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(54) Photothermographic elements adapted for laser exposure

(57) In a photothermographic element adapted for laser exposure, a photosensitive layer and a contiguous non-photosensitive layer have a difference in refractive index from 0.1 to 0.7, and these layers are concurrently coated and dried. The element is not only improved in brittleness, but prevents interference fringes from appearing when the element is subject to laser exposure for forming images.

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Description

[0001] This invention relates to photothermographic elements adapted for laser exposure.

BACKGROUND OF THE INVENTION

[0002] Typical prior art means for producing outputs of the image information of MRI and X-ray CT is to scan a photographic photosensitive material with a laser beam for exposure. In these years, semiconductor laser diodes having high output and stability are on widespread use as a light source, which give a certain allowance to the sensitivity of photographic photosensitive material as an output medium. From the standpoints of rapid processing and environmental protection, on the other hand, it is desired to reduce the silver coverage of photographic photosensitive material. To this end, an attempt is made to reduce the size of emulsion grains in order to maintain the desired maximum optical density (Dmax). Further, the photosensitive material used in a thermographic process or a system free of the fixing treatment to dissolve away silver halide is required to be free of haze.

[0003] In these photosensitive materials containing finer emulsion grains or having high transparency, however, interference fringes appear as a result of reflection of laser light within the material. The interference fringes are described in JP-B 10735/1994 as "non-contact interference fringes."

[0004] Referring to FIGS. 1 to 3, one typical laser scanning exposure procedure is illustrated. A laser light source 1 emits a laser beam 2 which is modulated by a modulator 3 in accordance with an image signal which is delivered from an image signal output unit 5 through a modulator drive circuit 4. The beam 2 then reaches a rotating polygon mirror 8 through a beam expander 6 and a cylindrical lens 7 where it is reflected toward a cylindrical mirror 10 through a fθ lens 9. The cylindrical mirror 10 reflects the laser beam 2 toward a photographic photosensitive material sheet 11. In this way, the sheet 11 is scanned with laser light in both a main scan direction depicted by arrow A and a sub-scan direction depicted by arrow B.

[0005] In the main scan direction A, the angle between the sheet 11 surface and the laser beam 2 varies with scanning operation as shown in FIG. 2, and this angle is generally designed to be perpendicular at the center of scanning operation. In the sub-scan direction B, the angle θ between the sheet 11 surface and the laser beam 2 is generally set off the perpendicular as shown in FIG. 3 in order to prevent the laser light reflected by the sheet 11 from being fed back to the laser apparatus. This offset angle from the perpendicular is only 1 or 2 degrees. Consequently, a region where the angle of an incident laser beam to the surface of the photosensitive material to be exposed is substantially perpendicular always exists in the conventional laser scanning operation. In such an exposure region where the angle of an incident laser beam is substantially perpendicular, the above-mentioned super-position of reflected laser beam can occur, failing to avoid the appearance of interference fringes.

SUMMARY OF THE INVENTION

[0006] An object of the present invention is to provide a photothermographic element which forms an image through laser exposure while preventing the appearance of interference fringes and which is satisfactory in brittleness.

[0007] This and other objects are achieved by the present invention which provides a photothermographic element adapted for laser exposure, comprising on a support at least one photosensitive layer containing a photosensitive silver halide and a binder and at least one non-photosensitive layer containing a binder. The difference in index of refraction between the photosensitive layer and the non-photosensitive layer disposed contiguous thereto is 0.10 to 0.70. The photosensitive layer and the non-photosensitive layer have been formed by concurrent coating in a multiple manner and drying. Preferably, the photosensitive layer and the non-photosensitive layer disposed contiguous thereto have been formed from aqueous coating solutions.

[0008] In one preferred embodiment, the photosensitive silver halide has a mean grain size from 0.01 μm to less than 0.1 μm and is contained in a silver coverage of 0.01 to 0.3 g/m^2. Typically, the photosensitive layer is a photothermographic layer further containing an organic silver salt and a reducing agent for silver ion. Preferably, the binder in the photosensitive layer comprises a polymer latex while the binder in the non-photosensitive layer comprises a water-soluble polymer.

