resulting slurry was stirred at 60° C. overnight and then cooled for use as desired.

Photosensitive coating compositions were prepared by dissolving 1,8-diazidonaphthalene (DAN) and iodoform in a sample of the above stock binder solution, in sufficient quantities to produce 0.7 N and 0.63 N concentrations, respectively. Uniform films of the resulting compositions having thicknesses of from about 0.2 to about 0.3 mil were uniformly applied to the surface of a polyester film substrate (Mylar® by E. I. du Pont de Nemours). The resulting photosensitive compositions were imaged by exposing them through a film transparency to a bank of black light fluorescent lamps transmitting light in the 300–380 nm. (peaking at 350 nm.) region for a period of from about 10 to about 30 seconds. The result was a gray-black image of excellent tonal range, resolution and acuity.

The above procedure was repeated using various spin-coupling agents in lieu of the iodoform. In each case an image of enhanced neutrality was achieved. The results are set forth in Table I below.

TABLE I

Ex. No.	Spin-coupling agent: Compound	Spin-coupling agent: Concentration N	Image color
1	Iodoform	0.63	Gray-black.
2	Carbontetra bromide	0.69	Blue-black.
3	1,2-diiodoethane	2.38	Do.
4	Iodobenzene	2.33	Purple-blue.
5	p-Chloroiodobenzene	2.51	Do.
6	1,3,5-tribromobenzene	2.56	Do.
7	1,4,5,8-tetrabromonaphthalene	0.15	Do.
8	9,10-dibromoanthracene	0.24	Do.
9	Ethyl iodide	3.8	Gray-black.
10	Propyl iodide	3.5	Do.

EXAMPLES 11–18

The general imaging procedure of Example 1 is repeated using a DAN concentration of about 0.67 and $(CH)_2I_2$ as a spin-coupling agent in a concentration of about 2.38 N. A blue-black image was produced by exposure to the ultraviolet source for a period of about 100 seconds.

The neutrality of image color produced by the presence of the spin-coupling agent is expressed by a ratio of the optical densities of the image at two arbitrarily chosen positions such as ΔOD, 460 nm. and ΔOD, 560 nm. In the case of the hypothetical black image, this ratio approaches unity.

This procedure is repeated with various spin-coupling agents at various concentrations. The results achieved in each case are set forth in Table II following.

TABLE II

Ex. No.	Spin-coupling agent Compound	Concentration N	Exposure time, seconds	ΔOD 460 nm.	ΔOD 560 nm.	ΔOD 460 / ΔOD 560	Color
11	$(CH_2)_2I_2$	2.38	100.2	0.67	0.75	0.89	Blue-black.
12	$(CH_2)_2I_2$	0.58	100.1	0.61	0.74	0.83	Do.
13	CHI_3	0.63	100.1	0.49	0.55	0.89	Gray-black.
14	CHI_3	0.24	100.3	0.46	0.72	0.64	Purple-black.
15	$Cu^{+2}AA^a$	0.11	100	1.00	1.25	0.80	Gray-black.
16	$Ni^{+2}AA^a$	0.13	100	0.65	1.20	0.54	Purple-black.
17	$Co^{+2}AA^a$	0.12	100	1.00	1.13	0.88	Gray-black.
18	$Mn^{+2}AA^a$	0.12	100	----------	----------	----------	Purple-black.

[a] Acetylacetonate.

EXAMPLES 19–25

The general procedure of Example 1 is repeated employing DAN concentrations of about 0.7 N. The results achieved with various spin-coupling agents and a control photosensitive composition prepared with the 1,8 - dialidonaphthalene (DAN) alone are set forth in Table III below.

