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(54) Photothermographic elements

(57) A photothermographic element has on a support a photothermographic layer which has been formed by applying a coating solution in which a photosensitive silver halide and a binder containing at least 50 wt% of a polymer latex having a surface acid content of 0.5-8 wt% are dispersed in a solvent containing at least 30 wt% of water, followed by drying. The photothermographic element can be prepared from an aqueous coating solution which is desirable from the ecological and safety standpoints while it has improved photographic properties.

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Description

[0001] This invention relates to photothermographic elements and more particularly, to photothermographic elements having improved photographic properties.

BACKGROUND OF THE INVENTION

[0002] Photothermographic technology is well known. In photothermographic elements having a photosensitive layer on a support, exposure is made to form latent images which are converted into visible images through heat development. The technology is disclosed, for example, in USP 3,152,904 and 3,457,075, D. Morgan and B. Shely, "Thermally Processed Silver Systems" in "Imaging Processes and Materials," Neblette, 8th Ed., Sturge, V. Walworth and A. Shepp Ed., page 2, 1969.

[0003] This technology well complies with the recently increasing social demand for simple processing and environmental protection.

[0004] In prior art photothermographic elements, photothermographic layers are formed by applying coating solutions based on organic solvents followed by drying. For example, USP 5,415,993 discloses a system of polyvinyl butyral as a binder in toluene and methyl ethyl ketone as a solvent. The use of organic solvents, however, is undesirable from the ecological and safety standpoints. One countermeasure proposed thus far is a technique of forming photothermographic layers using aqueous solvents. In connection with the aqueous coating of photothermographic layers, several patents disclose to use polymers as the binder. For example, JP-A 116114/1978 discloses gelatin, JP-A 151138/1975 discloses polyvinyl alcohol, JP-A 28737/1983 discloses polyvinyl acetal, USP 4,504,575 and 4,529,689 disclose polymer latexes, WO 97/04355 and WO 97/04356 disclose water-soluble polymers or water-dispersible polymers. These systems, however, fail to achieve satisfactory photographic performance because of increased fog or inferior image tone. There is a demand to have a photothermographic element that is formed without using organic solvents which are undesirable from the ecological and safety standpoints, and that exhibits satisfactory photographic properties.

SUMMARY OF THE INVENTION

[0005] An object of the invention is to provide a photothermographic element which has improved photographic properties and can be prepared by applying an aqueous solution which is desirable from the ecological and safety standpoints.

[0006] According to the invention, there is provided a photothermographic element comprising at least one photothermographic layer containing a photosensitive silver halide and a binder on at least one surface of a support. The element further contains an organic silver salt, preferably a silver salt of an organic carboxylic acid, and a reducing agent therefor. The photothermographic layer has been formed by applying an aqueous coating solution, followed by drying. In the coating solution, the binder containing at least 50% by weight of the binder of a polymer latex is dispersed in a solvent containing at least 30% by weight of the solvent of water. The polymer latex should have a surface acid content of 0.5% to 8% by weight, and preferably 1% to 4% by weight. Also preferably, the polymer latex has an equilibrium moisture content of 0.01% to 2% by weight at 25°C and RH 60%.

BRIEF DESCRIPTION OF THE DRAWING

[0007] The only figure, FIG. 1 is a graph of conductometric titration curve used when a surface acid content is determined.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The photothermographic element of the invention has at least one photothermographic layer (which is also referred to as photosensitive layer) on at least one surface of a support. The photosensitive layer contains a photosensitive silver halide and a binder. The element further contains an organic silver salt and a reducing agent therefor. The photosensitive layer may be a single layer or include two or more layers, preferably two to four layers.

[0009] According to the invention, at least one of the photo-sensitive layers contains a polymer latex in an amount of at least 50% by weight, preferably 70% to 100% by weight of the entire binder in the layer. The polymer latex should have a surface acid content of 0.5% to 8% by weight. Except for this, no particular limits are imposed on the polymer latex. Use may be made of acrylic resins, vinyl acetate resins, polyester resins, polyurethane resins, rubbery resins, vinyl chloride resins, vinylidene chloride resins, polyolefin resins, and copolymers thereof. Throughout the specification, the photosensitive layer in the photothermographic element of the invention and the polymer latex contained therein are often referred to as "inventive photo-sensitive layer" and "inventive polymer latex," respectively.

[0010] The "polymer latex" is a dispersion of a microparticulate water-insoluble hydrophobic polymer in a water-soluble dispersing medium. With respect to the dispersed state, a polymer emulsified in a dispersing medium, an emulsion polymerized polymer, a micelle dispersion, and a polymer having a hydrophilic structure in a part of its molecule so that the molecular chain itself is dispersed on a molecular basis are included. With respect to the polymer latex, reference is made to Okuda and Inagaki Ed., "Synthetic Resin Emulsion," Kobunshi Kankokai, 1978; Sugimura, Kataoka, Suzuki and Kasahara Ed., "Application of Synthetic Latex," Kobunshi Kankokai, 1993; and Muroi, "Chemistry of Synthetic Latex," Kobunshi Kankokai, 1970.

[0011] In the polymer latex, dispersed particles should preferably have a mean particle size of about 1 to 50,000 nm, more preferably about 5 to 1,000 nm. No particular limit is imposed on the particle size distribution of dispersed particles, and the polymer latex may have either a wide particle size distribution or a monodisperse particle size distribution.

[0012] The polymer latex used herein may be either a latex of the conventional uniform structure or a latex of the so-called core/shell type. In the latter case, better results are sometimes obtained when the core and the shell have different glass transition temperatures.

[0013] The inventive polymer latex should preferably have a minimum film-forming temperature (MFT) of about -30°C to 90°C, more preferably about 0°C to 70°C. A film-forming aid may be added in order to control the minimum film-forming temperature. The film-forming aid is also referred to as a plasticizer and includes organic compounds (typically organic solvents) for lowering the minimum film-forming temperature of a polymer latex. It is described in Muroi, "Chemistry of Synthetic Latex," Kobunshi Kankokai, 1970.

[0014] The polymer of the inventive polymer latex should preferably have an equilibrium moisture content at 25°C and RH 60% of up to 2% by weight, more preferably 0.01% to 2% by weight, most preferably 0.1% to 1.5% by weight. With respect to the definition and measurement of equilibrium moisture content, reference should be made to "Polymer Engineering Series No. 14, Polymer Material Test Methods," Edited by Japanese Polymer Society, Chijin Shokan Publishing K.K., for example.

[0015] The polymer may be linear or branched or crosslinked. The polymer may be either a homopolymer or a copolymer having two or more monomers polymerized together. The copolymer may be either a random copolymer or a block copolymer. The polymer preferably has a number average molecule weight Mn of about 5,000 to about 1,000,000, more preferably about 10,000 to about 500,000. Polymers with a too lower molecular weight would generally provide a low film strength after coating whereas polymers with a too higher molecular weight are difficult to form films.

[0016] Illustrative examples of the polymer latex which can be used as the binder in the photosensitive layer of the photothermographic element of the invention include latexes of methyl methacrylate/ethyl acrylate/(meth)acrylic acid copolymers, latexes of methyl methacrylate/2-ethylhexyl acrylate/styrene/(meth)acrylic acid copolymers, latexes of styrene/butadiene/(meth)acrylic acid copolymers, latexes of styrene/butadiene/itaconic acid copolymers, latexes of styrene/butadiene/divinyl benzene/(meth)acrylic acid copolymers, latexes of methyl methacrylate/vinyl chloride/(meth)acrylic acid copolymers, and latexes of vinylidene chloride/ethyl acrylate/acrylonitrile/(meth)acrylic acid copolymers. These polymers or polymer latexes are commercially available. Exemplary rubbery resins are LACSTAR 3307B and 7132C (Dai-Nippon Ink & Chemicals K.K.) and Nipol Lx416 (Nippon Zeon K.K.). These polymers may be used alone or in admixture of two or more.

[0017] In the inventive photosensitive layer, the polymer latex described above is used in an amount of at least 50% by weight of the entire binder. Preferably, the styrenebutadiene polymer latex is used in an amount of 70 to 100% by weight of the entire binder in the photosensitive layer.

[0018] The polymer latex used in the photosensitive layer of the photothermographic element of the invention should have a surface acid content of 0.5% to 8% by weight. The "surface acid content" of the polymer latex is the amount (expressed in percent) of carboxyl groups present on surfaces of latex particles based on the weight of polymer latex solids. The surface acid content of the polymer latex is 0.5% to 8% by weight, preferably 0.5% to 6% by weight, more preferably 1% to 4% by weight. Outside this range, higher surface acid contents can cause gelation whereas lower surface acid contents can give rise to the problems of a low sensitivity and low image density.

[0019] A surface acid content of at least 0.5% by weight is preferably achieved by copolymerizing the polymer latex with a monomer having a carboxyl group such as acrylic acid, methacrylic acid, itaconic acid, and maleic acid. Also useful are commercially available monomers such as Aronix M5400 and M5500 (Toa Synthetic Chemistry K.K.) and B-CEA (Daicell Chemical Industry K.K.). The amount of carboxyl groups introduced into the polymer is preferably 0.5 to 20% by weight, more preferably 0.8 to 15% by weight of the polymer. The amount of acid on polymer latex surfaces can be determined by conventional conductometric titration. An illustrative procedure of titration will be described later in Example.

[0020] In the inventive photosensitive layer, a hydrophilic polymer may be added in an amount of less than 50% by weight, preferably less than 30% by weight of the entire binder. Such hydrophilic polymers are gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and hydroxypropyl methyl cellulose.

[0021] In the inventive photosensitive layer, the total amount of binder is preferably 0.2 to 30 g/m^2, more preferably 1 to 15 g/m^2.

[0022] The inventive photosensitive layer is formed by applying an aqueous coating solution followed by drying. By the term "aqueous", it is meant that water accounts for at least 30% by weight of the solvent or dispersing medium of the coating solution. More preferably at least 50% by weight, most preferably 70 to 100% by weight of the solvent in the coating solution is water. The component other than water of the coating solution may be a water-miscible organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide or ethyl acetate. Exemplary solvent compositions include a 90/10 mixture of water/methanol, a 70/30 mixture of water/methanol, a 90/10 mixture of water/ethanol, a 90/10 mixture of water/isopropanol, a 95/5 mixture of water/dimethylformamide, a 80/15/5 mixture of water/methanol/dimethylformamide, and a 90/5/5 mixture of water/methanol/dimethylformamide, all expressed in a weight ratio.

Silver halide

[0023] A method for forming the photosensitive silver halide according to the invention is well known in the art. Any of the methods disclosed in *Research Disclosure* No. 17029 (June 1978) and USP 3,700,458, for example, may be used. Illustrative methods which can be used herein are a method of adding a halogen-containing compound to a pre-formed organic silver salt to convert a part of silver of the organic silver salt into photosensitive silver halide and a method of adding a silver-providing compound and a halogen-providing compound to a solution of gelatin or another polymer to form photosensitive silver halide grains and mixing the grains with an organic silver salt. The latter method is preferred in the practice of the invention.

[0024] The photosensitive silver halide should preferably have a smaller grain size for the purpose of minimizing white turbidity after image formation. Specifically, the grain size is up to 0.20 μm, preferably 0.01 μm to 0.15 μm, most preferably 0.02 μm to 0.12 μm. The term grain size designates the length of an edge of a silver halide grain where silver halide grains are regular grains of cubic or octahedral shape. Where silver halide grains are tabular, the grain size is the diameter of an equivalent circle having the same area as the projected area of a major surface of a tabular grain. Where silver halide grains are not regular, for example, in the case of spherical or rod-shaped grains, the grain size is the diameter of an equivalent sphere having the same volume as a grain.

[0025] The shape of silver halide grains may be cubic, octahedral, tabular, spherical, rod-like and potato-like, with cubic and tabular grains being preferred in the practice of the invention. Where tabular silver halide grains are used, they should preferably have an average aspect ratio of from 100:1 to 2:1, more preferably from 50:1 to 3:1. Silver halide grains having rounded corners are also preferably used. No particular limit is imposed on the face indices (Miller indices) of an outer surface of silver halide grains. Preferably silver halide grains have a high proportion of {100} face featuring high spectral sensitization efficiency upon adsorption of a spectral sensitizing dye. The proportion of {100} face is preferably at least 50%, more preferably at least 65%, most preferably at least 80%. Note that the proportion of Miller index {100} face can be determined by the method described in T. Tani, J. Imaging Sci., 29, 165 (1985), utilizing the adsorption dependency of {111} face and {100} face upon adsorption of a sensitizing dye.

[0026] The halogen composition of photosensitive silver halide is not critical and may be any of silver chloride, silver chlorobromide, silver bromide, silver iodobromide, silver iodochlorobromide, and silver iodide. Silver bromide or silver iodobromide is preferred in the practice of the invention. Most preferred is silver iodobromide preferably having a silver iodide content of 0.1 to 40 mol%, especially 0.1 to 20 mol%. The halogen composition in grains may have a uniform distribution or a non-uniform distribution wherein the halogen concentration changes in a stepped or continuous manner. Preferred are silver iodobromide grains having a higher silver iodide content in the interior. Silver halide grains of the core/shell structure are also useful. Such core/shell grains preferably have a multilayer structure of 2 to 5 layers, more preferably 2 to 4 layers.

[0027] Preferably the photosensitive silver halide grains used herein contain at least one complex of a metal selected from the group consisting of rhodium, rhenium, ruthenium, osmium, iridium, cobalt, mercury, and iron. The metal complexes may be used alone or in admixture of two or more complexes of a common metal or different metals. An appropriate content of the metal complex is 1×10^{-9} to 1×10^{-2} mol, more preferably 1×10^{-8} to 1×10^{-4} mol per mol of silver. Illustrative metal complex structures are those described in JP-A 225449/1995. Preferred among cobalt and iron complexes are hexacyano metal complexes. Illustrative, non-limiting examples of cobalt and iron complexes include hexacyano metal complexes such as complexes of ferrocyanate, ferricyanate, and hexacyanocobaltate ions. The distribution of the metal complex in silver halide grains is not critical. That is, the metal complex may be contained in silver halide grains uniformly or at a high concentration in either the core or the shell.

