(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 919 862 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.06.1999 Bulletin 1999/22

(51) Int Cl.^{6}: **G03C 1/498**

(21) Application number: **98203843.2**

(22) Date of filing: **14.11.1998**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **26.11.1997 US 979317**

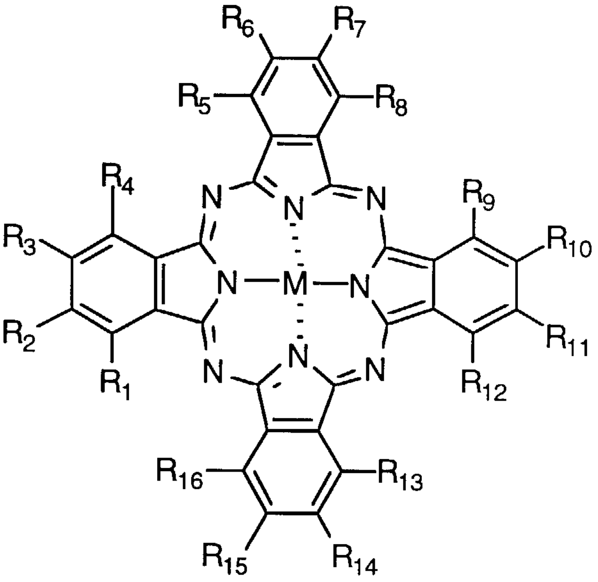
(71) Applicant: **EASTMAN KODAK COMPANY**
Rochester, New York 14650 (US)

(72) Inventors:
- **Weidner, Charles Harry**
  Rochester, New York 14650-2201 (US)
- **Java, Dorothy Theresa**
  Rochester, New York 14650-2201 (US)

(74) Representative:
Nunney, Ronald Frederick Adolphe et al
Kodak Limited,
Patents, W92-3A,
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)

(54) Photothermographic imaging element containing an antihalation dye

(57) This invention comprises a photothermographic imaging element comprising a support, an photothermographic imaging layer and at least one non-imaging layer positioned above the imaging layer, between the imaging layer and the support or on the side of the support opposite the imaging layer, wherein the non-imaging layer contains a dye of structure I:



(I)

wherein

M is a multi-valent metal atom;

R_1, R_4, R_5, R_8, R_9, R_{12},R_{13}, R_{16} independently represent a hydrogen atom, or a substituted or unsubstituted, branched or unbranched alkyl group;

Printed by Jouve, 75001 PARIS (FR)

(Cont. next page)

R_2, R_3, R_6, R_7, R_{10}, R_{11}, R_{14}, R_{15} independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted, branched or unbranched alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; or one or more of the adjacent pairs R_1 and R_2, R_2 and R_3, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12}, R_{13} and R_{14}, R_{14} and R_{15} and R_{15} and R_{16} taken together may represent the atoms necessary to form a substituted or unsubstituted aromatic or heteroaromatic ring.

Description

FIELD OF THE INVENTION

[0001] This invention relates to a photothermographic imaging element suited for use with a red or near-infrared laser. More specifically, this invention relates to a photothermographic imaging element comprising an antihalation dye.

BACKGROUND OF THE INVENTION

[0002] There is often desired for photosensitive emulsion layers or other layers of silver halide light-sensitive materials, colored layers that absorb light of specific wavelengths in order to provide filtration of unwanted wavelengths of light, absorb scattered light within a layer, or provide halation protection. These coloring layers can be located above the photosensitive layer, within the photosensitive layer, between the photosensitive layer and the support or on the opposite side of the support. When the colored layer is located in the latter three areas as described above, it is able to prevent unwanted back reflection of the light, thus providing halation protection to the photosensitive material.

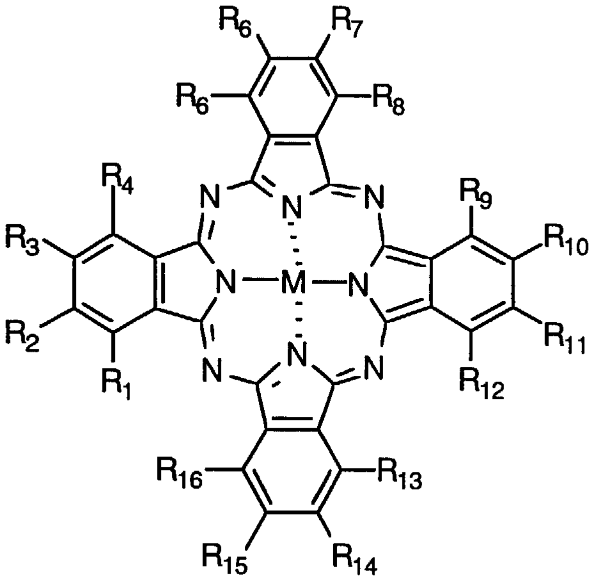
[0003] Antihalation is particularly important when a film is exposed using a laser because of the high intensity of light emitted by the laser necessitating high levels of dye to be used in order to provide adequate absorption of light. This can lead to undesirable coloration of the photographic element, particularly with regard to a photothermographic system where wet processing steps are unavailable to provide washout of the filtration dye.

PROBLEM TO BE SOLVED BY THE INVENTION

[0004] The problem to be solved by this invention is to provides a photothermographic element containing a dye that is useful for absorbing laser light in the red and near-infrared regions (i.e. in a wavelength range of 660 to 800 nm), that has very little extraneous absorption in unwanted areas of the visible spectrum, that is stable with time and that functions as an antihalation dye.