[0009] In a further preferred embodiment, an uppermost layer on the side where the photosensitive layer is situated contains a matte agent. More preferably, the matte agent has a mean particle size of 1 to 10 μm and is contained in the uppermost layer at a population of 200 to 10,000 particles/mm^2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 schematically illustrates a typical laser scanning exposure system.
FIG. 2 schematically illustrates the angle between a laser beam and a surface of photosensitive material to be exposed as viewed in one direction.
FIG. 3 schematically illustrates the exposure angle as viewed in another direction.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The photothermographic element of the present invention includes on a support at least one photosensitive layer containing a photosensitive silver halide and a binder and at least one non-photosensitive layer containing a binder. The photosensitive layer may be either a single layer or consist of two or more layers, preferably up to four layers. The non-photosensitive layer may be either a single layer or consist of two or more layers, preferably up to four layers.

[0012] According to the invention, the difference in index of refraction between at least one photosensitive layer and a non-photosensitive layer disposed contiguous thereto is from 0.10 to 0.70, preferably from 0.10 to 0.50, and more preferably from 0.10 to 0.40.

[0013] As long as the difference in index of refraction is within the above-defined range, either the photosensitive layer or the non-photosensitive layer may have a higher index of refraction. It is often preferred that the photosensitive layer has a higher index of refraction. As long as the difference in index of refraction is within the above-defined range, the indexes of refraction of the respective layers may have any values. It is often preferred that the photosensitive layer has an index of refraction of 1.50 to 2.60, more preferably 1.55 to 2.30, and most preferably 1.60 to 2.00, while the non-photosensitive layer has an index of refraction of 1.40 to 1.90, more preferably 1.45 to 1.80, and most preferably 1.50 to 1.65.

[0014] The index of refraction of a layer can be adjusted by dispersing in a binder a substance having a high index of refraction such as metals, metal salts, silver salts of organic acids, and metal oxides. However, adding a large amount of such a high index of refraction substance gives a higher pigment/binder ratio, detracting from the strength of a film (for example, rendering a film brittle). It is thus desired to adjust the pigment/binder ratio to about 1/1 or less. The index of refraction may be measured by well-known methods. It is recommended to measure an index of refraction with respect to the D line of a sodium lamp using an Abbe refractometer. For example, a film of the same composition as a layer to be measured for an index of refraction is formed on a glass substrate to a thickness of about 100 μm, and the film is peeled from the substrate and subject to measurement.

[0015] The photothermographic element of the invention may contain optional additives such as toners, coating aids and other auxiliary agents. The photosensitive element of the invention may be constructed as comprising a first photosensitive layer (which is generally a layer disposed adjacent to the support) containing an organic silver salt and silver halide and a second layer containing some other components or both the layers containing some other components. Also envisioned herein is a two-layer construction consisting of a single photosensitive layer containing all the components and a non-photosensitive protective topcoat. The protective layer may be constructed from a plurality of layers. It is acceptable to further include a non-photosensitive intermediate layer between the protective layer and the photosensitive layer. In the case of multi-color sensitive photothermographic material, a combination of two layers as mentioned just above may be employed for each color. Also a single layer may contain all necessary components as described in USP 4,708,928. In the case of multi-dye, multi-color sensitive photothermographic material, photosensitive layers are distinctly supported by providing a functional or non-functional barrier layer therebetween as described in USP 4,460,681. The present invention only requires that one photosensitive layer and one non-photosensitive layer disposed contiguous thereto have a difference in index of refraction within the above-specified range although it is preferred that all the photosensitive layers have a difference in index of refraction within the above-specified range from the respective non-photosensitive layers disposed contiguous thereto.

[0016] According to the invention, the photosensitive layer and the non-photosensitive layer are formed by concurrent coating and drying. Both the layers are preferably formed by coating aqueous coating solutions. Methods for forming a layer by coating an aqueous coating solution include a method of using a water-soluble polymer as the binder and a method of dispersing a hydrophobic polymer in water or a mixture of water and a water-miscible solvent (to form a polymer latex). In the practice of the invention, the latter method is preferred for the photosensitive layer, and the former method is preferred for the non-photosensitive layer.