[0028] Photosensitive silver halide grains may be desalted by any of well-known water washing methods such as noodle and flocculation methods although silver halide grains may be either desalted or not according to the invention.

[0029] The photosensitive silver halide grains used herein should preferably be chemically sensitized. Preferred chemical sensitization methods are sulfur, selenium, and tellurium sensitization methods which are well known in the art. Also useful are a noble metal sensitization method using compounds of gold, platinum, palladium, and iridium and a reduction sensitization method. In the sulfur, selenium, and tellurium sensitization methods, any of compounds well known for the purpose may be used. For example, the compounds described in JP-A 128768/1995 are useful. Exemplary tellurium sensitizing agents include diacyltellurides, bis(oxycarbonyl)tellurides, bis(carbamoyl)tellurides, bis(oxycarbonyl)ditellurides, bis(carbamoyl)ditellurides, compounds having a P=Te bond, tellurocarboxylic salts, Te-organyltellurocarboxylic esters, di(poly)tellurides, tellurides, telluroles, telluroacetals, tellurosulfonates, compounds having a P-Te bond, Te-containing heterocyclics, tellurocarbonyl compounds, inorganic tellurium compounds, and colloidal tellurium. The preferred compounds used in the noble metal sensitization method include chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide, and gold selenide as well as the compounds described in USP 2,448,060 and BP 618,061. Illustrative examples of the compound used in the reduction sensitization method include ascorbic acid, thiourea dioxide, stannous chloride, aminoiminomethane-sulfinic acid, hydrazine derivatives, boran compounds, silane compounds, and polyamine compounds. Reduction sensitization may also be accomplished by ripening the emulsion while maintaining it at pH 7 or higher or at pAg 8.3 or lower. Reduction sensitization may also be accomplished by introducing a single addition portion of silver ion during grain formation.

[0030] According to the invention, the photosensitive silver halide is preferably used in an amount of 0.01 to 0.5 mol, more preferably 0.02 to 0.3 mol, most preferably 0.03 to 0.25 mol per mol of the organic silver salt. With respect to a method and conditions of admixing the separately prepared photosensitive silver halide and organic silver salt in an image forming layer coating solution, any desired admixing method may be used insofar as the benefits of the invention are fully achievable.

Sensitizing dye

[0031] Preferably, the photosensitive silver halide according to the invention is spectrally sensitized with a sensitizing dye. There may be used any of sensitizing dyes which can spectrally sensitize silver halide grains in the desired wavelength region when adsorbed to the silver halide grains. The sensitizing dyes used herein include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, styryl dyes, hemicyanine dyes, oxonol dyes, and hemioxonol dyes. Useful sensitizing dyes which can be used herein are described in *Research Disclosure,* Item 17643 IV-A (December 1978, page 23), *ibid*., Item 1831 X (August 1979, page 437) and the references cited therein. It is advantageous to select a sensitizing dye having appropriate spectral sensitivity to the spectral properties of a particular light source of various laser imagers, scanners, image setters and process cameras.

[0032] Exemplary dyes for spectral sensitization to red light include compounds I-1 to I-38 described in JP-A 18726/1979, compounds I-1 to I-35 described in JP-A 75322/1994, compounds I-1 to I-34 described in JP-A 287338/1995, dyes 1 to 20 described in JP-B 39818/1980, compounds I-1 to I-37 described in JP-A 284343/1987, and compounds I-1 to I-34 described in JP-A 287338/1995 for red light sources such as He-Ne lasers, red semiconductor lasers and LED.

[0033] For semiconductor laser light sources in the wavelength range of 750 to 1,400 nm, spectral sensitization may be advantageously done with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol, and xanthene dyes. Useful cyanine dyes are cyanine dyes having a basic nucleus such as a thiazoline, oxazoline, pyrroline, pyridine, oxazole, thiazole, selenazole and imidazole nucleus. Preferred examples of the useful merocyanine dye contain an acidic nucleus such as a thiohydantoin, rhodanine, oxazolidinedione, thiazolinedione, barbituric acid, thiazolinone, malononitrile, and pyrazolone nucleus in addition to the above-mentioned basic nucleus. Among the above-mentioned cyanine and merocyanine dyes, those having an imino or carboxyl group are especially effective. A suitable choice may be made of well-known dyes as described, for example, in USP 3,761,279, 3,719,495, and 3,877,943, BP 1,466,201, 1,469,117, and 1,422,057, JP-B 10391/1991 and 52387/1994, JP-A 341432/1993, 194781/1994, and 301141/1994.

[0034] Especially preferred dye structures are cyanine dyes having a thioether bond-containing substituent group, examples of which are the cyanine dyes described in JP-A 58239/1987, 138638/1991, 138642/1991, 255840/1992, 72659/1993, 72661/1993, 222491/1994, 230506/1990, 258757/1994, 317868/1994, and 324425/1994, Publication of International Patent Application No. 500926/1995, and USP 5,541,054; dyes having a carboxylic group, examples of which are the dyes described in JP-A 163440/1991, 301141/1994 and USP 5,441,899; and merocyanine dyes, polynuclear merocyanine dyes, and polynuclear cyanine dyes, examples of which are the dyes described in JP-A 6329/1972, 105524/1974, 127719/1976, 80829/1977, 61517/1979, 214846/1984, 6750/1985, 159841/1988, 35109/1994, 59361/1994, 146537/1995, Publication of International Patent Application No. 50111/1993, BP 1,467,638, and USP 5,281,515.

[0035] Also useful in the practice of the invention are dyes capable of forming the J-band as disclosed in USP 5,510,236, 3,871,887 (Example 5), JP-A 96131/1990 and 48753/1984.

[0036] These sensitizing dyes may be used alone or in admixture of two or more. A combination of sensitizing dyes is often used for the purpose of supersensitization. In addition to the sensitizing dye, the emulsion may contain a dye which itself has no spectral sensitization function or a compound which does not substantially absorb visible light, but is capable of supersensitization. Useful sensitizing dyes, combinations of dyes showing supersensitization, and compounds showing supersensitization are described in *Research Disclosure*, Vol. 176, 17643 (December 1978), page 23, IV J and JP-B 25500/1974 and 4933/1968, JP-A 19032/1984 and 192242/1984.

[0037] The sensitizing dye may be added to a silver halide emulsion by directly dispersing the dye in the emulsion or by dissolving the dye in a solvent and adding the solution to the emulsion. The solvent used herein includes water, methanol, ethanol, propanol, acetone, methyl cellosolve, 2,2,3,3-tetrafluoropropanol, 2,2,2-trifluoroethanol, 3-methoxy-1-propanol, 3 -methoxy-1-butanol, 1-methoxy-2-propanol, N,N-dimethylformamide and mixtures thereof.

[0038] Also useful are a method of dissolving a dye in a volatile organic solvent, dispersing the solution in water or hydrophilic colloid and adding the dispersion to an emulsion as disclosed in USP 3,469,987, a method of dissolving a dye in an acid and adding the solution to an emulsion or forming an aqueous solution of a dye with the aid of an acid or base and adding it to an emulsion as disclosed in JP-B 23389/1969, 27555/1969 and 22091/1982, a method of forming an aqueous solution or colloidal dispersion of a dye with the aid of a surfactant and adding it to an emulsion as disclosed in USP 3,822,135 and 4,006,025, a method of directly dispersing a dye in hydrophilic colloid and adding the dispersion to an emulsion as disclosed in JP-A 102733/1978 and 105141/1983, and a method of dissolving a dye using a compound capable of red shift and adding the solution to an emulsion as disclosed in JP-A 74624/1976. It is also acceptable to apply ultrasonic waves to form a solution.

[0039] The time when the sensitizing dye is added to the silver halide emulsion according to the invention is at any step of an emulsion preparing process which has been ascertained effective. The sensitizing dye may be added to the emulsion at any stage or step before the emulsion is coated, for example, at a stage prior to the silver halide grain forming step and/or desalting step, during the desalting step and/or a stage from desalting to the start of chemical ripening as disclosed in USP 2,735,766, 3,628,960, 4,183,756, and 4,225,666, JP-A 184142/1983 and 196749/1985, and a stage immediately before or during chemical ripening and a stage from chemical ripening to emulsion coating as disclosed in JP-A 113920/1983. Also as disclosed in USP 4,225,666 and JP-A 7629/1983, an identical compound may be added alone or in combination with a compound of different structure in divided portions, for example, in divided portions during a grain forming step and during a chemical ripening step or after the completion of chemical ripening, or before or during chemical ripening and after the completion thereof. The type of compound or the combination of compounds to be added in divided portions may be changed.

[0040] The amount of the sensitizing dye used may be an appropriate amount complying with sensitivity and fog although the preferred amount is about 10^{-6}, to 1 mol, more preferably 10^{-4} to 10^{-1} mol per mol of the silver halide in the photosensitive layer.

Organic silver salt

[0041] The organic silver salt used herein is relatively stable to light, but forms a silver image when heated at 80°C or higher in the presence of an exposed photocatalyst (as typified by a latent image of photosensitive silver halide) and a reducing agent. The organic silver salt may be of any desired organic compound containing a source capable of reducing silver ion. Preferred are silver salts of organic acids, typically long chain aliphatic carboxylic acids having 10 to 30 carbon atoms, especially 15 to 28 carbon atoms. Also preferred are complexes of organic or inorganic silver salts with ligands having a stability constant in the range of 4.0 to 10.0. The silver-providing substance preferably constitutes about 5 to 70% by weight of the image forming layer. Preferred organic silver salts include silver salts of organic compounds having a carboxyl group. Examples include silver salts of aliphatic carboxylic acids and silver salts of aromatic carboxylic acids though not limited thereto. Preferred examples of the silver salt of aliphatic carboxylic acid include silver behenate, silver arachidate, silver stearate, silver oleate, silver laurate, silver caproate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartrate, silver linolate, silver butyrate, silver camphorate and mixtures thereof.

[0042] Silver salts of compounds having a mercapto or thion group and derivatives thereof are also useful. Preferred examples of these compounds include a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, a silver salt of 2-mercaptobenzimidazole, a silver salt of 2-mercapto-5-aminothiadiazole, a silver salt of 2-(ethylglycolamido)-benzothiazole, silver salts of thioglycolic acids such as silver salts of S-alkylthioglycolic acids wherein the alkyl group has 12 to 22 carbon atoms, silver salts of dithiocarboxylic acids such as a silver salt of dithioacetic acid, silver salts of thioamides, a silver salt of 5-carboxyl-1-methyl-2-phenyl-4-thiopyridine, silver salts of mercaptotriazines, a silver salt of 2-mercaptobenzoxazole as well as silver salts of 1,2,4-mercaptothiazole derivatives such as a silver salt of 3-amino-5-benzylthio-1,2,4-thiazole as described in USP 4,123,274 and silver salts of thion compounds such as a silver salt of 3-(3-carboxyethyl)-4-methyl-4-thiazoline-2-thion as described in USP 3,301,678. Compounds containing an imino group may also be used. Preferred examples of these compounds include silver salts of benzotriazole and derivatives thereof, for example, silver salts of benzotriazoles such as silver methyl-benzotriazole, silver salts of halogenated benzotriazoles such as silver 5-chlorobenzotriazole as well as silver salts of 1,2,4-triazole and 1-H-tetrazole and silver salts of imidazole and imidazole derivatives as described in USP 4,220,709. Also useful are various silver acetylide compounds as described, for example, in USP 4,761,361 and 4,775,613.

[0043] The organic silver salt which can be used herein may take any desired shape although needle crystals having a minor axis and a major axis are preferred. In the practice of the invention, grains should preferably have a minor axis of 0.01 μm to 0.20 μm and a major axis of 0.10 μm to 5.0 μm, more preferably a minor axis of 0.01 μm to 0.15 μm and a major axis of 0.10 μm to 4.0 μm. The grain size distribution of the organic silver salt is desirably monodisperse. The monodisperse distribution means that a standard deviation of the length of minor and major axes divided by the length, respectively, expressed in percent, is preferably up to 100%, more preferably up to 80%, most preferably up to 50%. It can be determined from the measurement of the shape of organic silver salt grains using an image obtained through a transmission electron microscope. Another method for determining a monodisperse distribution is to determine a standard deviation of a volume weighed mean diameter. The standard deviation divided by the volume weighed mean diameter, expressed in percent, which is a coefficient of variation, is preferably up to 100%, more preferably up to 80%, most preferably up to 50%. It may be determined by irradiating laser light, for example, to organic silver salt grains dispersed in liquid and determining the autocorrelation function of the fluctuation of scattering light relative to a time change, and obtaining the grain size (volume weighed mean diameter) therefrom.

[0044] The organic silver salt used herein is preferably desalted. The desalting method is not critical. Any well-known method may be used although well-known filtration methods such as centrifugation, suction filtration, ultrafiltration, and flocculation/water washing are preferred.

[0045] In the practice of the invention, the organic silver salt is prepared into a solid particle dispersion using a dispersant, in order to provide fine particles of small size and free of flocculation. A solid particle dispersion of the organic silver salt may be prepared by mechanically dispersing the salt in the presence of dispersing aids by well-known comminuting means such as ball mills, vibrating ball mills, planetary ball mills, sand mills, colloidal mills, jet mills, roller mills, microfluidizers, nanomizers and Gaulin homogenizers. Of these, microfluidizers, nanomizers and Gaulin homogenizers are preferably used.