SUMMARY OF THE INVENTION

[0005] This invention comprises a photothermographic imaging element comprising a support, a photothermographic imaging layer and at least one non-imaging layer positioned above the imaging layer, between the imaging layer and the support or on the side of the support opposite the imaging layer, wherein the non-imaging layer contains a dye of structure **I**:



(I)

wherein

M is a multi-valent metal atom;

R_1, R_4, R_5, R_8, R_9, R_{12},R_{13}, R_{16} independently represent a hydrogen atom, or a substituted or unsubstituted, branched or unbranched alkyl group;

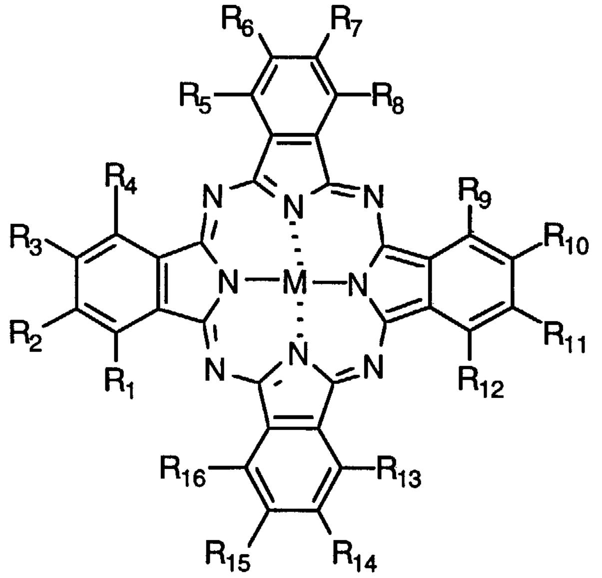
R_2, R_3, R_6, R_7, R_{10}, R_{11}, R_{14}, R_{15} independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted, branched or unbranched alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; or one or more of the adjacent pairs R_1 and R_2, R_2 and R_3, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12}, R_{13} and R_{14}, R_{14} and R_{15} and R_{15} and R_{16} taken together may represent the atoms necessary to form a substituted or unsubstituted aromatic or heteroaromatic ring.

ADVANTAGEOUS EFFECT OF THE INVENTION

[0006] A particular advantage of the dyes utilized in the preparation of a photothermographic element in accordance with the invention is the solubility of the dyes which allows coating of the antihalation element in a variety of polymeric binders. Another advantage is the excellent absorption of these dyes at the desired wavelengths as evidenced by their state-of-the-art properties as antihalation dyes in a photothermographic element. Another advantage is the stability of these dyes with time, both under hydrolytic and photolytic conditions.

DETAILED DESCRIPTION OF THE INVENTION

[0007] As mentioned above, the dyes utilized in the photothermographic element of this invention is a dye of structure I:



(I)

wherein

M is a multi-valent metal atom;

R_1, R_4, R_5, R_8, R_9, R_{12},R_{13}, R_{16} independently represent a hydrogen atom, or a substituted or unsubstituted, branched or unbranched alkyl group;

R_2, R_3, R_6, R_7, R_{10}, R_{11}, R_{14}, R_{15} independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted, branched or unbranched alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; or one or more of the adjacent pairs R_1 and R_2, R_2 and R_3, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12}, R_{13} and R_{14}, R_{14} and R_{15} and R_{15} and R_{16} taken together may represent the atoms necessary to form a substituted or unsubstituted aromatic or heteroaromatic ring.

M is preferably a multi-valent metal atom selected from the group consisting of: Mg, Ca, Sr, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, B, Al, Sn, Pb, Mo, Pd and Pt. Particularly preferred are Mg, Ni, Zn, and Cu.

[0008] Alkyl and alkoxy groups preferably contain 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms. Alkyl groups include, for example, methyl, ethyl, propyl, isopropyl, butyl sec. butyl, tert. butyl, heptyl or decyl. Alkoxy groups include, for example, methoxy, ethoxy, propoxy, or tert. butoxy. Aryl and aryloxy groups preferably contain 6 to 12 carbon atoms, more preferably 5 to 8 carbon atoms. Aryl groups that can be used include, for example, phenyl, tolyl, naphthyl, 2,4-dimethylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 2-isopropylphenyl, 3-isopropylphenyl, 4-isopropylphenyl, 4-tert-butylphenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-ethoxyphenyl, 4-ethoxyphenyl, or 4-isopropoxyphenyl. Aryloxy groups, include, for example, phenoxy, substituted phenoxy such as 2-methylphenoxy, 4-methylphenoxy, 2-ethylphenoxy, 4-ethylphenoxy, 4-eumylphenoxy, 4-isopropylphenoxy, 4-tert-butyl-phenoxy, 2-chlorophenoxy, or 4,-chlorophenoxy.

[0009] Aromatic ring structures include, for example phenyl, 1,2-naphthyl, 2,3-naphthyl, or phenanthryl. Heteroaromatic rings include, for example, pyridine, pyrazine, pyridazine and pyrimidine.