TABLE III

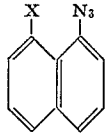
Ex. No.	Spin-coupling agent— Compound	Concentration	ΔOD 460 mμ	ΔOD 560 mμ	ΔOD 700	ΔOD 460 / ΔOD 560	ΔOD 700 / ΔOD 560
19	----------	----------	0.36	0.95	0.27	0.36	0.284
20	CHI_3	0.63	0.72	0.75	0.49	0 96	0.65
21	CBr_4	0.69	0.52	0.60	0.38	0.87	0.63
22	$(CH_2)_2I_2$	2.38	0.68	0.84	0.55	0.81	0.65
23	$Cu^{+2}AA^a$	0.11	0 76	0.95	0.46	0.80	0.48
24	$Co^{+2}AA^a$	0.12	1.00	1.14	0.62	0.88	0.54
25	$N^{+2}AA^a$	0.13	0.62	1.14	0.39	0.54	0.34

[a] Acetylacetonate.

The relative degrees of image broadening are also graphically depicted by means of FIG. 1, in which the optical densities of the images produced are plotted as a function of wavelength. It is readily apparent that in each case modification of the image produced to a more neutral color was achieved by means of the addition of a spin-coupling agent.

I claim:

1. A photosensitive material suitable for the formation of images comprising a photographic substrate having a photosensitive coating deposited thereon, said coating comprising a film-forming plastic having uniformly dispersed therein in admixture at least one photosensitive aromatic azido compound of the structure:



wherein X is selected from the group consisting of azido, hydroxy, trifluoroacetamido, amino and



wherein R is lower alkyl of from C_1–C_6 and at least one external heavy-atom spin-orbital coupling agent consisting of an alkyl halide, and aryl halide, and a paramagnetic metal chelate.

2. The material according to claim **1** wherein said coupling agent has a paramagnetic metal atom and the aromatic azido compound is selected from the group consisting of 1,8-diazidonaphthalene, 1-acetamido-8-azidonaphthalene, 1 - azido-8-trifluoracetamidonaphthalene, 1-amino-8-azidonaphthalene and 1 - azido-8-hydroxynaphthalene.

3. The material according to claim **1** wherein said coupling agent has a halide atom and the aromatic azido compound is selected from the group consisting of 1,8-diazidonaphthalene, 1-acetamido-8-azidonaphthalene, 1-azido-8-trifluoroacetamidonaphthalene, 1-amino-8-azidonaphthalene and 1-azido-8-hydroxynaphthalene.

4. The material according to claim **2** wherein the heavy-atom is a metal chelate corresponding to the reaction product of a metal ion selected from the group consisting of Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Mn^{+3} and Fe^{+3} with an organic ligand selected from the group consisting of acetylacetone 2,6-dimethylheptanedione, 4,6-nonanedione.

5. The material according to claim **4** wherein the organic ligand is acetylacetone.

6. The material according to claim **3** wherein the halide is selected from the group consisting of iodo and bromo substituted C_1–C_{12} alkanes.

7. The material according to claim **1** further comprising a sensitizer selected from the group consisting of ultraviolet and visible light sensitizers within said coating.

8. The material according to claim **7** wherein the sensitizer is selected from the group consisting of fluorenone and benzoanthrone.

9. A dry imaging process comprising the consecutive steps of :(A) imaging the material of claim **1** by irradiation with image activating radiation to produce a visible image, and (B) heating the material to evaporate the unreacted aromatic azido compound.

10. The process according to claim **9** wherein said coupling agent has at least one paramagnetic metal atom.

11. The process according to claim **9** wherein said coupling agent has at least one halide atom.

12. The process according to claim **9** wherein said coupling agent is a metal chelate corresponding to the re-

action product of a paramagnetic ion selected from the group consisting of Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Mn^{+3}, and Fe^{+3} with an organic ligand selected from the group consisting of acetylacetone, 2,6-dimethylheptanedione and 4,6-nonanedione.

13. The process according to claim **12** wherein the organic ligand is acetylacetone.

14. The process according to claim **9** wherein the heavy atom compound is selected from the group consisting of iodo and bromo substituted C_1–C_{12} alkanes.

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