[0046] The dispersant used in the preparation of a solid microparticulate dispersion of the organic silver salt may be selected from synthetic anionic polymers such as polyacrylic acid, copolymers of acrylic acid, copolymers of maleic acid, copolymers of maleic acid monoester, and copolymers of acryloylmethylpropanesulfonic acid; semi-synthetic anionic polymers such as carboxymethyl starch and carboxymethyl cellulose; anionic polymers such as alginic acid and pectic acid; anionic surfactants as described in JP-A 92716/1977 and WO 88/04794; the compounds described in Japanese Patent Application No. 350753/1995; well-known anionic, nonionic and cationic surfactants; and well-known polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methyl cellulose, as well as naturally occurring high molecular weight compounds such as gelatin.

[0047] In general, the dispersant is mixed with the organic silver salt in powder or wet cake form prior to dispersion. The resulting slurry is fed into a dispersing machine. Alternatively, a mixture of the dispersant with the organic silver salt is subject to heat treatment or solvent treatment to form a dispersant-bearing powder or wet cake of the organic silver salt. It is acceptable to effect pH control with a suitable pH adjusting agent before, during or after dispersion.

[0048] Rather than mechanical dispersion, fine particles can be formed by roughly dispersing the organic silver salt in a solvent through pH control and thereafter, changing the pH in the presence of dispersing aids. An organic solvent can be used as the solvent for rough dispersion although the organic solvent is usually removed at the end of formation of fine particles.

[0049] The thus prepared dispersion may be stored while continuously stirring for the purpose of preventing fine particles from settling during storage. Alternatively, the dispersion is stored after adding hydrophilic colloid to establish a highly viscous state (for example, in a jelly-like state using gelatin). An antiseptic agent may be added to the dispersion in order to prevent the growth of bacteria during storage.

[0050] The organic silver salt is used in any desired amount, preferably about 0.1 to 5 g/m^2, more preferably about 1 to 3 g/m^2, as expressed by a silver coverage per square meter of the photothermographic element.

Reducing agent

[0051] The photothermographic element of the invention contains a reducing agent for the organic silver salt. The reducing agent for the organic silver salt may be any of substances, preferably organic substances, that reduce silver ion into metallic silver. Conventional photographic developing agents such as Phenidone®, hydroquinone and catechol are useful although hindered phenols are preferred reducing agents. The reducing agent should preferably be contained in an amount of 5 to 50 mol%, more preferably 10 to 40 mol% per mol of silver on the image forming layer-bearing side. The reducing agent may take the form of a precursor which is modified so as to exert its effective function only at the time of development.

[0052] For photothermographic elements using organic silver salts, a wide range of reducing agents are disclosed, for example, in JP-A 6074/1971, 1238/1972, 33621/1972, 46427/1974, 115540/1974, 14334/1975, 36110/1975, 147711/1975, 32632/1976, 1023721/1976, 32324/1976, 51933/1976, 84727/1977, 108654/1980, 146133/1981, 82828/1982, 82829/1982, 3793/1994, USP 3,667,958, 3,679,426, 3,751,252, 3,751,255, 3,761,270, 3,782,949, 3,839,048, 3,928,686, 5,464,738, German Patent No. 2321328, and EP 692732. Exemplary reducing agents include amidoximes such as phenylamidoxime, 2-thienylamidoxime, and p-phenoxyphenyl-amidoxime; azines such as 4-hydroxy-3,5-dimethoxy-benzaldehydeazine; combinations of aliphatic carboxylic acid arylhydrazides with ascorbic acid such as a combination of 2,2-bis(hydroxymethyl)propionyl-β-phenylhydrazine with ascorbic acid; combinations of polyhydroxybenzenes with hydroxylamine, reductone and/or hydrazine, such as combinations of hydroquinone with bis(ethoxyethyl)hydroxylamine, piperidinohexosereductone or formyl-4-methylphenyl-hydrazine; hydroxamic acids such as phenylhydroxamic acid, p-hydroxyphenylhydroxamic acid, and β-anilinehydroxamic acid; combinations of azines with sulfonamidophenols such as a combination of phenothiazine with 2,6-dichloro-4-benzene-sulfonamidephenol; α-cyanophenyl acetic acid derivatives such as ethyl-α-cyano-2-methylphenyl acetate and ethyl-α-cyanophenyl acetate; bis-β-naphthols such as 2,2-dihydroXy-1,1-binaphthyl, 6,6-dibromo-2,2-dihydroxy-1,1-binaphthyl, and bis(2-hydroxy-1-naphthyl)methane; combinations of bis-β-naphthols with 1,3-dihydroxybenzene derivatives such as 2,4-dihydroxybenzophenone and 2,4-dihydroxyacetophenone; 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones such as dimethylaminohexosereductone, anhydrodihydroaminohexosereductone and anhydrodihydropiperidonehexosereductone; sulfonamidephenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidephenol and p-benzenesulfonamidephenol; 2-phenylindane-1,3-dione, etc.; chromans such as 2,2-dimethyl-7-t-butyl-6-hydroxychroman; 1,4-dihydropyridines such as 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine; bisphenols such as bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methyl-phenyl)propane, 4,4-ethylidene-bis(2-t-butyl-6-methylphenol), 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-propane; ascorbic acid derivatives such as 1-ascorbyl palmitate and ascorbyl stearate; aldehydes and ketones such as benzil and diacetyl; 3-pyrazolidones and certain indane-1,3-diones; and chromanols (tocopherols). Preferred reducing agents are bisphenols and chromanols.

[0053] The reducing agent may be added in any desired form such as solution, powder or solid particle dispersion. The solid particle dispersion of the reducing agent may be prepared by well-known comminuting means such as ball mills, vibrating ball mills, sand mills, colloidal mills, jet mills, roller mills, microfluidizers, nanomizers and Gaulin homogenizers. Dispersing aids may be used for facilitating dispersion.

Toner

[0054] A higher optical density is sometimes achieved when an additive known as a "toner" for improving images is contained. The toner is also sometimes advantageous in forming black silver images. The toner is preferably used in an amount of 0.1 to 50 mol%, especially 0.5 to 20 mol% per mol of silver on the image forming layer-bearing side. The toner may take the form of a precursor which is modified so as to exert its effective function only at the time of development.

[0055] For photothermographic elements using organic silver salts, a wide range of toners are disclosed, for example, in JP-A 6077/1971, 10282/1972, 5019/1974, 5020/1974, 91215/1974, 2524/1975, 32927/1975, 67132/1975, 67641/1975, 114217/1975, 3223/1976, 27923/1976, 14788/1977, 99813/1977, 1020/1978, 76020/1978, 156524/1979, 156525/1979, 183642/1986, and 56848/1992, JP-B 10727/1974 and 20333/1979, USP 3,080,254, 3,446,648, 3,782,941, 4,123,282, 4,510,236, BP 1,380,795, and Belgian Patent No. 841,910. Examples of the toner include phthalimide and N-hydroxyphthalimide; cyclic imides such as succinimide, pyrazolin-5-one, quinazolinone, 3-phenyl-2-pyrazolin-5-one, 1-phenylurazol, quinazoline and 2,4-thiazolidinedione; naphthalimides such as N-hydroxy-1,8-naphthalimide; cobalt complexes such as cobaltic hexamine trifluoroacetate; mercaptans as exemplified by 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole, and 2,5-dimercapto-1,3,4-thiadiazole; N-(aminomethyl)aryldicarboxyimides such as (N,N-dimethylaminomethyl)phthalimide and N,N-(dimethylaminomethyl)-naphthalene-2,3-dicarboxyimide; blocked pyrazoles, isothiuronium derivatives and certain photo-bleach agents such as N,N'-hexamethylenebis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)-bis(isothiuroniumtrifluoroacetate) and 2-tribromomechyl-sulfonyl-benzothiazole; 3-ethyl-5-{(3-ethyl-2-benzo-thiazolinylidene)-1-methylethylidene}-2-thio-2, 4-oxazolidinedione; phthalazinone, phthalazinone derivatives or metal salts, or derivatives such as 4-(1-naphthyl)-phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxy-phthalazinone and 2,3-dihydro-1,4-phthalazinedione; combinations of phthalazinones with phthalic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid and tetrachlorophthalic anhydride); phthalazine, phthalazine derivatives or metal salts such as 4-(1-naphthyl)phthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine; combinations of phthalazine with phthalic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid and tetrachlorophthalic anhydride); quinazolinedione, benzoxazine or naphthoxazine derivatives; rhodium complexes which function not only as a tone regulating agent, but also as a source of halide ion for generating silver halide in situ, for example, ammonium hexachlororhodinate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodinate (III); inorganic peroxides and persulfates such as ammonium peroxide disulfide and hydrogen peroxide; benzoxazine-2,4-diones such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidine and asym-triazines such as 2,4-dihydroxypyrimidine and 2-hydroxy-4-aminopyrimidine; azauracil and tetraazapentalene derivatives such as 3,6-dimercapto-1,4-diphenyl-1H,4H-2,3a,5,6a-tetraazapentalene, and 1,4-di(o-chlorophenyl)-3,6-

dimercapto-1H,4H-2,3a,5,6a-tetraazapentalene.

[0056] The toner may be added in any desired form, for example, as a solution, powder and solid particle dispersion. The solid particle dispersion of the toner is prepared by well-known finely dividing means such as ball mills, vibrating ball mills, sand mills, colloid mills, jet mills, and roller mills. Dispersing aids may be used in preparing the solid particle dispersion.

Antifoggant

[0057] With antifoggants, stabilizers and stabilizer precursors, the silver halide emulsion and/or organic silver salt according to the invention can be further protected against formation of additional fog and stabilized against lowering of sensitivity during shelf storage. Suitable antifoggants, stabilizers and stabilizer precursors which can be used alone or in combination include thiazonium salts as described in USP 2,131,038 and 2,694,716, azaindenes as described in USP 2,886,437 and 2,444,605, mercury salts as described in USP 2,728,663, urazoles as described in USP 3,287,135, sulfocatechols as described in USP 3,235,652, oximes, nitrons and nitroindazoles as described in BP 623,448, polyvalent metal salts as described in USP 2,839,405, thiuronium salts as described in USP 3,220,839, palladium, platinum and gold salts as described in USP 2,566,263 and 2,597,915, halogen-substituted organic compounds as described in USP 4,108,665 and 4,442,202, triazines as described in USP 4,128,557, 4,137,079, 4,138,365 and 4,459,350, and phosphorus compounds as described in USP 4,411,985.

[0058] Preferred antifoggants are organic halides, for example, the compounds described in JP-A 119624/1975, 120328/1975, 121332/1976, 58022/1979, 70543/1981, 99335/1981, 90842/1984, 129642/1986, 129845/1987, 208191/1994, 5621/1995, 2781/1995, 15809/1996, USP 5,340,712, 5,369,000, and 5,464,737.

[0059] The antifoggant may be added in any desired form such as solution, powder or solid particle dispersion. The solid particle dispersion of the antifoggant may be prepared by well-known comminuting means such as ball mills, vibrating ball mills, sand mills, colloidal mills, jet mills, and roller mills. Dispersing aids may be used for facilitating dispersion.

[0060] It is sometimes advantageous to add a mercury (II) salt to an emulsion layer as an antifoggant though not necessary in the practice of the invention. Mercury (II) salts preferred to this end are mercury acetate and mercury bromide. The mercury (II) salt is preferably added in an amount of 1×10^{-9} mol to 1×10^{-3} mol, more preferably 1×10^{-8} mol to 1×10^{-4} mol per mol of silver coated.

[0061] Still further, the photothermographic element of the invention may contain a benzoic acid type compound for the purposes of increasing sensitivity and restraining fog. Any of benzoic acid type compounds may be used although examples of the preferred structure are described in USP 4,784,939 and 4,152,160, Japanese Patent Application Nos. 98051/1996, 151241/1996, and 151242/1996. The benzoic acid type compound may be added to any site in the photothermographic element, preferably to a layer on the same side as the photosensitive layer, and more preferably an organic silver salt-containing layer. The benzoic acid type compound may be added at any step in the preparation of a coating solution. Where it is contained in an organic silver salt-containing layer, it may be added at any step from the preparation of the organic silver salt to the preparation of a coating solution, preferably after the preparation of the organic silver salt and immediately before coating. The benzoic acid type compound may be added in any desired form including powder, solution and fine particle dispersion. Alternatively, it may be added in a solution form after mixing it with other additives such as a sensitizing dye, reducing agent and toner. The benzoic acid type compound may be added in any desired amount, preferably 1×10^{-6} mol to 2 mol, more preferably 1×10^{-3} mol to 0.5 mol per mol of silver.

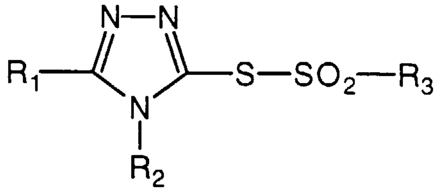
[0062] In the photothermographic element of the invention, mercapto, disulfide and thion compounds may be added for the purposes of retarding or accelerating development to control development, improving spectral sensitization efficiency, and improving storage stability before and after development.

[0063] Where mercapto compounds are used herein, any structure is acceptable. Preferred are structures represented by Ar-S-M and Ar-S-S-Ar wherein M is a hydrogen atom or alkali metal atom, and Ar is an aromatic ring or fused aromatic ring having at least one nitrogen, sulfur, oxygen, selenium or tellurium atom. Preferred hetero-aromatic rings are benzimidazole, naphthimidazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, benzotellurazole, imidazole, oxazole, pyrrazole, triazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine pyrazine, pyridine, purine, quinoline and quinazolinone rings. These hetero-aromatic rings may have a substituent selected from the group consisting of halogen (e.g., Br and Cl), hydroxy, amino, carboxy, alkyl groups (having at least 1 carbon atom, preferably 1 to 4 carbon atoms), and alkoxy groups (having at least 1 carbon atom, preferably 1 to 4 carbon atoms). Illustrative, non-limiting examples of the mercapto-substituted hetero-aromatic compound include 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercapto-5-methylbenzimidazole, 6-ethoxy-2-mercaptobenzothiazole, 2,2'-dithiobis(benzothiazole), 3-mercapto-1,2,4-triazole, 4,5-diphenyl-2-imidazolethiol, 2-mercaptoimidazole, 1-ethyl-2-mercaptobenzimidazole, 2-mercaptoquinoline, 8-mercaptopurine, 2-mercapto-4(3H)-quinazolinone, 7-trifluoromethyl-4-quinolinethiol, 2,3,5,6-tetrachloro-4-pyridinethiol, 4-amino-6-hydroxy-2-mercaptopyrimidine monohydrate, 2-amino-5-mercapto-1,3,4-thiadiazole, 3-amino-5-mercapto-1,2,4-triazole, 4-hydroxy-2-mercaptopyrimidine, 2-mercaptopyrimidine, 4,6-diamino-2-mercaptopyrimidine, 2-mercapto-4-methylpyrimidine hydrochloride, 3-mercapto-5-phenyl-1,2,4-triazole, and 2-mercapto-4-phenyloxazole.