[0010] When reference in this application is made to a particular moiety it is to be understood that the moiety may itself be unsubstituted or substituted with one or more substituents (up to the maximum possible number). For example, "alkyl group" refers to a substituted or unsubstituted alkyl, while "benzene group" refers to a substituted or unsubstituted benzene (with up to six substituents). Generally, unless otherwise specifically stated, substituent groups usable on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for the photothermographic utility. Examples of substituents on any of the mentioned groups can include known substituents, such as: halogen, for example, chloro, fluoro, bromo, iodo; alkoxy, particularly those "lower alkyl" (that is, with 1 to 6 carbon atoms, for example, methoxy, ethoxy; substituted or unsubstituted alkyl, particularly lower alkyl (for example, methyl, trifluoromethyl); thioalkyl (for example, methylthio or ethylthio), particularly either of those with 1 to 6 carbon atoms; substituted and unsubstituted aryl, particularly those having from 6 to 20 carbon atoms (for example, phenyl); and substituted or unsubstituted heteroaryl, particularly those having a 5 or 6-membered ring containing 1 to 3 heteroatoms selected from N, O, or S (for example, pyridyl, thienyl, furyl, pyrrolyl); acid or acid salt groups such as any of those described below; and others known in the art. Alkyl substituents may specifically include "lower alkyl" (that is, having 1-6 carbon atoms), for example, methyl, or ethyl. Further, with regard to any alkyl group or alkylene group, it will be understood that these can be branched or unbranched and include ring structures.

[0011] Dyes of structure I are known and some are commercially available. The dyes can be made by the methods outlined in *The Phthalocyanines,* Vol. I and II, Moser, F.H. and Thomas, A.L., CRC Press, Boca Raton, Florida, 1983 or by the method of Wöhrle, D.; Schnurpfeil, G.; Knothe, G. Dyes and Pigments 1992, *18*, 91.

[0012] Illustrative dyes for use in the photothermographic element of this invention are represented, but not limited to, the examples shown in Table 1 (the peak absorption (λmax) of the dyes dissolved in acetone (or toluene) is also given in Table 1):

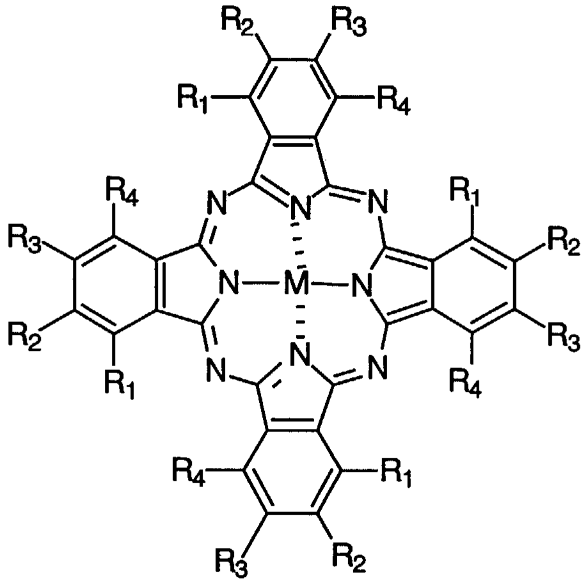
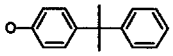
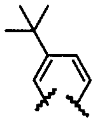
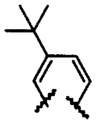
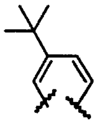
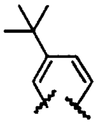
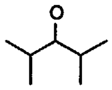


Table 1

Dye	R_1/R_4	R_2/R_3	M	Sol'n. λ_{max}
1	H	*t*-butyl	Co	661 nm
2	H	*t*-butyl	Cu	677 nm (toluene)
3	H	*t*-butyl	Fe	684 nm
4	H	*t*-butyl	Mg	672 nm
5	H	*t*-butyl	Ni	669 nm
6	H	*t*-butyl	Zn	671 nm
7	H		Cu	681 nm
8	H	OPh	Ni	672 nm
9	H		Ni	766 nm
10	H		Zn	755 nm
12	H		Cu	770 nm
12	H		Mg	769 nm
13		H	Mg	702 nm
14	H	$(CH_3)_3CO$	Mg	677 nm
15	H	$(CH_3)_3CO$	Zn	676 nm
16	H	$(CH_3)_3CO$	Cu	680 nm (toluene)
17	F	F	Zn	630 nm

[0013] The photothermographic element of this invention typically comprises a support, a photothermographic layer, a backing layer, an overcoat layer and various interlayers, such as, subbing layers, and filter layers. The antihalation dye used in accordance with this invention can be in any of the layers of the photothermographic element. In preferred embodiments of the invention, the dye is incorporated into a backing layer (e.g. a pelloid layer) or a layer between the support and the photothermographic layer.

[0014] The layers of a photothermographic element are generally prepared from a solution containing a binder and other components to give the layer the desired properties in an appropriate solvent. In accordance with this invention, an antihalation dye is dissolved in a solvent together with a binder for incorporation into the desired layer of the photothermographic element. The binder can be a hydrophobic binder preferably polymethyl methacrylate, polystyrene, polyvinyl butyral, or cellulose acetate butyrate. Preferred solvents for use with a hydrophobic binder are aromatic solvents, such as, toluene or xylene, ketone solvents, such as, methyl ethyl ketone, and methyl isobutyl ketone, tetrahydrofuran, ethyl acetate, chlorinated solvents such as dichloromethane. The solvent can contain water, if desired. In other embodiments of the invention the binder is a hydrophilic binder, preferably gelatin. The hydrophilic binder is generally dissolved in an aqueous medium for incorporation into the desired layer of the photothermographic element.

[0015] The dye is preferably used in an amount of 10 to 10,000 ppm (parts per million), more preferably 10 to 1,000 ppm, based on the amount of binder in the layer.