[0017] The inventive photosensitive layer is preferably 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, preferably at least 50% by weight, more preferably 70 to 100% by weight of the solvent or dispersing medium of the coating solution. 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.

[0018] In the inventive photosensitive layer, a polymer latex to be described below preferably constitutes more than 50% by weight, more preferably 70 to 100% by weight of the entire binder. This photosensitive layer is sometimes referred to as "inventive photosensitive layer" and the polymer latex used as the binder therefor is referred to as "inventive polymer latex," hereinafter. The term "polymer latex" used herein 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. 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 dispersion may have either a wide particle size distribution or a monodisperse particle size distribution.

[0019] The inventive 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.

[0020] 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.

[0021] Polymers used in the inventive polymer latex include acrylic resins, vinyl acetate resins, polyester resins, polyurethane resins, rubbery resins, vinyl chloride resins, vinylidene chloride resins, polyolefin resins, and copolymers thereof. 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 100,000. 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.

[0022] The polymer of the inventive polymer latex should preferably have an equilibrium moisture content at 25°C and RH 60% of 0.01 to 2% by weight, more preferably 0.02 to 1% 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.

[0023] Illustrative examples of the polymer latex which can be used as the binder in the image-forming layer of the photothermographic element of the invention include latexes of methyl methacrylate/ethyl acrylate/methacrylic acid copolymers, latexes of methyl methacrylate/2-ethylhexyl acrylate/styrene/acrylic acid copolymers, latexes of styrene/butadiene/acrylic acid copolymers, latexes of styrene/butadiene/divinyl benzene/methacrylic acid copolymers, latexes of methyl methacrylate/vinyl chloride/acrylic acid copolymers, and latexes of vinylidene chloride/ethyl acrylate/acrylonitrile/methacrylic acid copolymers. These polymers or polymer latexes are commercially available. Exemplary acrylic resins are Sebian A-4635, 46583 and 4601 (Daicell Chemical Industry K.K.) and Nipol LX811, 814, 820, 821 and 857 (Nippon Zeon K.K.). Exemplary polyester resins are FINETEX ES650, 611, 675, and 850 (Dai-Nippon Ink & Chemicals K.K.) and WD-size and WMS (Eastman Chemical Products, Inc.). Exemplary polyurethane resins are HYDRAN AP10, 20, 30 and 40 (Dai-Nippon Ink & Chemicals K. K.). Exemplary rubbery resins are LACSTAR 7310K, 3307B, 4700H and 7132C (Dai-Nippon Ink & Chemicals K.K.) and Nipol LX416, 410, 438C and 2507 (Nippon Zeon K.K.). Exemplary vinyl chloride resins are G351 and G576 (Nippon Zeon K.K.). Exemplary vinylidene chloride resins are L502 and L513 (Asahi Chemicals K.K.). Exemplary olefin resins are Chemipearl S120 and SA100 (Mitsui Petro-Chemical K.K.). These polymers may be used alone or in admixture of two or more.

[0024] 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.

[0025] 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. To the photosensitive layer, crosslinking agents for crosslinking, surfactants for ease of application, and other addenda may be added.

[0026] The coating solution for the photosensitive layer according to the invention is preferably a thixotropic fluid. Thixotropy is a structural property that a gel reduces its viscosity as the share rate increases. In measuring the viscosity of a liquid, any meter may be used. A fluid spectrometer RFS commercially available from Rheometrics Far East K.K. is preferred. Viscosity measurement is made at 25°C.

[0027] The photosensitive layer coating solution according to the invention should preferably have a viscosity of 400 mPa • s to 100,000 mPa • s at a shear rate of 0.1 s^{-1}, more preferably 500 to 20,000 mPa • s at a shear rate of 0.1 s^{-1}. The solution should also preferably have a viscosity of 1 mPa • s to 200 mPa • s at a shear rate of 1,000 s^{-1}, more preferably 5 to 80 mPa • s at a shear rate of 1,000 s^{-1};

[0028] A variety of systems are known to exert thixotropy. Reference should be made to, for example, Kobunshi Kankokai Ed., "Rheology," and Muroi and Morino, "Polymer Latex," (published by Kobunshi Kankokai). In order for a fluid to exert thixotropy, the fluid should contain a multiplicity of fine solid particles. Thixotropy can be enhanced by containing thickening linear polymers, using fine solid particles having anisotropy and a high aspect ratio, or using alkaline thickening agents or surfactants.