[0064] These mercapto compounds are preferably added to the emulsion layer in amounts of 0.001 to 1.0 mol, more preferably 0.01 to 0.3 mol per mol of silver.

[0065] In the photothermographic element according to one preferred embodiment of the invention, a compound of the following general formula (1) or (2) is used for minimizing changes of photographic properties under varying development conditions.

Formula (1):



Herein R_1, R_2, and R_3 are independently hydrogen, aliphatic hydrocarbon groups or aryl groups.

[0066] The aliphatic hydrocarbon groups represented by R_1 in formula (1) include normal, branched or cyclic alkyl groups (preferably of 1 to 20 carbon atoms, more preferably 3 to 16 carbon atoms, most preferably 5 to 12 carbon atoms), alkenyl groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 12 carbon atoms), and alkynyl groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 12 carbon atoms), which may have substituents.

[0067] Examples of the substituents include aryl groups (preferably of 6 to 30 carbon atoms, more preferably 6 to 20 carbon atoms, most preferably 6 to 12 carbon atoms, such as phenyl, p-methylphenyl, and naphthyl), amino groups (preferably of 0 to 20 carbon atoms, more preferably 0 to 10 carbon atoms, most preferably 0 to 6 carbon atoms, such as amino, methylamino, dimethylamino, diethylamino, and dibenzylamino), alkoxy groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms, most preferably 1 to 8 carbon atoms, such as methoxy, ethoxy, butoxy, and dodecyloxy), aryloxy groups (preferably of 6 to 20 carbon atoms, more preferably 6 to 16 carbon atoms, most preferably 6 to 12 carbon atoms, such as phenyloxy and 2-naphthyloxy), acyl groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as acetyl, benzoyl, formyl, and pivaloyl), alkoxycarbonyl groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 12 carbon atoms, such as methoxycarbonyl and ethoxcarbonyl), aryloxycarbonyl groups (preferably of 7 to 20 carbon atoms, more preferably 7 to 16 carbon atoms, most preferably 7 to 10 carbon atoms, such as phenoxycarbonyl), acyloxy groups (preferably of 1 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 10 carbon atoms, such as acetoxy and benzoyloxy), acylamino groups (preferably of 1 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 10 carbon atoms, such as acetylamino, butyrylamino, and benzoylamino), alkoxycarbonylamino groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 16 carbon atoms, most preferably 2 to 12 carbon atoms, such as methoxycarbonylamino), aryloxycarbonylamino groups (preferably of 7 to 20 carbon atoms, more preferably 7 to 16 carbon atoms, most preferably 7 to 12 carbon atoms, such as phenyloxycarbonylamino), sulfonylamino groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as methanesulfonylamino and benzenesulfonylamino), sulfamoyl groups (preferably of 0 to 20 carbon atoms, more preferably 0 to 16 carbon atoms, most preferably 0 to 12 carbon atoms, such as sulfamoyl, methylsulfamoyl, dimethylsulfamoyl, and phenylsulfamoyl), carbamoyl groups (preferably of 0 to 20 carbon atoms, more preferably 0 to 16 carbon atoms, most preferably 0 to 12 carbon atoms, such as carbamoyl, diethylcarbamoyl, and phenylcarbamoyl), ureido groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as ureido, methylureido, and phenylureido), alkylthio groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as methylthio and ethylthio), arylthio groups (preferably of 6 to 20 carbon atoms, more preferably 6 to 16 carbon atoms, most preferably 6 to 12 carbon atoms, such as phenylthio), sulfonyl groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as mesyl and tosyl), sulfinyl groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as methanesulfinyl and benzenesulfinyl), phosphoramide groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 16 carbon atoms, most preferably 1 to 12 carbon atoms, such as diethylphosphoramide and phenylphosphoramide), hydroxy groups, mercapto groups, halogen atoms (e.g., fluorine, chlorine, bromine, and iodine atoms), cyano groups, sulfo groups, carboxy groups, nitro groups, hydroxamic groups, sulfino groups, hydrazino groups, sulfonylthio groups, thiosulfonyl groups, and heterocyclic groups (e.g., imidazolyl, pyridyl, furyl, piperidyl, and morpholyl). These substituents may, in turn, be further substituted. Where there is more than one substituent, they may be identical or different.

[0068] Preferred substituents on the aliphatic hydrocarbon groups represented by R_1 are aryl, alkoxy, heterocyclic cyano, alkoxycarbonyl groups and halogen atoms. Cyano, alkoxycarbonyl, alkoxy groups and halogen atoms are more preferred.

[0069] The aryl groups represented by R_1 are preferably monocyclic or fused ring aryl groups having 6 to 30 carbon atoms, more preferably monocyclic or fused ring aryl groups having 6 to 20 carbon atoms, for example, phenyl and naphthyl, with the phenyl being especially preferred. The aryl groups represented by R_1 may have substituents thereon. Examples of such substituents include those described above as the substituents on the aliphatic hydrocarbon groups represented by R_1 as well as alkyl groups (preferably of 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms, most preferably 1 to 8 carbon atoms, such as methyl, ethyl, isopropyl, tert-butyl, n-octyl, tert-amyl, dodecyl, and cyclohexyl), alkenyl groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 12 carbon atoms, most preferably 2 to 8 carbon atoms, such as vinyl, allyl, 2-butenyl, and 3-pentenyl), and alkynyl groups (preferably of 2 to 20 carbon atoms, more preferably 2 to 12 carbon atoms, most preferably 2 to 8 carbon atoms, such as propargyl and 3-pentynyl).

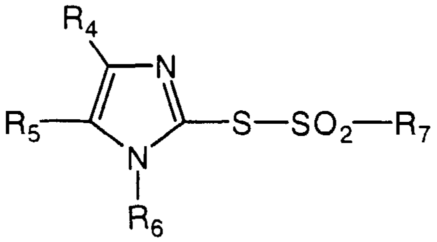
[0070] Preferred substituents on the aryl groups represented by R_1 are alkyl, aryl, alkoxy, aryloxy, acyl, alkoxycarbonyl, acyloxy, acylamino, alkoxycarbonylamino, aryloxycarbonyl-amino, sulfonylamino, sulfamoylamino, carbamoylamino, ureido, alkylthio, arylthio, sulfonyl, nitro, sulfonylthio, halogen, and cyano. Of these, alkyl, alkoxy, aryloxy, acyl, alkoxycarbonyl, nitro, acylamino, alkylthio, halogen and cyano are more preferred.

[0071] The groups represented by R_1 are preferably alkyl groups, and more preferably normal alkyl groups.

[0072] The aliphatic hydrocarbon and aryl groups represented by R_2 in formula (1) are as defined above for R_1, with their illustrative examples being also the same. Most preferably, R_2 is phenyl.

[0073] The aliphatic hydrocarbon and aryl groups represented by R_3 in formula (1) are as defined above for R_1, with their illustrative examples being also the same. Most preferably, R_3 represents alkyl (such as butyl) and phenyl.

Formula (2):



Herein R_4 and R_5 are independently hydrogen, aliphatic hydrocarbon groups or aryl groups, R_6 and R_7 are independently aliphatic hydrocarbon groups or aryl groups.

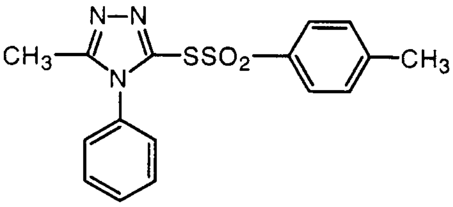
[0074] The aliphatic hydrocarbon and aryl groups represented by R_4 and R_5 in formula (2) are as defined above for R_1 in formula (1), with their illustrative examples being also the same. Most preferably, R_4 and R_5 are hydrogen, alkyl (such as methyl, ethyl and butyl) and phenyl.

[0075] The aliphatic hydrocarbon and aryl groups represented by R_6 and R_7 in formula (2) are as defined above for R_1 in formula (1), with their illustrative examples being also the same. Most preferably, R_6 and R_7 are alkyl (such as methyl, butyl and hexyl) and phenyl.

[0076] Illustrative examples of the compounds of formulae (1) and (2) are given below. The compounds which can be used herein are not limited thereto.

[0077] Illustrative examples of the compound of formula (1) are given below.

(T-1)



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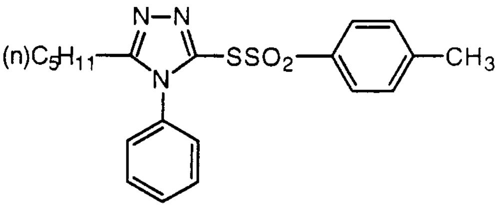

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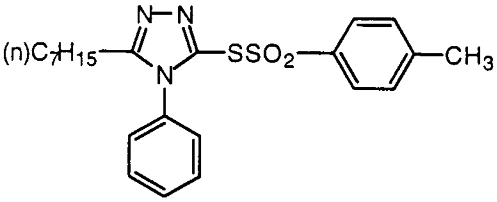

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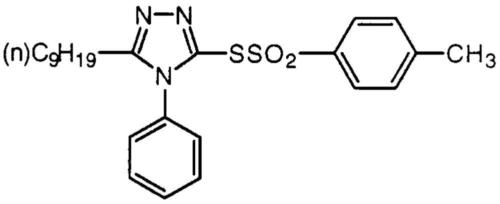

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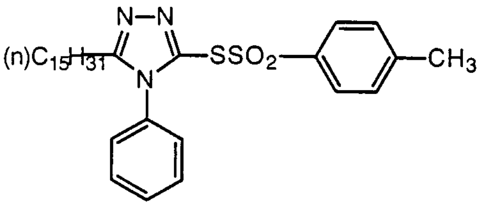

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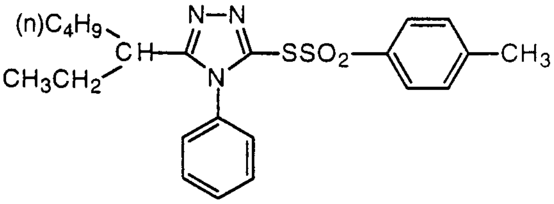

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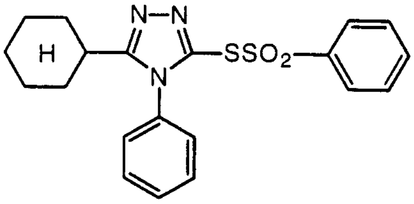

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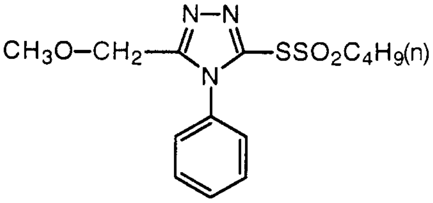

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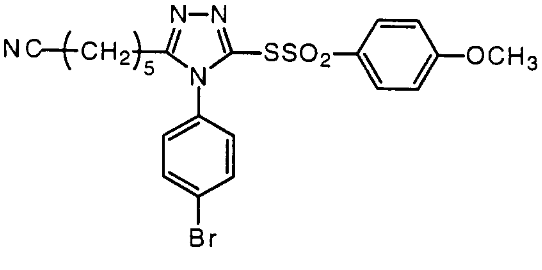

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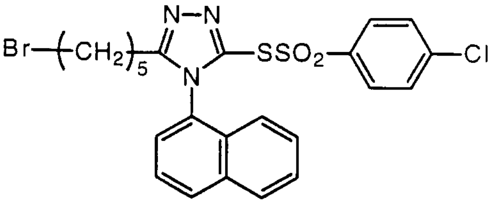

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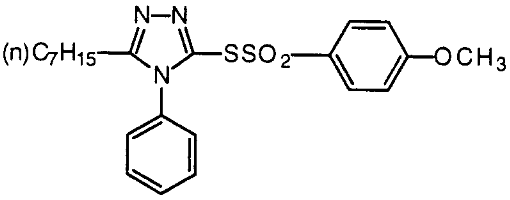

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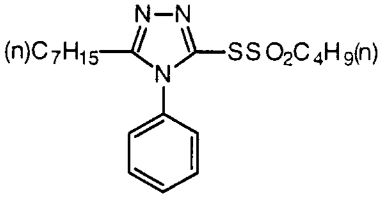

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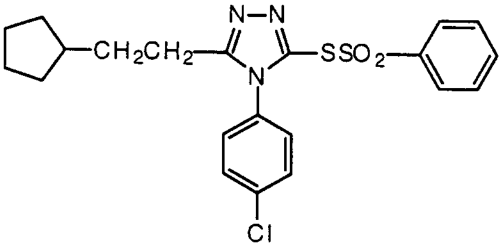

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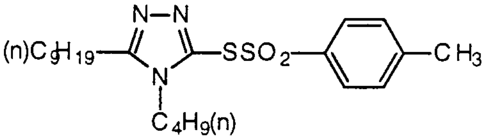