[0016] Typical photothermographic elements of this invention comprise at least one photothermographic layer containing in reactive association in a binder, preferably a binder comprising hydroxyl groups, (a) photographic silver halide prepared in situ and/or ex situ, (b) an image-forming combination comprising (i) an organic silver salt oxidizing agent, preferably a silver salt of a long chain fatty acid, such as silver behenate, with (ii) a reducing agent for the organic silver salt oxidizing agent, preferably a phenolic reducing agent, and (c) an optional toning agent. References describing such imaging elements include, for example, U.S. Patents 3,457,075; 4,459,350; 4,264,725 and 4,741,992 and Research Disclosure, June 1978, Item No. 17029.

[0017] In the photothermographic material it is believed that the latent image silver from the silver halide acts as a catalyst for the described image-forming combination upon processing. A preferred concentration of photographic silver halide is within the range of 0.01 to 10 moles of photographic silver halide per mole of silver behenate in the photothermographic material. Other photosensitive silver salts are useful in combination with the photographic silver halide if desired. Preferred photographic silver halides are silver chloride, silver bromide, silver bromochloride, silver bromoiodide, silver chlorobromoiodide, and mixtures of these silver halides. Very fine grain photographic silver halide is especially useful. The photographic silver halide can be prepared by any of the known procedures in the photographic art. Such procedures for forming photographic silver halides and forms of photographic silver halides are described in, for example, Research Disclosure, December 1978, Item No. 17029 and Research Disclosure, June 1978, Item No. 17643. Tabular grain photosensitive silver halide is also useful, as described in, for example, U.S. Patent No. 4,435,499. The photographic silver halide can be unwashed or washed, chemically sensitized, protected against the formation of fog, and stabilized against the loss of sensitivity during keeping as described in the above Research Disclosure publications. The silver halides can be prepared in situ as described in, for example, U.S. Patent No. 4,457,075, or prepared ex situ by methods known in the photographic art.

[0018] The photothermographic element typically comprises an oxidation-reduction image forming combination that contains an organic silver salt oxidizing agent, preferably a silver salt of a long chain fatty acid. Such organic silver salts are resistant to darkening upon illumination. Preferred organic silver salt oxidizing agents are silver salts of long chain fatty acids containing 10 to 30 carbon atoms. Examples of useful organic silver salt oxidizing agents are silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate, and silver palmitate. Combinations of organic silver salt oxidizing agents are also useful. Examples of useful organic silver salt oxidizing agents that are not organic silver salts of fatty acids are silver benzoate and silver benzotriazole.

[0019] The optimum concentration of organic silver salt oxidizing agent in the photothermographic element will vary depending upon the desired image, particular organic silver salt oxidizing agent, particular reducing agent and particular photothermographic element. A preferred concentration of organic silver salt oxidizing agent is within the range of 0.1 to 100 moles of organic silver salt oxidizing agent per mole of silver halide in the element. When combinations of organic silver salt oxidizing agents are present, the total concentration of organic silver salt oxidizing agents is preferably within the described concentration range.

[0020] A variety of reducing agents are useful in the photothermographic element. Examples of useful reducing agents in the image-forming combination include substituted phenols and naphthols, such as bis-beta-naphthols; polyhydroxybenzenes, such as hydroquinones, pyrogallols and catechols; aminophenols, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid reducing agents, such as ascorbic acid, ascorbic acid ketals and other ascorbic acid derivatives; hydroxylamine reducing agents; 3-pyrazolidone reducing agents, such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone; and sulfonamidophenols and other organic reducing agents known to be useful in photothermographic elements, such as described in U.S. Patent 3,933,508, U.S. Patent 3,801,321 and Research Disclosure, June 1978, Item No. 17029. Combinations of organic reducing agents are also useful in the photothermographic element.

[0021] Preferred organic reducing agents in the photothermographic element are sulfonamidophenol reducing agents, such as described in U.S. Patent 3,801,321. Examples of useful sulfonamidophenol reducing agents are 2,6-dichloro-4-benzene- sulfonamidophenol; benzenesulfonamidophenol; and 2,6-dibromo-4-benzenesulfonamidophenol, and combinations thereof.

[0022] An optimum concentration of organic reducing agent in the photothermographic element varies depending upon such factors as the particular photothermographic element, desired image, processing conditions, the particular organic silver salt and the particular oxidizing agent.

[0023] The photothermographic element preferably comprises a toning agent, also known as an activator-toner or toner-accelerator. Combinations of toning agents are also useful in the photothermographic element. Examples of useful toning agents and toning agent combinations are described in, for example, Research Disclosure, June 1978, Item No. 17029 and U.S. Patent No. 4,123,282. Examples of useful toning agents include, for example, phthalimide, N-hydroxyphthalimide, N-potassium-phthalimide, succinimide, N-hydroxy-1,8-naphthalimide, phthalazine, 1-(2H)-phthalazinone and 2-acetylphthalazinone.

[0024] Post-processing image stabilizers and latent image keeping stabilizers are useful in the photothermographic element. Any of the stabilizers known in the photothermographic art are useful for the described photothermographic element. Illustrative examples of useful stabilizers include photolytically active stabilizers and stabilizer precursors as described in, for example, U.S. Patent 4,459,350. Other examples of useful stabilizers include azole thioethers and blocked azolinethione stabilizer precursors and carbamoyl stabilizer precursors, such as described in U.S. Patent 3,877,940.