Silver halide

[0029] The amount of photosensitive silver halide used is preferably 0.01 to 0.3 g/m^2, more preferably 0.02 to 0.2 g/m^2. No particular limits are imposed on the method of mixing a separately prepared photosensitive silver halide in a image-forming layer coating solution and the mixing conditions insofar as the benefits of the invention are achievable.

[0030] A method for forming the photosensitive silver halide 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 preparing an organic silver salt and adding a halogen-containing compound to the 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.

[0031] The photosensitive silver halide should preferably have a smaller mean grain size for the purpose of minimizing white turbidity after image formation. Specifically, the mean grain size is preferably from 0.01 μm to less than 0.1 μm, more preferably from 0.01 μm to 0.08 μm, further preferably from 0.01 μm to 0.06 μm, and most preferably from 0.03 μm to 0.06 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.

[0032] 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 photosensitive 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.

[0033] 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.

[0034] 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. The metal complex is preferably contained in an amount of $1x10^{-9}$ to $1x10^{-2}$ mol, more preferably $1x10^{-8}$ to $1x10^{-3}$ mol per mol of silver. Illustrative metal complex structures are those described in JP-A 225449/1995. The cobalt and iron compounds are preferably hexacyano metal complexes while illustrative, non-limiting examples include ferricyanate, ferrocyanate, 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 to form a uniform phase or at a high concentration in either the core or the shell.

[0035] 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.

[0036] 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 heterocycles, 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, borane 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.

[0037] In one preferred embodiment of the invention, the photosensitive layer contains an organic silver salt and a reducing agent for silver ion.

Organic silver salt

[0038] 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 of silver.

[0039] The organic silver salt which can be 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, more preferably silver salts of organic carboxylic acids, typically silver salts of 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. A silver-providing substance is preferably used in an amount of about 5 to 70% by weight of the photosensitive 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.

[0040] 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-thione 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 methylbenzotriazole, 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.

[0041] 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 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 auto-correlation function of the fluctuation of scattering light relative to a time change, and obtaining the grain size (volume weighed mean diameter) therefrom.

[0042] 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.

[0043] In the practice of the invention, the organic silver salt is prepared into a solid microparticulate dispersion using a dispersant, in order to provide fine particles of small size and free of flocculation. A solid micro-particulate 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, micro-fluidizers, nanomizers, and Gaulin homogenizers. Preferred are micro-fluidizers, nanomizers, and Gaulin homogenizers.

[0044] 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 methylcellulose, as well as naturally occurring high molecular weight compounds such as gelatin.

[0045] 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.

[0046] 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.

[0047] 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.

Reducing agent

[0048] 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.

[0049] 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-phenoxyphenylamidoxime; 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-methylphenylhydrazine; 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; αcyanophenyl 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 anhydrodihydropiperidone-hexosereductone; 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-methylphenyl)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.

[0050] 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, micro-fluidizers, nanomizers, and Gaulin homogenizers. Dispersing aids may be used for facilitating dispersion.

Sensitizing dye

[0051] Preferably, the photosensitive silver halide used herein is spectrally sensitized with a sensitizing dye. Spectral sensitization in the red to infrared region is especially preferred.

[0052] There may be used any of sensitizing dyes which can spectrally sensitize silver halide grains in a 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.

[0053] 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.

[0054] 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.

[0055] 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, 59381/1994, 146537/1995, Publication of International Patent Application No. 50111/1993, BP 1,467,638, and USP 5,281,515.

[0056] 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.

[0057] 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.

[0058] 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.

[0059] 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.

[0060] 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.

[0061] 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.

Toner

[0062] 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.

[0063] For photothermographic imaging 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-dimercapto-pyrimidine, 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-tribromomethyl-sulfonyl-benzothiazole; 3-ethyl-5-((3-ethyl-2-benzothiazolinylidene)-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.