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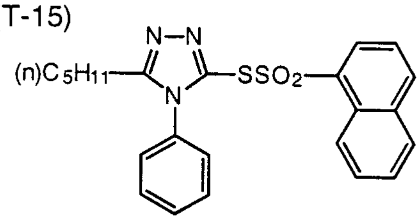

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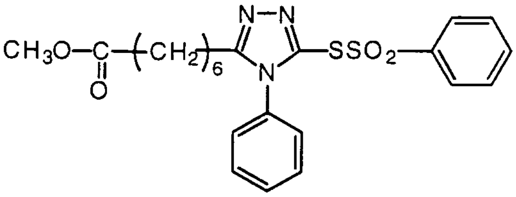

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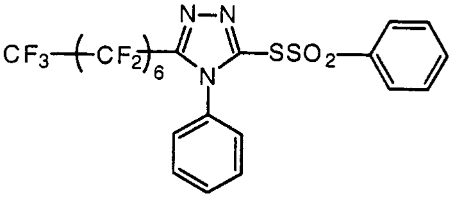

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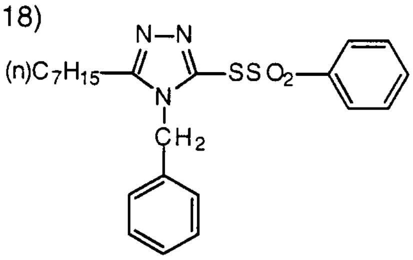

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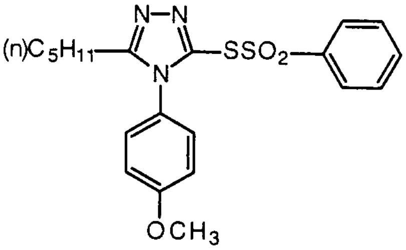

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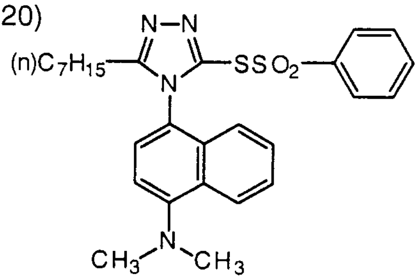

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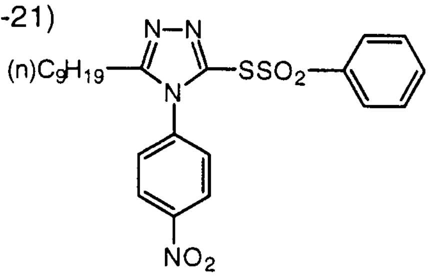

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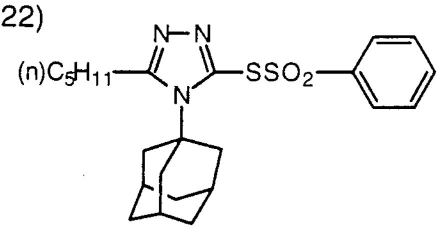

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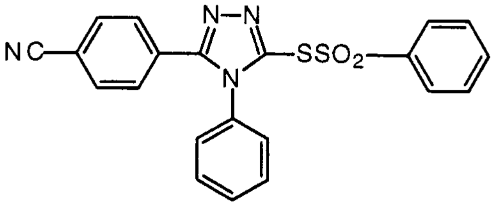

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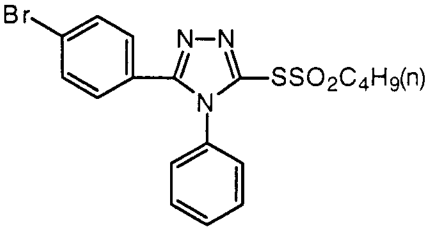

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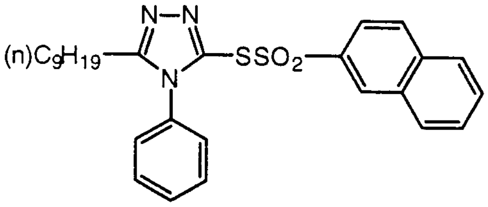

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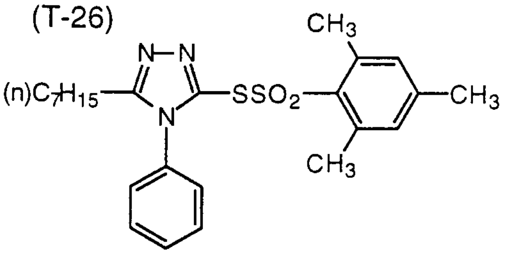

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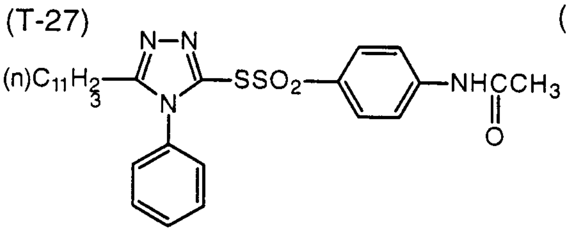

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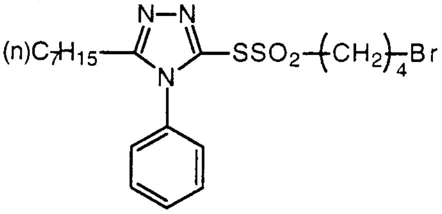

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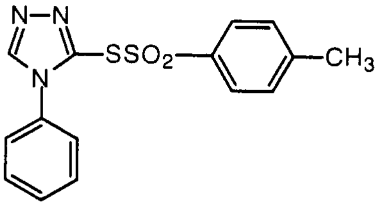
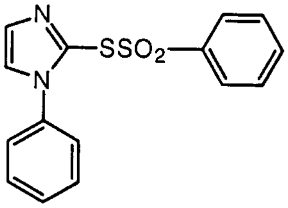
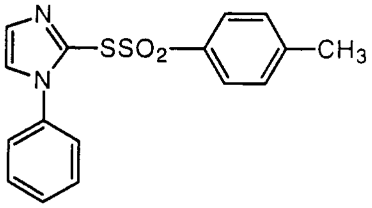


[0078] Illustrative examples of the compound of formula (2) are given below.

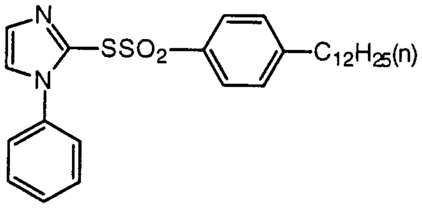
(I-1)



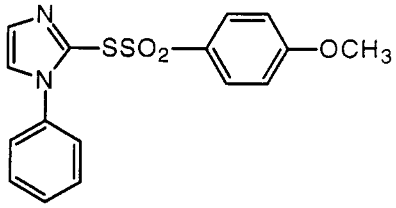
(I-2)



(I-3)



(I-4)



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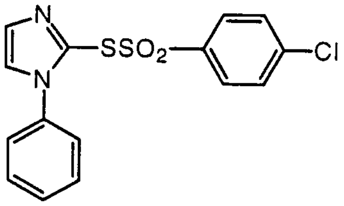

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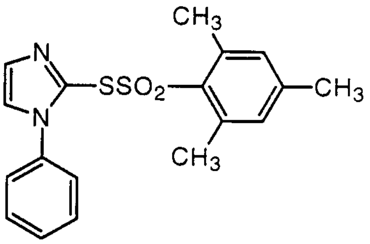

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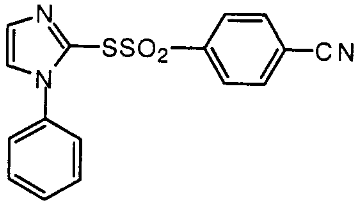

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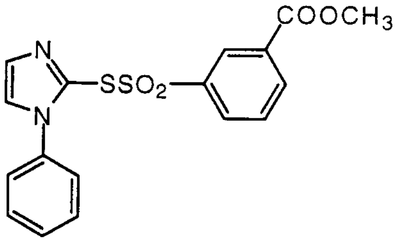

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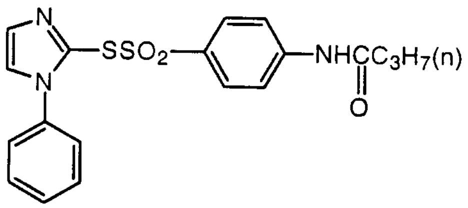

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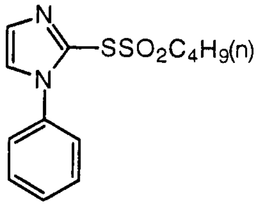

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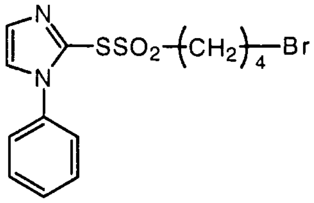

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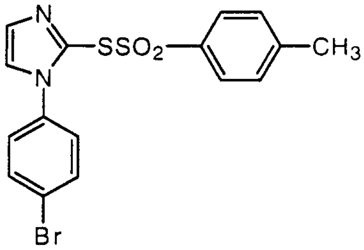

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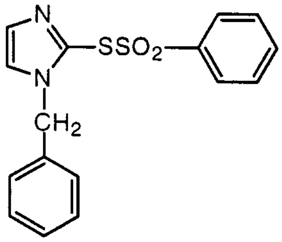

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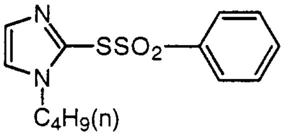

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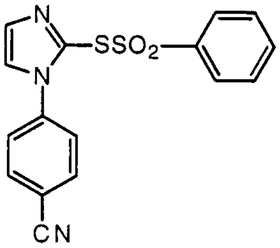

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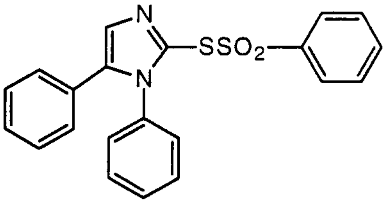

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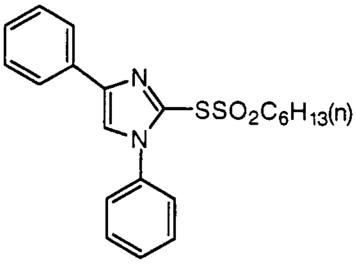

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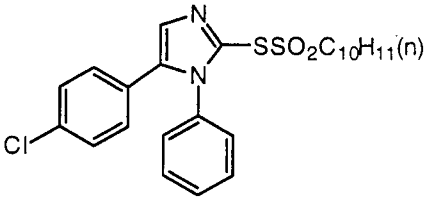

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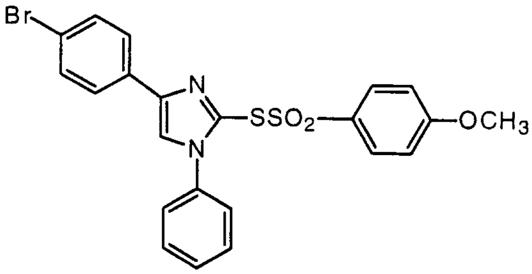

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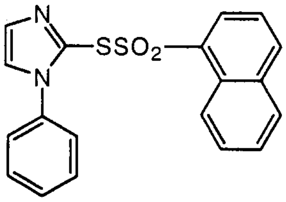

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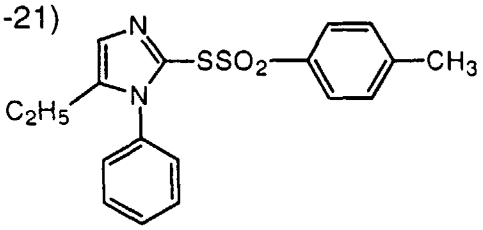

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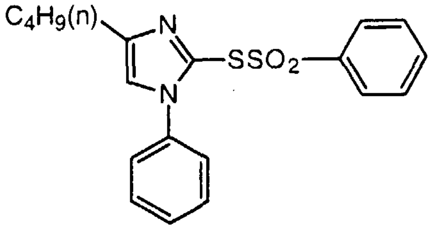

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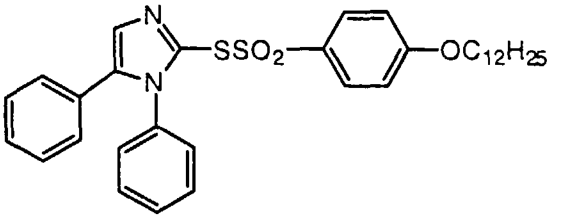

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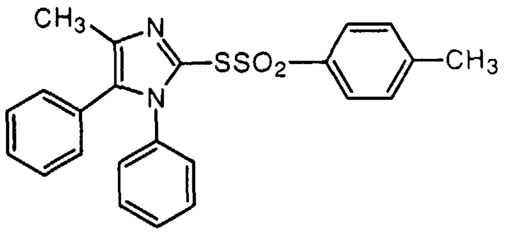

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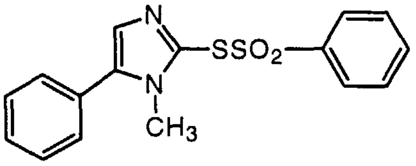


[0079] The compounds of formulae (1) and (2) can be readily synthesized through reaction of mercaptotriazoles or mercaptoimidazoles with acid chlorides. Alternatively, they can be readily synthesized by methods as described in "New Experimental Chemistry Series," Vol. 14, pp. 1801-1803 (Japan Chemical Society Ed.), for example, disproportionation reaction of sulfinic acids, oxidation of disulfides, reaction of disulfides with sulfinic acid salts, and reaction of sulfinic acid salts with sulfinyl halides.

[0080] The compounds of formula (1) and/or (2) may be used alone or in admixture of two or more. They may be used in an appropriate amount for their purpose, preferably 0.1 to 40 mol%, more preferably 0.5 to 10 mol% based on the total amount of silver salts used.