[0025] The photothermographic elements as described preferably contain various colloids and polymers alone or in combination as vehicles and binders and in various layers. Useful materials are hydrophilic or hydrophobic. They are transparent or translucent and include both naturally occurring substances, such as gelatin, gelatin derivatives, cellulose derivatives, polysaccharides, such as dextran, or gum arabic; and synthetic polymeric substances, such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone) and acrylamide polymers. Other synthetic polymeric compounds that are useful include dispersed vinyl compounds such as in latex form and particularly those that increase dimensional stability of photographic elements. Effective polymers include water insoluble polymers of acrylates, such as alkylacrylates and methacrylates, acrylic acid, sulfoacrylates, and those that have cross-linking sites. Preferred high molecular weight materials and resins include poly(vinyl butyral), cellulose acetate butyrate, poly(methylmethacrylate), poly(vinylpyrrolidone), ethyl cellulose, polystyrene, poly(vinylchloride), chlorinated rubbers, polyisobutylene, butadiene-styrene copolymers, copolymers of vinyl chloride and vinyl acetate, copolymers of vinylidene chloride and vinyl acetate, poly(vinyl alcohol) and polycarbonates.

[0026] Photothermographic elements can contain addenda that are known to aid in formation of a useful image. The photothermographic element can contain development modifiers that function as speed increasing compounds, sensitizing dyes, hardeners, antistatic agents, plasticizers and lubricants, coating aids, brighteners, other absorbing and filter dyes, such as described in Research Disclosure, December 1978, Item No. 17643 and Research Disclosure, June 1978, Item No. 17029.

[0027] The photothermographic element can comprise a variety of supports. Examples of useful supports are poly (vinylacetal) film, polystyrene film, poly(ethyleneterephthalate) film, poly(ethylene naphthalate) film, polycarbonate film, and related films and resinous materials, as well as paper, glass, metal, and other supports that withstand the thermal processing temperatures.

[0028] The layers of the photothermographic element are coated on a support by coating procedures known in the photographic art, including dip coating, air knife coating, curtain coating or extrusion coating using hoppers. If desired, two or more layers are coated simultaneously.

[0029] Spectral sensitizing dyes are useful in the photothermographic element to confer added sensitivity to the element. Useful sensitizing dyes are described in, for example, Research Disclosure, June 1978, Item No. 17029 and Research Disclosure, December 1978, Item No. 17643.

[0030] A photothermographic element as described preferably comprises a thermal stabilizer to help stabilize the photothermographic element prior to exposure and processing. Such a thermal stabilizer provides improved stability of the photothermographic element during storage. Preferred thermal stabilizers are 2-bromo-2-arylsulfonylacetamides, such as 2-bromo-2-p-tolysulfonylacetamide; 2-(tribromomethyl sulfonyl)benzothiazole; and 6-substituted-2,4-bis(tribromomethyl)-s-triazines, such as 6-methyl or 6-phenyl-2,4-bis(tribromomethyl)-s-triazine.

[0031] A photothermographic element typically has a transparent protective layer comprising a film forming binder, preferable a hydrophilic film forming binder. Such binders include, for example, crosslinked polyvinyl alcohol, gelatin, or poly(silicic acid). Particularly preferred are binders comprising poly(silicic acid) alone or in combination with a water-soluble hydroxyl-containing monomer or polymer as described in the US Patent No. 4,828,971.

[0032] The term "protective layer" is used in this application to mean a transparent, image insensitive layer that can be an overcoat layer, that is a layer that overlies the image sensitive layer(s), or a backing layer, that is a layer that is on the opposite side of the support from the image sensitive layer(s). The imaging element can contain an adhesive interlayer between the protective layer and the underlying layer(s). The protective layer is not necessarily the outermost layer of the imaging element.

[0033] The protective layer can contain an electrically conductive layer having a surface resistivity of less than 5 x 10^{11} ohms/square. Such electrically conductive overcoat layers are described in US Patent No. 5,547,821.

[0034] A photothermographic imaging element generally includes at least one transparent protective layer containing matte particles. Either organic or inorganic matte particles can be used. Examples of organic matte particles are often in the form of beads, of polymers such as polymeric esters of acrylic and methacrylic acid, e.g., poly(methylmethacrylate), styrene polymers and copolymers. Examples of inorganic matte particles are of glass, silicon dioxide, titanium dioxide, magnesium oxide, aluminum oxide, barium sulfate, and calcium carbonate. Matte particles and the way they are used are further described in U.S. Patent Nos. 3,411,907, 3,754,924, 4,855,219, 5,279,934, 5,288,598, 5,378,577, 5,750,328 and 5,563,226.

[0035] A wide variety of materials can be used to prepare the protective layer that is compatible with the requirements of photothermographic elements. The protective layer should be transparent and should not adversely affect sensitometric characteristics of the photothermographic element such as minimum density, maximum density and photographic speed. Useful protective layers include those comprised of poly(silicic acid) and a water-soluble hydroxyl containing monomer or polymer that is compatible with poly(silicic acid) as described in U.S. Patent 4,741,992 and 4,828,971. A combination of poly(silicic acid) and poly(vinyl alcohol) is particularly useful. Other useful protective layers include those formed from polymethylmethacrylate, acrylamide polymers, cellulose acetate, crosslinked polyvinyl alcohol, terpolymers of acrylonitrile, vinylidene chloride, and 2-(methacryloyloxy)ethyl-trimethylammonium methosulfate, crosslinked gelatin, polyesters and polyurethanes.