[0064] 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

[0065] 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.

[0066] 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.

[0067] 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.

[0068] 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 nmol to 1 mmol, more preferably 10 nmol to 100 μmol per mol of silver coated.

[0069] 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 photosensitive element, preferably to a layer on the same side as the photosensitive layer serving as the image forming 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 μmol to 2 mol, more preferably 1 mmol to 0.5 mol per mol of silver.

[0070] In the 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.

[0071] 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.

[0072] 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.

[0073] In the photosensitive 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.

Contrast enhancer

[0074] In the photothermographic element 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.

[0075] A contrast enhancement accelerator may be used along with the contrast enhancer for the purpose of forming ultrahigh contrast images. Exemplary are the amine compounds described in USP 5,545,505, specifically AM-1 to AM-5; hydroxamic acid type compounds described in USP 5,545,507, specifically HA-1 to HA-11, acrylonitriles described in USP 5,545,507, specifically CN-1 to CN-13, hydrazine compounds described in USP 5,558,983, specifically CA-1 to CA-6, 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.

[0076] With respect to the synthesis method, addition method and addition amount of these contrast enhancers and contrast enhancement accelerators, reference should be made to the above-referred patents.

Protective layer

[0077] A surface protective layer may be provided in the imaging element according to the present invention for the purpose of preventing sticking of an image forming layer. The protective layer is situated remote from the support with respect to the image forming layer and may consist of two or more layers.

[0078] Of the protective layers, at least one layer should preferably contain gelatin in an amount of at least 50% by weight, more preferably at least 70% by weight of the binder, and especially, the outermost layer should preferably contain gelatin in an amount of at least 50% by weight, more preferably at least 70% by weight of the binder.

[0079] 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 ease of application, and other addenda are optionally added to the surface protective layer.

[0080] 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.

[0081] 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.

[0082] 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), "Liquid Mixing Technology," Nikkan Kogyo Shinbun, 1989, Chap. 8.

[0083] In the image forming 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.

[0084] In the image forming layer or emulsion layer according to the invention, 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.

[0085] In the 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 invention. 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 (e.g., 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] In the practice of the invention, a matte agent may be added to the one-side photosensitive element for improving transportation efficiency. Preferably the outermost layer is matted for effectively preventing occurrence of interference fringes. 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 agent particles having a particle size of 1 μm to 10 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 photosensitive material 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.

[0090] 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.

[0091] In the element 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 on the photosensitive layer side because the occurrence of interference fringes is restrained. Also preferably, the matte agent is contained in a layer functioning as the so-called protective layer. The amount of the matte agent added is preferably 200 to 10,000 particles/mm^2, more preferably 300 to 8,000 particles/mm^2.

[0092] In the practice of the invention, the binder used in the non-photosensitive intermediate layer, non-photosensitive protective layer and 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), poly(methyl 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.

[0093] The non-photosensitive intermediate layer or non-photosensitive protective layer which is disposed contiguous to the photosensitive layer preferably contains 50%, more preferably 70 to 100% by weight of the binder of a water-soluble polymer. For the intermediate layer, non-protein water-soluble polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and water-soluble polyvinyl butyral are preferable. For the protective layer, water-soluble polymers, especially gelatin, are preferable.

[0094] The back layer preferably exhibits a maximum absorbance of 0.3 to 2, more preferably 0.5 to 2 in the desired 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.

[0095] A backside resistive heating layer as described in USP 4,460,681 and 4,374,921 may be used in a photothermographic imaging system according to the present invention.

[0096] In the practice of the invention, a hardener may be used in various layers such as the photosensitive layer, protective layer and back 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.

[0097] A surfactant may be used in various layers for the purposes of improving coating and electric charging properties. The surfactants used herein may be nonionic, anionic, cationic and fluorinated ones. Examples include sodium dodecylbenzene sulfonate, sodium p-tert-octylphenoxyethoxyethylsulfonate, sodium di(2-ethyl)hexylsulfosuccinate, sodium lauryl sulfate, saponin, nonylphenoxypolyethoxyethanol, fluorinated polymer surfactants as described in JP-A 170950/1987 and USP 5,380,644, fluorinated surfactants as described in JP-A 244945/1985 and 188135/1988, polysiloxane surfactants as described in USP 3,885,965, and polyalkylene oxide and anionic surfactants as described in JP-A 301140/1994.