[0081] The compound of formula (1) or (2) may be added in any suitable form, for example, as a solution, emulsion, solid particle dispersion, or a state mordanted with a polymeric mordant. Preferably, the compound is added in a solid particle dispersion or similar form without using organic solvents. The solid particle dispersion may be prepared by well-known dispersion techniques. Exemplary dispersing machines which can be used are sand mills, attritors, pearl mills, super mills, ball mills, impellers, dispersers, KD mills, colloidal mills, dynatrons, three-roll mills, pressure kneaders, Manton Gaulin, and microfluidizers. With respect to the solid particle dispersion apparatus and technology, reference should be made to Kajiuchi and Usui, "Dispersion Rheology and Dispersing Technology," Shinzan Publishing K.K., 1991, pp 357-403 and Tokai Section of the Chemical Engineering Society Ed., "Progress of Chemical Engineering," Vol. 24, Maki Publishing K.K., 1990, pp 184-185. In the solid particle dispersion, dispersed particles usually have a mean particle size of 0.05 to 10.0 μm, preferably 0.05 to 5 μm, more preferably 0.05 to 1.0 μm, most preferably 0.1 to 0.6 μm.

[0082] In the image forming layer, polyhydric alcohols (e.g., glycerin and diols as described in USP 2,960,404), fatty acids and esters thereof as described in USP 2,588,765 and 3,121,060, and silicone resins as described in BP 955,061 may be added as a plasticizer and lubricant.

[0083] In the practice of the invention, contrast enhancers may be used for forming ultrahigh contrast images. Included are hydrazine derivatives as described in USP 5,464,738, 5,496,695, 5,512,411, 5,536,622, Japanese Patent Application Nos. 228627/1995, 215822/1996, 130842/1996, 148113/1996, 156378/1996, 148111/1996, and 148116/1996; compounds having a quaternary nitrogen atom as described in Japanese Patent Application No.

83566/1996, and acrylonitrile compounds as described in USP 5,545,515. Illustrative examples are compounds 1 to 10 in USP 5,464,738, compounds H-1 to H-28 in USP 5,496,695, compounds I-1 to I-86 in Japanese Patent Application No. 215822/1996, compounds H-1 to H-62 in 130842/1996, compounds I-1 to I-21 in 148113/1996, compounds 1 to 50 in 148111/1996, compounds 1 to 40 in 148116/1996, and compounds P-1 to P-26 and T-1 to T-18 in 83566/1996, and compounds CN-1 to CN-13 in USP 5,545,515.

[0084] Also in the practice of the invention, ultrahigh contrast promoting agents may be used in combination with the contrast enhancers for forming ultrahigh contrast images. Such ultrahigh contrast promoting agents include the amine compounds described in USP 5,545,505, specifically Compounds AM-1 to AM-5 therein, the hydroxamic acids described in USP 5,545,507, specifically HA-1 to HA-11 therein, the acrylonitriles described in USP 5,545,507, specifically CN-1 to CN-13 therein, the hydrazine compounds described in USP 5,558,983, specifically CA-1 to CA-6 therein, the onium salts described in Japanese Patent Application No. 132836/1996, specifically A-1 to A-42, B-1 to B-27 and C-1 to C-14.

[0085] The synthesis methods, addition methods, and addition amounts of these ultrahigh contrast enhancers and ultrahigh contrast promoting agents are as described in the above-listed patents.

[0086] In the inventive photosensitive layer, a variety of dyes and pigments may be used from the standpoints of improving tone and preventing irradiation. Any desired dyes and pigments may be used in the inventive photosensitive layer. Useful pigments and dyes include those described in Colour Index and both organic and inorganic, for example, pyrazoloazole dyes, anthraquinone dyes, azo dyes, azomethine dyes, oxonol dyes, carbocyanine dyes, styryl dyes, triphenylmethane dyes, indoaniline dyes, indophenol dyes, and phthalocyanine dyes. The preferred dyes used herein include anthraquinone dyes leg., Compounds 1 to 9 described in JP-A 341441/1993 and Compounds 3-6 to 3-18 and 3-23 to 3-38 described in JP-A 165147/1993), azomethine dyes (e.g., Compounds 17 to 47 described in JP-A 341441/1993), indoaniline dyes (e.g., Compounds 11 to 19 described in JP-A 289227/1993, Compound 47 described in JP-A 341441/1993 and Compounds 2-10 to 2-11 described in JP-A 165147/1993), and azo dyes (e.g., Compounds 10 to 16 described in JP-A 341441/1993). The dyes and pigments may be added in any desired form such as solution, emulsion or solid particle dispersion or in a form mordanted with polymeric mordants. The amounts of these compounds used are determined in accordance with the desired absorption although the compounds are generally used in amounts of 1 μg to 1 g per square meter of the imaging element.

Protective layer

[0087] A surface protective layer may be provided in the photothermographic element according to the present invention for the purpose of preventing sticking of the image forming layer. The protective layer is situated far from the image forming layer on the support and may include two or more layers.

[0088] At least one of protective layers preferably contains gelatin in an amount of at least 50% by weight, especially at least 70% by weight of the binder. More preferably, gelatin constitutes at least 50% by weight, especially at least 70% by weight of the binder in the outermost layer.

[0089] In the surface protective layer, any desired anti-sticking material may be used. Examples of the anti-sticking material include wax, silica particles, styrene-containing elastomeric block copolymers (e.g., styrene-butadiene-styrene and styrene-isoprene-styrene), cellulose acetate, cellulose acetate butyrate, cellulose propionate and mixtures thereof. Surfactants for facilitating application, and other addenda are optionally added to the surface protective layer.

[0090] A hardener may be used in the protective layer in the practice of the invention. In the absence of a hardener, the layer is less resistant to water and becomes tacky or dissolved with water droplets, which is obstructive to handling as an image forming element.

[0091] Examples of the hardener are described in T.H. James, "The Theory of the Photographic Process," Fourth Edition, Macmillan Publishing Co., Inc., 1977, pp. 77-87, and include polyvalent metal ions described on page 78, polyisocyanates as described in USP 4,281,060 and JP-A 208193/1994, epoxy compounds as described in USP 4,791,042, and vinyl sulfones as described in JP-A 89048/1987. Of these, polyvalent metal ions such as chromium and aluminum ions are especially preferred. The amount of the hardener used may be sufficient to achieve the desired purpose although it is preferably 1 μmol to 1 mmol, more preferably 5 μmol to 200 μmol per gram of gelatin based on the overall amount of gelatin which is present on the side of the support where the image forming layer is formed.

[0092] The hardener is added as a solution. The time when the solution of the hardener is added to the protective layer coating solution should be from 30 minutes to immediately before application, preferably from 10 minutes to 10 seconds before application. No particular limits are imposed on the mixing procedure and conditions insofar as the benefits of the invention are achievable. Illustrative mixing procedures include a procedure of adding the hardener solution to a tank at a flow rate, mixing in the tank and pumping the solution to a coater at a delivery rate, the tank being designed to provide a desired average residence time as calculated from the flow rate and the delivery rate; and a procedure using the static mixer described in N. Harnby, M.F. Edwards & A.W. Nienow (translated by Takahashi), "Livid Mixing Technology," Nikkan Kogyo Shinbun, 1989, Chap. 8.

[0093] In the photosensitive layer or a protective layer therefor according to the invention, there may be used light absorbing substances and filter dyes as described in USP 3,253,921, 2,274,782, 2,527,583, and 2,956,879. The dyes may be mordanted as described in USP 3,282,699. The filer dyes are used in such amounts that the layer may have an absorbance of 0.1 to 3, especially 0.2 to 1.5 at the exposure wavelength.

[0094] In the inventive photosensitive layer, there may be used matte agents, for example, starch, titanium dioxide, zinc oxide, and silica as well as polymer beads including beads of the type described in USP 2,992,101 and 2,701,245. The emulsion layer side surface may have any degree of matte insofar as no star dust failures occur although a Bekk smoothness of 200 to 10,000 seconds, especially 300 to 10,000 seconds is preferred.

[0095] In the practice of the invention, an antihalation layer may be disposed on the side of the photosensitive layer remote from the light source. The antihalation layer preferably has a maximum absorbance of 0.3 to 2 in the desired wavelength range, more preferably an absorbance of 0.5 to 2 at the exposure wavelength, and an absorbance of 0.001 to less than 0.5 in the visible region after processing, and is also preferably a layer having an optical density of 0.001 to less than 0.3.

[0096] Where an antihalation dye is used in the invention, it may be selected from various compounds insofar as it has the desired absorption in the wavelength range, is sufficiently low absorptive in the visible region after processing, and provides the antihalation layer with the preferred absorbance profile. Exemplary antihalation dyes are given below though the dyes are not limited thereto. Useful dyes which are used alone are described in JP-A 56458/1984, 216140/1990, 13295/1995, 11432/1995, USP 5,380,635, JP-A 68539/1990, page 13, lower-left column, line 1 to page 14, lower-left column, line 9, and JP-A 24539/1991, page 14, lower-left column to page 16, lower-right column. It is further preferable in the practice of the invention to use a dye which will decolorize during processing. Illustrative, non-limiting, examples of decolorizable dyes are disclosed in JP-A 139136/1977, 132334/1978, 501480/1981, 16060/1982, 68831/1982, 101835/1982, 182436/1984, 36145/1995, 199409/1995, JP-B 33692/1973, 16648/1975, 41734/1990, USP 4,088,497, 4,283,487, 4,548,896, and 5,187,049.

[0097] In one preferred embodiment, the photothermographic element of the invention is a one-side photosensitive element having at least one photosensitive layer containing a silver halide emulsion on one side and a back layer on the other side of the support.

[0098] In the practice of the invention, a matte agent may be added to the one-side photosensitive element for improving transportation efficiency. The matte agents used herein are generally microparticulate water-insoluble organic or inorganic compounds. There may be used any desired one of matte agents, for example, well-known matte agents including organic matte agents as described in USP 1,939,213, 2,701,245, 2,322,037, 3,262,782, 3,539,344, and 3,767,448 and inorganic matte agents as described in USP 1,260,772, 2,192,241, 3,257,206, 3,370,951, 3,523,022, and 3,769,020. Illustrative examples of the organic compound which can be used as the matte agent are given below; exemplary water-dispersible vinyl polymers include polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, acrylonitrile-α-methylstyrene copolymers, polystyrene, styrene-divinyl-benzene copolymers, polyvinyl acetate, polyethylene carbonate, and polytetrafluoroethylene; exemplary cellulose derivatives include methyl cellulose, cellulose acetate, and cellulose acetate propionate; exemplary starch derivatives include carboxystarch, carboxynitrophenyl starch, urea-formaldehyde-starch reaction products, gelatin hardened with well-known curing agents, and hardened gelatin which has been coaceruvation hardened into microcapsulated hollow particles. Preferred examples of the inorganic compound which can be used as the matte agent include silicon dioxide, titanium dioxide, magnesium dioxide, aluminum oxide, barium sulfate, calcium carbonate, silver chloride and silver bromide desensitized by a well-known method, glass, and diatomaceous earth. The aforementioned matte agents may be used as a mixture of substances of different types if necessary. The size and shape of the matte agent are not critical. The matte agent of any particle size may be used although matte agents having a particle size of 0.1 μm to 30 μm are preferably used in the practice of the invention. The particle size distribution of the matte agent may be either narrow or wide. Nevertheless, since the haze and surface luster of coating are largely affected by the matte agent, it is preferred to adjust the particle size, shape and particle size distribution of a matte agent as desired during preparation of the matte agent or by mixing plural matte agents.

[0099] In the practice of the invention, the back layer should preferably have a degree of matte as expressed by a Bekk smoothness of 10 to 250 seconds, more preferably 50 to 180 seconds.

[0100] In the practice of the invention, the matte agent is preferably contained in an outermost surface layer, a layer functioning as an outermost surface layer, a layer close to the outer surface or a layer functioning as a so-called protective layer.

[0101] In the practice of the invention, the binder used in the back layer is preferably transparent or translucent and generally colorless. Exemplary binders are naturally occurring polymers, synthetic resins, polymers and copolymers, and other film-forming media, for example, gelatin, gum arabic, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), polylmethyl methacrylate), polyvinyl chloride, poly(methacrylic acid), copoly(styrene-maleic anhydride), copoly(styrene-acrylonitrile), copoly(styrene-butadiene), polyvinyl acetals (e.g., polyvinyl formal and polyvinyl butyral), polyesters, polyurethanes, phenoxy resins, poly(vinylidene chloride), polyepoxides, polycarbonates, poly(vinyl acetate), cellulose esters, and polyamides. The binder may be dispersed in water, organic solvent or emulsion to form a dispersion which is coated to form a layer.

[0102] The back layer preferably exhibits a maximum absorbance of 0.3 to 2, more preferably 0.5 to 2 in the predetermined wavelength range and an absorbance of 0.001 to less than 0.5 in the visible range after processing. Further preferably, the back layer has an optical density of 0.001 to less than 0.3. Examples of the antihalation dye used in the back layer are the same as previously described for the antihalation layer.

[0103] A backside resistive heating layer as described in USP 4,460,681 and 4,374,921 may be used in a photographic thermographic image system according to the present invention.

[0104] According to the invention, a hardener may also be used in various layers such as back layers other than the image forming layer and protective layer. Examples of the hardener are described in T.H. James, "The Theory of the Photographic Process," Fourth Edition, Macmillan Publishing Co., Inc., 1977, pp. 77-87, and include polyvalent metal ions described on page 78, polyisocyanates as described in USP 4,281,060 and JP-A 208193/1994, epoxy compounds as described in USP 4,791,042, and vinyl sulfones as described in JP-A 89048/1987.