[0036] Particularly preferred protective layers are described in above-mentioned U.S. Patent Nos. 5,310,640 and 5,547,821

[0037] The photothermographic elements are exposed by means of various forms of energy, including those to which the photographic silver halides are sensitive, e.g., include ultraviolet, visible and infrared regions of the electromagnetic spectrum as well as electron beam and beta radiation, gamma ray, x-ray, alpha particle, neutron radiation and other forms of corpuscular wave-like radiant energy in either non-coherent (random phase) or coherent (in phase) forms produced by lasers. Exposures are monochromatic, orthochromatic, or panchromatic depending upon the spectral sensitization of the photographic silver halide. Imagewise exposure is preferably for a time and intensity sufficient to produce a developable latent image in the photothermographic element.

[0038] After imagewise exposure of the photothermographic element, the resulting latent image is developed merely by overall heating the element to thermal processing temperature. This overall heating merely involves heating the photothermographic element to a temperature within the range of 90°C. to 180°C. until a developed image is formed, such as within 0.5 to 60 seconds. By increasing or decreasing the thermal processing temperature a shorter or longer time of processing is useful. A preferred thermal processing temperature is within the range of 100°C. to 140°C.

[0039] Heating means known in the photothermographic imaging arts are useful for providing the desired processing temperature for the exposed photothermographic element. The heating means is, for example, a simple hot plate, iron, roller, heated drum, microwave heating means, or heated air.

[0040] Thermal processing is preferably carried out under ambient conditions of pressure and humidity. Conditions outside of normal atmospheric pressure and humidity are useful.

[0041] The components of the photothermographic element can be in any location in the element that provides the desired image. If desired, one or more of the components can be in one or more layers of the element. For example, in some cases, it is desirable to include certain percentages of the reducing agent, toner, stabilizer and/or other addenda in the overcoat layer over the photothermographic imaging layer of the element. This, in some cases, reduces migration of certain addenda in the layers of the element.

[0042] It is necessary that the components of the imaging combination be "in association" with each other in order to produce the desired image. The term "in association" herein means that in the photothermographic element the photographic silver halide and the image forming combination are in a location with respect to each other that enables the desired processing and forms a useful image.

[0043] The following examples illustrate the preparation of dyes of structure I and their evaluation in photothermographic elements.

Example 1

Synthesis of Dye 4

[0044] A mixture of 25 parts of 4-tert-butylphthalonitrile, and 3.1 parts of magnesium chloride in 220 parts of n-pentanol was treated with 22.7 parts of 1,8-diazabicyclo[5.4.0]undec-7-ene, and subsequently heated to reflux for 18 h. The mixture was cooled, poured into 2500 parts of a 4:1 methanol/water mixture, stirred for 1 h, and then the dark precipitate was filtered and washed well with 1000 parts of methanol. Drying under vacuum provided 21.5 parts of dye 4 suitable for use in the present invention, λ_{max}-672 nm (acetone), $\varepsilon = 26.9 \times 10^4$.

Example 2

Synthesis of Dye 6

[0045] A mixture of 3 parts of 4-tert-butylphthalonitrile, and 0.7 parts of zinc chloride in 25 parts of n-pentanol was treated with 2.5 parts of 1,8-diazabicyclo[5.4.0]undec-7-ene, and heated to reflux for 18 h. After cooling, the mixture was poured into 250 parts of a 4:1 methanol/water mixture, and stirred for 1 h. The dark precipitate was filtered, washed with an additional 150 parts of methanol, and dried under vacuum to provide 2.9 parts of dye 6, λ_{max}-671 nm (acetone), $\varepsilon = 28.8 \times 10^4$.

Example 3

Synthesis of Dye 2

[0046] A mixture of 5 parts of 4-tert-butylphthalonitrile, and 0.9 parts of copper(II) chloride was treated with 4.5 parts of 1,8-diazabicyclo[5.4.0]undec-7-ene, and heated to reflux for 18 h. After cooling, the mixture was poured into 250 parts of a 4:1 methanol/water mixture, and stirred for 1 h. The dark precipitate was 521 filtered, washed with an additional 150 parts of methanol, and dried under vacuum to provide 4.5 parts of dye 2, λ_{max}-677 nm (toluene), $\varepsilon = 25.8 \times 10^4$.

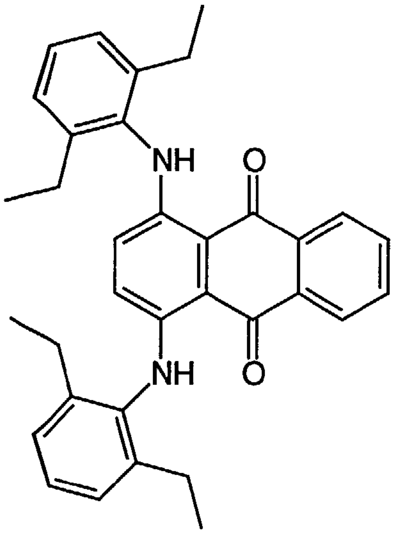
[0047] The other examples of the present invention can be made in an analogous fashion, from the appropriately substituted phthalonitrile and a multi-valent metal salt.