[0098] Examples of the solvent used herein are described in "New Solvent Pocket Book," Ohm K.K., 1994, though not limited thereto. The solvent used herein should preferably have a boiling point of 40 to 180°C. Exemplary solvents include hexane, cyclohexane, toluene, methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, ethyl acetate, 1,1,1-trichloroethane, tetrahydrofuran, triethylamine, thiophene, trifluoroethanol, perfluoropentane, xylene, n-butanol, phenol, methyl isobutyl ketone, cyclohexanone, butyl acetate, diethyl carbonate, chlorobenzene, dibutyl ether, anisole, ethylene glycol diethyl ether, N,N-dimethylformamide, morpholine, propanesultone, perfluorotributylamine, and water.

Support

[0099] According to the invention, the thermographic photographic emulsion may be coated on a variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, polyethylene naphthalate film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or resinous materials, as well as glass, paper, metals, etc. Often used are flexible substrates, typically paper supports, specifically baryta paper and paper supports coated with partially acetylated α-olefin polymers, especially polymers of α-olefins having 2 to 10 carbon atoms such as polyethylene, polypropylene, and ethylene-butene copolymers. The supports are either transparent or opaque, preferably transparent.

[0100] The photosensitive element of the invention may have an antistatic or electroconductive layer, for example, a layer containing soluble salts (e.g., chlorides and nitrates), an evaporated metal layer, or a layer containing ionic polymers as described in USP 2,861,056 and 3,206,312 or insoluble inorganic salts as described in USP 3,428,451.

[0101] A method for producing color images using the photothermographic element of the invention is as described in JP-A 13295/1995, page 10, left column, line 43 to page 11, left column, line 40. Stabilizers for color dye images are exemplified in BP 1,326,889, USP 3,432,300, 3,698,909, 3,574,627, 3,573,050, 3,764,337, and 4,042,394.

[0102] In preparing the photothermographic element of the invention, the photosensitive layer and the non-photosensitive layer contiguous thereto are concurrently applied in an overlapping manner and dried. Various coating procedures may be used. Exemplary procedures include extrusion coating, slide coating, curtain coating, dip coating, knife coating, flow coating, and extrusion coating using a hopper of the type described in USP 2,681,294. The coating techniques recommended in the invention are extrusion coating and slide coating as described in Stephan F. Kistler and Peter M. Schweizer, LIQUID FILM COATING, CHAPMA & HALL, 1997, pp. 399-536, and especially slide coating. Exemplary slider coaters used in slide coating are shown in Figure 11b.1 on page 427. Also useful are the methods described on pages 399-536 and the methods described in USP 2,761,791 and BP 837,095.

[0103] In the photothermographic element of the invention, there may be contained additional layers, for example, a dye accepting layer for accepting a mobile dye image, an opacifying layer when reflection printing is desired, a protective topcoat layer, and a primer layer well known in the photothermographic art. The photosensitive material of the invention is preferably such that only a single sheet of the photosensitive material can form an image. That is, it is preferred that a functional layer necessary to form an image such as an image receiving layer does not constitute a separate member.

[0104] The photosensitive element of the invention may be developed by any desired method although it is generally developed by heating after imagewise exposure. The preferred developing temperature is about 80 to 250°C, more preferably 100 to 140°C. The preferred developing time is about 1 to 180 seconds, more preferably about 10 to 90 seconds.

[0105] The preferred light source for exposure is a laser, for example, a gas laser, YAG laser, dye laser or semiconductor laser. A semiconductor laser combined with a second harmonic generating device is also useful.

[0106] Exposure may be carried out in combination with a technique for preventing generation of interference fringes. Known techniques for preventing generation of interference fringes are a technique of obliquely directing laser light to a photosensitive material as disclosed in JP-A 113548/1993 and the utilization of a multi-mode laser as disclosed in WO 95/31754. These techniques are preferably used herein.