Support

[0105] In the photothermographic element of the invention, a variety of supports may be used. A choice may be made from well-known supports including polyesters (e.g., polyethylene terephthalate and polynaphthalene terephthalate), polyolefins (e.g., polyethylene and polypropylene), cellulose derivatives (e.g., cellulose diacetate and cellulose triacetate), styrene polymers (e.g., polystyrene and poly-α-methylstyrene), and polycarbonate. Among others, polyesters, especially biaxially oriented polyethylene terephthalate (PET) is preferred as the support from the standpoints of strength and cost. A polyester film is preferably stretched at a draw ratio of about 2 to 8, especially about 3 in both longitudinal and transverse directions. After stretching in both longitudinal and transverse directions, the film may be heat treated at about 80 to about 200°C for about 10 seconds to about 20 minutes.

[0106] The thickness of the support is preferably about 20 to 500 μm, more preferably about 50 to 300 μm.

[0107] If desired, the support is dyed with any of well-known dyestuffs or pigments. The support is preferably dyed to such an extent that the dyed support may have an optical density of about 0.1 to 1.5, more preferably about 0.2 to 1.0 at the absorption wavelength of the dyestuff or pigment used.

[0108] The support used herein may be subject to surface treatment such as UV treatment, corona treatment, glow treatment or flame treatment, if desired. With respect to these surface treatments, reference is made to Tsunoda's report in "Collected Papers on Polymers," Vol. 35, page 229, 1978 and Hatada's report in "Surface Science, Vol. 5, page 408, 1984.

[0109] Optionally the support is provided with a subbing layer. The subbing layer is based on a binder which is preferably a polyester or styrene-butadiene copolymer. Other additives such as matte agents, surfactants, crosslinking agents and dyestuffs are added to the subbing layer, if desired.

[0110] In constructing the photothermographic element according to the invention, the respective layers can be formed by various coating procedures including dip coating, air knife coating, flow coating, and extrusion coating using a hopper of the type described in USP 2,681,294. If desired, two or more layers may be concurrently coated by the methods described in USP 2,761,791 and BP 837,095.

EXAMPLE

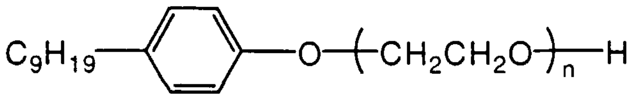
[0111] Examples of the present invention are given below by way of illustration and not by way of limitation.

Example 1

Undercoat coating solution A

[0112] An undercoat coating solution A was prepared by adding 2.5 g of polystyrene microparticulates having a mean particle size of 0.4 μm and 20 ml of a 1 wt% solution of Surfactant A to 200 ml of a 30 wt% water dispersion of a polyester copolymer Pesresin A-515GB (Takamatsu Yushi K.K.). Distilled water was added to a total volume of 1,000 ml.

Surfactant A



n ≒8.5

Undercoat coating solution B

[0113] An undercoat coating solution B was prepared by adding 200 ml of a 30 wt% water dispersion of a styrene-butadiene copolymer (styrene/butadiene/itaconic acid = 47/50/3 in weight ratio) and 0.1 g of polystyrene microparticulates having a mean particle size of 2.5 μm to 680 ml of distilled water. Distilled water was added to a total volume of 1,000 ml.

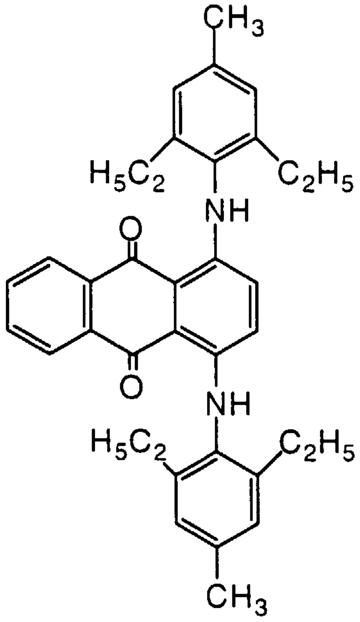
Undercoat coating solution C

[0114] An undercoat coating solution C was prepared by dissolving 10 g of inert gelatin in 500 ml of distilled water and adding thereto 40 g of a 40 wt% water dispersion of tin oxide-antimony oxide composite microparticulates as described in JP-A 20033/1986. Distilled water was added to a total volume of 1,000 ml.

Subbed support

[0115] The support used was a biaxially oriented PET film of 175 μm thick tinted with a Blue Dyestuff, which was subject to corona discharge treatment on one surface (photosensitive layer side) thereof. On the treated surface the support, the undercoat coating solution A was applied by means of a bar coater in a wet coverage of 5 cc/m^2, followed by drying at 180°C for 5 minutes. The undercoat layer had a dry thickness of about 0.3 μm.

Blue Dyestuff



[0116] Next, the support was subject to corona discharge treatment on the back surface thereof. On the treated back surface, the undercoat coating solution B was applied by means of a bar coater in a wet coverage of 5 cc/m^2, followed by drying at 180°C for 5 minutes to form a back undercoat having a dry thickness of about 0.3 μm. Further, the undercoat coating solution C was applied onto the back undercoat by means of a bar coater in a wet coverage of 3 cc/m^2, followed by drying at 180°C for 5 minutes to form a second back undercoat having a dry thickness of about 0.03 μm. The subbed support was completed in this way.

Organic acid silver dispersion

[0117] while a mixture of 7 grams of stearic acid, 4 gram of arachidic acid, 36 grams of behenic acid, and 850 ml of distilled water was vigorously stirred at 90°C, 187 ml of 1N NaOH aqueous solution was added. Reaction was carried out for 120 minutes. After 65 ml of 1N nitric acid was added, the solution was cooled to 50°C. with more vigorous stirring, 125 ml of an aqueous solution containing 21 grams of silver nitrate was added over 100 seconds. The solution was left to stand for 20 minutes. Thereafter, the solids were separated by suction filtration and washed with water until the water filtrate reached a conductivity of 30 μS/cm. To the thus obtained solids, 100 grams of a 10 wt% aqueous solution of polyvinyl alcohol PVA205 (Kurare K.K.) was added. Water was further added to a total weight of 270 grams. This was roughly dispersed in an automated mortar, obtaining a crude organic acid silver dispersion. This crude organic acid silver dispersion was dispersed in a nanomizer (manufactured by Nanomizer K.K.) under an impact pressure of 1,000 kg/cm^2, obtaining an organic acid silver dispersion. The thus obtained organic acid silver dispersion contained needle grains of organic acid silver having a mean minor diameter of 0.04 μm, a mean major diameter of 0.8 μm and a coefficient of variation of 30%.

Reducing agent dispersion

[0118] A slurry was obtained by adding 850 grams of water to 100 grams of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane and 50 grams of hydroxypropyl cellulose and thoroughly mixing them. This slurry was introduced into a vessel together with 840 grams of zirconia beads having an average diameter of 0.5 mm. A dispersing machine (1/4G Sand Grinder Mill by Imex K.K.) was operated for 5 hours for dispersion, obtaining a reducing agent dispersion.

Organic polyhalogenated compound dispersion

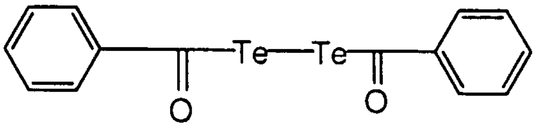
[0119] A slurry was obtained by adding 940 grams of water to 50 grams of tribromomethylphenylsulfone and 10 grams of hydroxypropyl cellulose and thoroughly mixing them. This slurry was introduced into a vessel together with 840 grams of zirconia beads having an average diameter of 0.5 mm. A dispersing machine (1/4G Sand Grinder Mill by Imex K.K.) was operated for 5 hours for dispersion, obtaining a dispersion of the organic polyhalogenated compound.

Silver halide grains

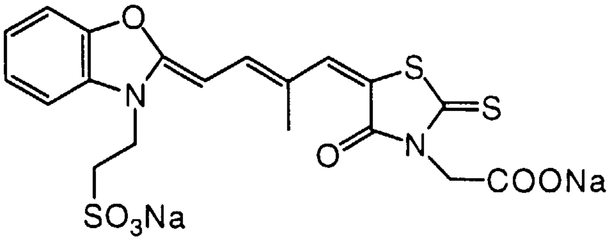
[0120] In 700 ml of water were dissolved 22 grams of phthalated gelatin and 30 mg of potassium bromide. The solution was adjusted to pH 5.0 at a temperature of 35°C. To the solution, 159 ml of an aqueous solution containing 18.6 grams of silver nitrate and 0.9 gram of ammonium nitrate and an aqueous solution containing potassium bromide and potassium iodide in a molar ratio of 92:8 were added over 10 minutes by the controlled double jet method while maintaining the solution at pAg 7.7. Then, 476 ml of an aqueous solution containing 55.4 grams of silver nitrate and 2 grams of ammonium nitrate and an aqueous solution containing 10 μmol/liter of dipotassium hexachloroiridate and 1 mol/liter of potassium bromide were added over 30 minutes by the controlled double jet method while maintaining the solution at pAg 7.7. After 1 gram of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added, the pH of the solution was lowered to cause flocculation and sedimentation for desalting. The solution was adjusted to pH 5.9 and pAg 8.2 by adding 0.1 gram of phenoxyethanol. There were obtained cubic grains of silver iodobromide having an iodide content of 8 mol% in the core and 2 mol% on the average, a mean grain size of 0.05 μm, a coefficient of variation of the projected area of 8%, and a (100) face proportion of 85%.

[0121] The thus obtained silver halide grains were heated at 60°C, to which 85 μmol of sodium thiosulfate, 11 μmol of 2,3,4,5,6-pentafluorophenyldiphenylphosphine selenide, 15 μmol of Tellurium Compound, 3 μmol of chloroauric acid, and 270 μmol of thiocyanic acid were added per mol of silver. The emulsion was ripened for 120 minutes and then quenched to 40°C. Then, 100 μmol of Chromophore and 500 μmol of 2-mercapto-5-methylbenzimidazole were added to the emulsion, which was quenched to 30°C, completing the preparation of a silver halide emulsion.

Tellurium Compound



Chromophore



Emulsion layer coating solution

[0122] An emulsion layer coating solution was prepared by mixing 1,350 grams of the organic acid silver dispersion, 140 cc of a 20 wt% aqueous solution of PVA205, 37 cc of a 10 wt% aqueous solution of phthalazine, 220 grams of the reducing agent dispersion, 61 grams of the organic polyhalogenated compound dispersion, 1,100 grams of a binder (P-1 to P-5 shown below and in Table 1), and 120 grams of the silver halide emulsion, the dispersions being as prepared above.

Binder

[0123]

P-1 -$(St)_{70}$-$(Bu)_{27}$-$(AA)_3$- latex
mean molecular weight 73,000
mean particle size 128 nm

P-2 -$(St)_{68}$-$(Bu)_{29}$-$(IA)_3$- latex
mean molecular weight 32,000
mean particle size 120 nm

P-3 -$(St)_{68}$-$(Bu)_{27}$-$(MAA)_5$- latex
mean molecular weight 119,000
mean particle size 108 nm

P-4 -$(MMA)_{70}$-$(EA)_{25}$-$(AA)_5$-latex
mean molecular weight 42,000
mean particle size 142 nm

P-5 -$(MMA)_{30}$-$(St)_{40}$-$(2EHA)_{25}$-$(MAA)_5$- latex
mean molecular weight 31,000
mean particle size 136 nm

[0124] Abbreviations represent the following monomers.

St: styrene Bu: butadiene
AA: acrylic acid IA: itaconic acid
MAA: methacrylic acid MMA: methyl methacrylate

EA: ethyl acrylate 2EHA: 2-ethylhexyl acrylate

Emulsion surface intermediate layer coating solution

[0125] In 900 cc of water was dissolved 100 grams of modified polyvinyl alcohol MP203 (Kurare K.K.). Further added was 2 cc of a 5 wt% aqueous solution of a sodium salt of di(2-ethylhexyl) sulfosuccinate.

Emulsion surface protective layer coating solution

[0126] A coating solution for the protective layer was prepared by dissolving 145 grams of inert gelatin in 1,110 cc of warm water, and adding thereto 400 grams of 20 wt% poly(ethyl acrylate) latex, 57 cc of 1N sulfuric acid, 10 cc of a 5 wt% aqueous solution of a sodium salt of di(2-ethylhexyl) sulfosuccinate, and 280 cc of a 10 wt% methanol solution of phthalic acid.

Emulsion surface overcoat layer coating solution

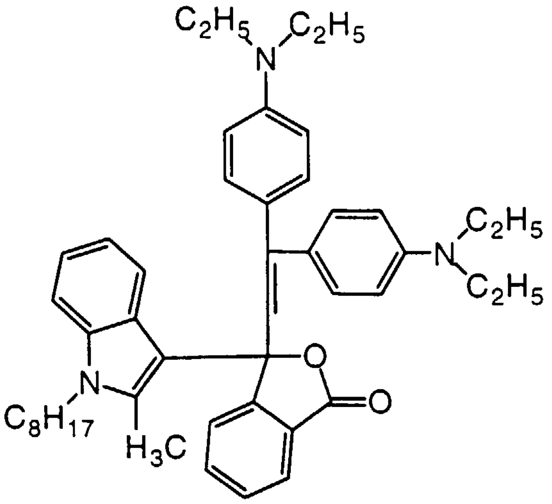
[0127] A coating solution for the overcoat layer was prepared by dissolving 129 grams of inert gelatin in 1,650 cc of warm water, adding thereto 130 grams of a gelatin dispersion containing 12 wt% of microparticulate poly(methyl methacrylate) having a mean particle size of 2.5 μm, 65 cc of 1N sulfuric acid, and 20 cc of a 5 wt% aqueous solution of a sodium salt of di(2-ethylhexyl) sulfosuccinate to form a matted solution, and adding a 2 wt% aqueous solution of chromium (III) potassium sulfate dodecahydrate (as a hardener) to the matted solution at a ratio of 0.3:1.