Example 4

[0048] The following components were mixed to form an emulsion (A):

Component	**Grams**
Silver Behenate dispersion (contains 26.4% by weight silver behenate in 8.5% by weight methyl ethyl ketone (MEK) / toluene (80:20) solution of polyvinylbutyral (Butvar™ B-76 available from Monsanto Co., USA)	877.8
Silver bromide (silver bromide emulsion contains 45.9 g Ag in 9% by weight MEK solution of Butvar B-76) containing sodium Iodide (NaI) (0.1% by weight)	127.1
Sensitizing dye (0.17% by weight solution in MEK / 2-ethoxy ethanol (90:10))	64.4
Succinimide (toner)	3.5
phthalimide (toner)	14.0
SF-96 (10% by weight SF-96 in MEK. SF-96™ a silicone available from General Electric Co., U.S.A.)	1.6
2-Bromo-2-[(4-methylphenyl)sulfonyl] acetamide	2.6
Naphthyl triazine (print-up stabilizer)	0.6
Palmitic acid (10% by weight in 10.5% by weight MEK solution of Butvar B-76)	30.6
N (4-hydroxyphenyl)benzenesulfonamide (12% by weight in 10.5% by weight MEK solution of Butvar B-76)	350.0
Butvar B-76 (10.5% by weight in MEK / Toluene 65:35)	105.2

[0049] The resulting photothermographic solution silver halide composition was coated at a wet laydown of 68.6 grams/m^2 on a blue (0.16 overall visual density) poly-(ethyleneterephthalate) film support, containing 250 ppm of dye C-1.



C-1

[0050] The coating was permitted to dry and was then overcoated with the following composition (B):

Component	Grams
Distilled Water	226.4
Polyvinyl Alcohol (PVA) (6.2% by weight in distilled water) (binder)	443.0
Tetraethyl Orthosilicate (35.4% by weight in methanol / water (53:47)) (hardener)	251.6
p-Toluene Sulfonic Acid (1N solution in distilled water)	3.1
para-isononylphenoxy polyglycidol, Olin 10G™ available from Olin Corp., USA (10% by weight in distilled water)	10.0
Silica (1.5 micron) (matting agent)	3.0

[0051] The resulting overcoat formulation (B) was coated at a wet laydown of 40.4 grams/m^2. The coating was permitted to dry.

Example 5

(Invention example)

[0052] An emulsion (A) was prepared as described in Example 4, coated on clear support, except that on the pelloid side of the film an Antihalation dye was coated with the following formulation:

Component	Grams
Phthalocyanine Dye #4 (Table 1) (2.3% by weight in Acetone) (Antihalation dye)	12.5
Butvar B-76 (6.0% by weight in MEK / Toluene (80:20)) (binder)	191.4
SF-96 (10% by weight SF-96 in MEK.) (surfactant)	0.3

The resulting composition was coated at a wet laydown of 50.8 grams/m^2 on a poly(ethyleneterephthalate) film support. The coating was permitted to dry and was then overcoated with the same overcoat composition (B) in Example 1. The resulting pelloid overcoat formulation was coated at a wet laydown of 40.4 grams/m^2. The coating was permitted to dry.

Example 6

(Invention example)

[0053] An emulsion (A) was prepared as described in Example 4, coated on clear support, except that on the pelloid side of the film an Antihalation dye was coated with the following formulation:

Component	Grams
Phthalocyanine Dye #4 (Table 1) (2.3% by weight	17.5
Butvar B-76 (6.2% by weight in MEK / Toluene80:20) (binder)	186.4
SF-96 (10% by weight SF-96 in MEK.) (surfactant)	0.3

The resulting composition was coated at a wet laydown of 50.8 grams/m^2 on a poly(ethyleneterephthalate) film support. The coating was permitted to dry and was then overcoated with the same overcoat composition (B) in Example 1. The resulting pelloid overcoat formulation was coated at a wet laydown of 40.4 grams/m^2. The coating was permitted to dry.

Example 7

Invention example

[0054] An emulsion (A) was prepared as described in Example 4, coated on clear support, except that on the pelloid side of the film an Antihalation dye was coated with the following formulation:

Component	Grams
Phthalocyanine Dye #4 (Table 1) (2.3% by weight in acetone) (Antihalation dye)	21.2
Butvar B-76 (6.3% by weight in MEK / Toluene 80:20) (binder)	182.7
SF-96 (10% by weight SF-96 in MEK.) (surfactant)	0.3

[0055] The resulting composition was coated at a wet laydown of 50.8 grams/m^2 on a poly(ethyleneterephthalate) film support. The coating was permitted to dry and was then overcoated with the same overcoat composition (B) in Example 1. The resulting pelloid overcoat formulation was coated at a wet laydown of 40.4 grams/m^2. The coating was permitted to dry.

Example 8

[0056] The dyes of the invention may also be coated as solid particle dispersions in a hydrophilic layer.

Ingredient	Amount
Dye 4	1.0 g
0.437% aqueous TX 200	23.0 g
1.8 mm Zirbeads[1]	60 cc

[1] Zirconium oxide beads commercially available from Zircoa

[0057] The dye and TX 200 (octylphenoxyethylene oxide sulfonate, commercially available from Rohm and Haas) solution were combined in a clean, dry 120 cc amber bottle and the pH was recorded. The pH was adjusted to <5 if needed, and the Zirbeads (zirconia beads)were then added, the bottle was sealed and milled on a SWECO vibratory mill for 5 days. Filter off Zirbeads to provide a dye slurry used in the next step.

[0058] The gel was melted at a temperature of 45°C or greater, the Olin 10G was added to this, followed by the dye slurry, and finally water in the amounts shown in the table. The final pH of the melt was recorded, and they were chill set for future coatings. The hardener solution was added to the melt just prior to coating. This solid particle dispersion (SPD) may be coated on the backside of the support as a pelloid layer, between the support and the emulsion, between the support and an interlayer, or between a polymeric underlayer and the emulsion.