[0107] Upon exposure of the photosensitive element of the invention, exposure is preferably made by overlapping laser light so that no scanning lines are visible, as disclosed in SPIE, Vol. 169, Laser Printing 116-128 (1979), JP-A 51043/1992, and WO 95/31754.

EXAMPLE

[0108] Examples of the present invention are given below by way of illustration and not by way of limitation.

Example 1

Organic acid silver dispersion

[0109] 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 93°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 by 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 0.9 μm and a coefficient of variation of 35%.

Reducing agent dispersion

[0110] 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

[0111] 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

[0112] 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%.

[0113] 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.

Emulsion layer coating solution

[0114] An emulsion layer coating solution was prepared by mixing 1,500 grams of the organic acid silver dispersion, 130 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, 1,000 grams of LACSTAR 3307B SBR latex (Dai-Nippon Ink & Chemicals K.K.), and 120 grams of the silver halide emulsion, the dispersions being as prepared above. The amount of silver halide coated was to give a silver coverage of 0.1 g/m^2.

Emulsion surface intermediate layer coating solution

[0115] 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. Further, the organic acid silver dispersion was added so as to give an index of refraction as reported in Table 1.

Emulsion surface protective layer-1 coating solution

[0116] 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 protective layer-2 coating solution

[0117] A coating solution for the protective layer was continuously prepared by dissolving 129 grams of inert gelatin in 1,650 cc of warm water, adding thereto 100 grams of a gelatin dispersion containing 12 wt% of micro-particulate 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 flow rate ratio of 0.3:1.

Back layer coating solution

[0118] 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.).

[0119] An organic solvent phase was prepared by mixing and dissolving 2.1 grams of a Basic Dye Precursor, 7.9 grams of an Acidic Substance, 0.1 gram of a Dyestuff, 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.

[0120] 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

[0121] 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.

Undercoating solution A

[0122] An undercoating solution A was prepared by adding 50 grams of microparticulate polystyrene having a mean particle size of 0.2 μm and 20 ml of 1 wt% Surfactant A to 200 ml of a 30% polyester copolymer water dispersion Pesresin A-515GB (Takamatsu Yushi K.K.) and adding distilled water thereto to a total volume of 1,000 ml.

Undercoating solution B

[0123] An undercoating solution B was prepared by adding 200 ml of a 30% styrene-butadiene copolymer water dispersion (styrene/butadiene/itaconic acid = 47/50/3 in weight ratio) and 0.1 gram of microparticulate polystyrene having a mean particle size of 2.5 μm to 680 ml of distilled water and adding distilled water thereto to a total volume of 1,000 ml.

Undercoating solution C

[0124] An undercoating solution C was prepared by dissolving 10 grams of inert gelatin in 500 ml of distilled water, adding thereto 40 grams of a 40 wt% water dispersion of composite tin oxide-antimony oxide microparticulates as described in JP-A 20033/1986 and adding distilled water thereto to a total volume of 1,000 ml.

Undercoated support

[0125] One surface (photosensitive side) of a biaxially oriented polyethylene terephthalate support of 175 μm thick tinted with a Blue Dyestuff was subjected to corona discharge treatment. The undercoating solution A was applied to the treated surface by means of a bar coater to a wet coverage of 5 cc/m^2, followed by drying at 180°C for 5 minutes. The coating had a dry thickness of about 0.3 μm.

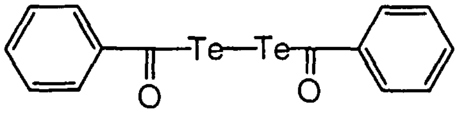
[0126] The rear or back surface of the support was subjected to corona discharge treatment. The undercoating solution B was applied to the back surface by means of a bar coater to a wet coverage of 5 cc/m^2, followed by drying at 180°C for 5 minutes to give a dry thickness of about 0.3 μm. The undercoating solution C was applied onto the undercoat B by means of a bar coater to a wet coverage of 3 cc/m^2, followed by drying at 180°C for 5 minutes to give a dry thickness of about 0.03 μm.