Back layer coating solution

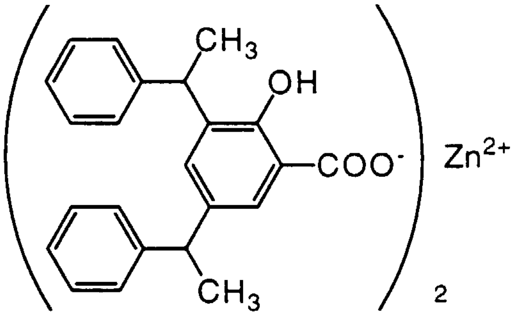
[0128] A base solution was prepared by dispersing 10 grams of a salt of N,N',N'',N'''-tetraethylguanidine and 4-carboxysulfonyl-phenylsulfone in a molar ratio of 1:2 as a solid base in 10 grams of polyvinyl alcohol PVA205 (Kurare K.K.) and 88 grams of water in a dispersing machine (1/16G Sand Grinder Mill by Imex K.K.).

[0129] An organic solvent phase was prepared by mixing and dissolving 2.1 grams of a Basic Dye Precursor, 79 grams of an Acidic Substance, and 10 grams of ethyl acetate. This organic solvent phase was mixed with an aqueous solution phase consisting of 10 grams of polyvinyl alcohol PVA205 (Kurare K.K.) and 80 grams of water, emulsified and dispersed at room temperature, obtaining a dyestuff solution having a mean particle size of 2.5 μm.

Basic Dye Precursor



Acidic Substance



[0130] A back surface coating solution was prepared by mixing 39 grams of the base solution, 26 grams of the dyestuff solution, and 36 grams of a 10 wt% aqueous solution of polyvinyl alcohol PVA205 (Kurare K.K.).

Back surface protective layer coating solution

[0131] A back surface protective layer coating solution was prepared by dissolving 20 grams of gelatin, 0.6 gram of polymethyl methacrylate having a mean particle size of 7 μm, 0.4 gram of sodium dodecylbenzenesulfonate, and 1 gram of X-22-2809 silicone compound (by Shin-Etsu Silicone K.K.) in 480 grams of water.

Thermographic image-forming element

[0132] Onto the back side of the subbed support, the back layer coating solution in a flow rate to provide an optical density of 0.7 at 647 nm and the back surface protective layer coating solution in an amount of 50 g/m^2 were concurrently applied in a multiple manner, using a coater as shown in Figure 11b.1 on page 427 of Stephan F. Kistler and Peter M. Schweizer, LIQUID FILM COATING, CHAPMAN & HALL, 1997. Then onto the surface of the support opposite to the back surface, the emulsion layer coating solution, intermediate layer coating solution, protective layer coating solution and overcoat layer coating solution were concurrently coated in the described order from the substrate side in amounts of 82 cc/m^2, 6.5 cc/m^2, 12.5 cc/m^2, and 12 cc/m^2, respectively. This was passed through a chilled zone at 10°C (dew point $\leq$ 0°C) and dried by blowing air at 30°C and RH 40% at a wind velocity of 20 m/sec.

Photographic properties

[0133] After a sample was aged for 10 days at 25°C, it was exposed at an incident angle of 30° by means of a laser sensitometer equipped with a 647-nm Kr laser (maximum power 500 mW) and developed at 120°C for 15 seconds. The thus obtained image was measured for optical density by means of a densitometer. Reported are Dmin and sensitivity (S) which is the reciprocal of an exposure providing a density higher by 1.0 than Dmin and expressed in a relative value based on a sensitivity of 100 for sample No. 101.

Measurement of moisture content of binder

[0134] A solution or dispersion of the binder used in the photosensitive layer was coated on a glass plate and dried at 50°C for one hour to form a model polymer film of 100 μm thick. The model polymer film was stripped from the glass plate and allowed to stand at 25°C and RH 60% for 3 days before its weight (W1) was measured. The model polymer film was then allowed to stand at 25°C in vacuum for 3 days. Immediately thereafter, the film was placed in a weighing bottle having a known weight (W2). From the weight (W3) of the bottle, the weight of the dry polymer film was calculated ($W0 = W3 - W2$). The equilibrium moisture content (Weq) at 25°C and RH 60% of the polymer was calculated according to the equation: $Weq = (W1 - W0)/W0 \times 100\%$ by weight .

Measurement of surface acid content

[0135] A dispersion of the binder (polymer latex) used in the photosensitive layer was adjusted to a latex concentration of 10% by weight and a volume of 50 ml. By slowly adding 0.1N HCl, the solution was adjusted to pH 2.5. Then a 0.1N NaOH solution was added dropwise to the solution at a rate of 0.05 ml/drop. A conductivity was measured at 1 minute of dropwise addition. From this conductometric titration, a titration curve was drawn as shown in FIG. 1.

[0136] The titration curve includes an initial conductivity decline straight line segment A, a conductivity rise segment after the start of neutralization of carboxyl groups (normally broken into two straight lines B1 and B2), and a conductivity rise straight line segment C after the completion of neutralization. From an intersection P1 between straight lines A and B1 and an intersection P2 between straight lines B2 and C, the distance a between P1 and P2 is determined. The surface acid content is computed according to the following equation:

$$\text{Surface acid content} = [\{45 \times (a/1000) \times 0.1\}/5] \times 100\%$$

wherein 45 is the molecular weight of a carboxyl group, a is the distance between the two inflection points P1 and P2 in FIG. 1, representing the amount of NaOH, 0.1 is the molar concentration of NaOH, and 5 is the solids content of the latex.

[0137] The results are shown in Table 1.

Table 1

Sample No.	Binder in photosensitive layer	moisture content (%)	Surface acid content (%)	Dmin	S
101	P-1	1.0	1.9	0.18	100
102*	Q-1	1.0	0.1	0.25	55
103	P-2	0.9	2.4	0.18	105
104*	Q-2	0.8	0.1	0.26	60
105	P-3	0.8	2.8	0.17	100
106*	Q-3	0.8	0.1	0.25	65
107	P-4	1.1	3.5	0.20	85
108*	Q-4	1.1	0.1	0.28	50
109	P-5	1.2	3.4	0.21	80
110*	Q-5	1.1	0.1	0.28	45
111*	Q-6	1.2	0.3	0.27	50

* comparison

Comparative Example 1

[0138] Photosensitive element samples were prepared as in Example 1 except that binders Q-1 to Q-6 were used in the preparation of the emulsion layer coating solution.

[0139] Note that binders Q-1 to Q-5 correspond to binders P-1 to P-5 in Example 1, respectively. The mean molecular weight is the same while the acid monomer is omitted.

Q-6 -$(MMA)_{31.4}$-$(St)_{41.9}$-$(2EHA)_{26.2}$-$(MAA)_{0.5}$- latex
mean molecular weight 34,000
mean particle size 130 nm

[0140] Abbreviations are the same as above.

[0141] These photosensitive element samples were examined as in Example 1, with the results shown in Table 1.

[0142] It is evident from Table 1 that the photothermographic elements falling within the scope of the invention have low fog and high sensitivity.

[0143] There has been described a photothermographic element wherein a photothermographic layer has been formed by applying a coating solution in which a binder containing at least 50% by weight of a polymer latex characterized by a surface acid content is dispersed in a solvent containing at least 30% by weight of water, followed by drying. The photothermographic element can be prepared from an aqueous coating solution which is desirable from the ecological and safety standpoints while it has improved photographic properties.

[0144] Japanese Patent Application No. 311459/1997 is incorporated herein by reference.

[0145] Reasonable modifications and variations are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined by the claims.

Claims

1. A photothermographic element comprising at least one photothermographic layer on at least one surface of a support, said photothermographic layer containing a photosensitive silver halide and a binder, said element further comprising an organic silver salt and a reducing agent therefor,
   wherein said photothermographic layer has been formed by applying a coating solution in which the binder containing at least 50% by weight of the binder of a polymer latex having a surface acid content of 0.5% to 8% by weight is dispersed in a solvent containing at least 30% by weight of the solvent of water, followed by drying.

2. The photothermographic element of claim 1 wherein the polymer latex has an equilibrium moisture content of 0.01% to 2% by weight at 25°C and RH 60%.

3. The photothermographic element of claim 1 or 2 wherein the organic silver salt is a silver salt of an organic carboxylic acid.

4. The photothermographic element of any one of claims 1 to 3 wherein the polymer latex has a surface acid content of 0.5% to 6% by weight.

5. The photothermographic element of claim 4 wherein the polymer latex has a surface acid content of 1% to 4% by weight.

6. The photothermographic element of any one of claims 1 to 5 wherein the binder contains 70% to 100% by weight of the polymer latex.

7. The photothermographic element of any one of claims 1 to 6 wherein the polymer of the polymer latex is selected from the group consisting of acrylic resins, vinyl acetate resins, polyester resins, polyurethane resins, rubbery resins, vinyl chloride resins, vinylidene chloride resins, polyolefin resins, and copolymers thereof.

8. The photothermographic element of any one of claims 1 to 7 wherein the polymer of the polymer latex is selected from the group consisting of methyl methacrylate/ethyl acrylate/(meth)acrylic acid copolymers, methyl methacrylate/2-ethylhexyl acrylate/styrene/(meth)acrylic acid copolymers, styrene/butadiene/(meth)acrylic acid copolymers, styrene/butadiene/itaconic acid copolymers, styrene/butadiene/divinyl benzene/(meth)acrylic acid copolymers, methyl methacrylate/vinyl chloride/(meth)acrylic acid copolymers, and vinylidene chloride/ethyl acr-

ylate/acrylonitrile/(meth)acrylic acid copolymers.

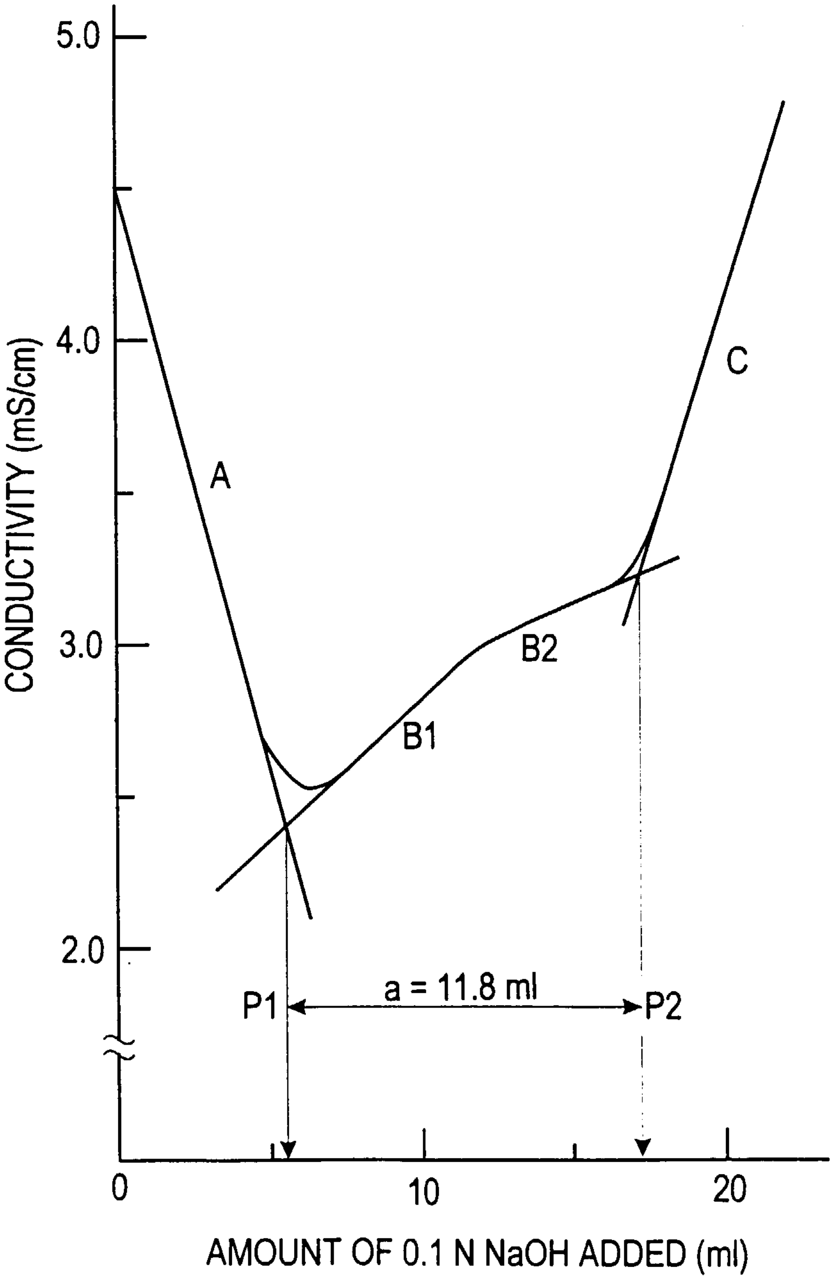
9. The photothermographic element of any one of claims 1 to 8 wherein a styrene-butadiene polymer latex is contained in the photothermographic layer in an amount of 70% to 100% by weight of the entire binder.

10. The photothermographic element of any one of claims 1 to 9 wherein the polymer latex is given a surface acid content of 0.5% to 8% by weight by copolymerizing the polymer latex with a monomer having a carboxyl group, thereby introducing 0.5 to 20% by weight of carboxyl groups into the polymer.

11. The photothermographic element of claim 10 wherein the monomer having a carboxyl group is acrylic acid, methacrylic acid, itaconic acid or maleic acid

12. The photothermographic element of claim 10 wherein the copolymerization introduces 0.8 to 15% by weight of carboxyl groups into the polymer.

FIG. 1


5.0
4.0
3.0
2.0
CONDUCTIVITY (mS/cm)
A
B1
B2
C
P1
P2
a = 11.8 ml
0
10
20
AMOUNT OF 0.1 N NaOH ADDED (ml)