Ingredient	Amount
Dye slurry	13.18 g
gelatin (G9461, 12.5%)	18.0 g
Olin 10G	1.35 g
water	51.21 g
hardener solution 1.25 g in 5 g water	6.25 g

The examples were exposed using a 683 nm 30 mw laser and processed at 123°C for 5 sec to produce a developed silver image. The developed silver image had a maximum density of 3.5 with a relative Log E speed of 1.00 measured at a density of 1.0 above D_{min}.

[0059] The SMPTE patterns from the exposed and developed examples were visually evaluated on a light box and graded according to their sharpness and overall appearance:

1- unacceptable- heavy flaring, blurred edges, text unreadable
2- marginally acceptable- edges sharp, text blurred
3- acceptable- sharp edges, sharp high contrast text.

The results are tabulated in Table 2.

Table 2

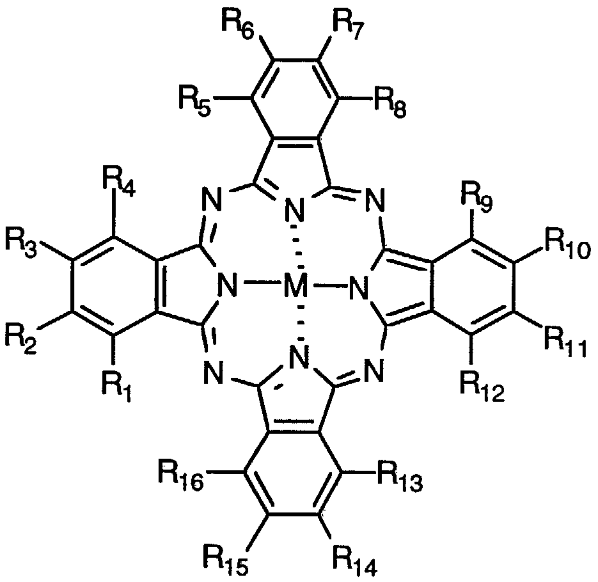
Example	Visual density (D_{min})	Density @ peak	SMPTE resolution	Remarks
4	0.24	0.26	1	comparative
5	0.15	1.0	2	invention
6	0.17	1.4	3	invention
7	0.20	1.7	3	invention

As can be readily seen, the examples of the present invention provide sharp images without increasing the visual density significantly.

[0060] The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. A photothermographic imaging element comprising a support bearing an photothermographic imaging layer and at least one non-imaging layer positioned above the imaging layer, between the imaging layer and the support or on the side of the support opposite the imaging layer, wherein the non-imaging layer contains a dye of structure **I**:



(I)

wherein

M is a multi-valent metal atom;

R_1, R_4, R_5, R_8, R_9, R_{12},R_{13}, R_{16} independently represent a hydrogen atom, or a substituted or unsubstituted, branched or unbranched alkyl group;

R_2, R_3, R_6, R_7, R_{10}, R_{11}, R_{14}, R_{15} independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted, branched or unbranched alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted aryloxy group; or one or more of the adjacent pairs R_1 and R_2, R_2 and R_3, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, R_8 and R_9, R_9 and R_{10}, R_{10} and R_{11}, R_{11} and R_{12}, R_{13} and R_{14}, R_{14} and R_{15} and R_{15} and R_{16} taken together may represent the atoms necessary to form a substituted or unsubstituted aromatic or heteroaromatic ring.

2. A photothermographic element according to claim 1, wherein the non-imaging layer containing the dye of structure (I) is a pelloid layer on the side of the support opposite the photothermographic layer.

3. A photothermographic element according to claim 1, wherein the non-imaging layer containing the dye of structure (I) is an antihalation layer positioned between the support and the photothermographic layer and the antihalation layer contains a dye of structure (I).

4. A photothermographic element according to claim 1, wherein at least one of R_2 or R_3 is a tertiary alkyl.

5. A photothermographic element according to claim 1, M is Mg, Ni, Zn, or Cu.

6. A photothermographic element according to claim 1, wherein the dye absorbs at a wavelength between 630 and 800 nm.

7. A photothermographic element according to claim 1, wherein the layer containing the dye comprises a hydrophobic binder.

8. A photothermographic element according to claim 1, wherein the layer containing the dye comprises a hydrophilic binder.

9. A photothermographic element according to claim 9, wherein the hydrophilic binder is gelatin.

10. A photothermographic element according to claim 1, wherein the photothermographic element comprises at least

two dyes of structure (I).

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 3843

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 258 129 A (IKENOUE SHINPEI ET AL) 24 March 1981 * claim 7 * ---	1-10	G03C1/498
E	EP 0 889 355 A (AGFA GEVAERT NV) 7 January 1999 * the whole document * ---	1-10	
A	EP 0 655 645 A (MINNESOTA MINING & MFG) 31 May 1995 * the whole document * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 March 1999	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03 82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 20 3843

26-03-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4258129 A	24-03-1981	JP 1006227 C	24-07-1980
		JP 52024520 A	24-02-1977
		JP 54042762 B	15-12-1979
		JP 51051941 A	07-05-1976
		DE 2635541 A	23-06-1977
		GB 1543266 A	28-03-1979
		DE 2548880 A	16-06-1976
		GB 1515167 A	21-06-1978
EP 0889355 A	07-01-1999	NONE	
EP 0655645 A	31-05-1995	JP 7199394 A	04-08-1995
		US 5468599 A	21-11-1995

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82