Thermographic image-forming element

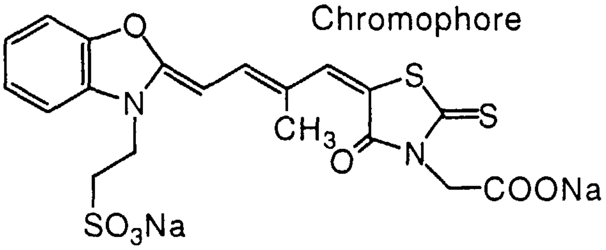
[0127] Onto the back side of the undercoated support, the back layer coating solution in an amount to provide an optical density of 0.7 at 647 nm and the back surface protective layer coating solution in an amount of 50 g/m^2 were concurrently applied in an overlapping manner, using a coater as shown in Figure 11b.1 on page 427 of Stephan F. Kistler and Peter M. Schweizer, LIQUID FILM COATING, CHAPMA & 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-1 coating solution and protective layer-2 coating solution were concurrently or sequentially 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 ≤ 0°C) and dried by blowing air at 30°C and EH 40% at a wind velocity of 20 m/sec. In the column of coating mode in Table 1, concurrent coating means that the four layers on the emulsion side were concurrently coated in an overlapping manner, and sequential coating means that the emulsion layer was first coated and dried before the remaining three layers were concurrently coated and dried. The coating amount of protective layer-2 coating solution corresponded to a silver coverage of 2.1 g/m^2 and polymethyl methacrylate particles were contained in that layer at a population of 7,700 particles/mm^2.

[0128] Some of the chemical agents used in the preparation of the element are shown below.

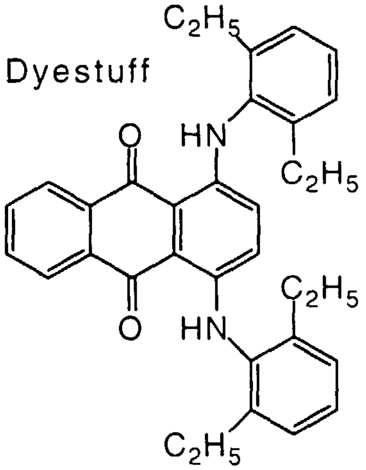
Tellurium Compound



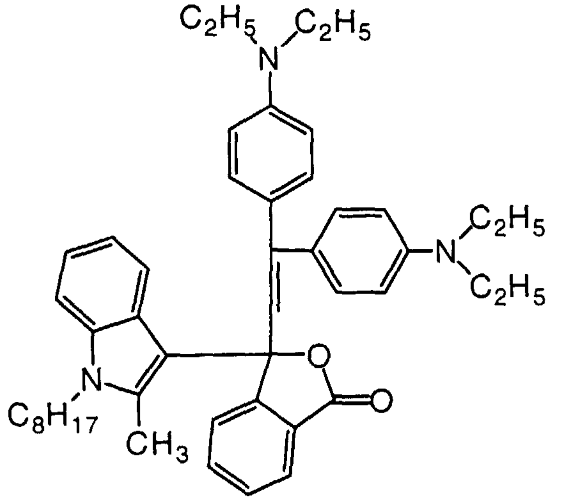
Chromophore



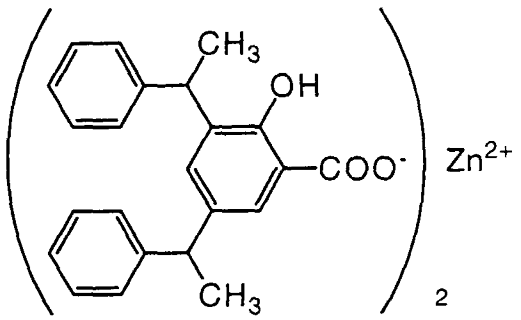
Dyestuff



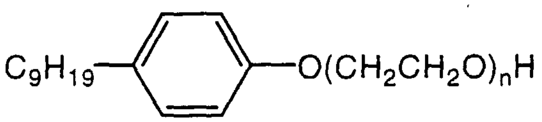
Basic Dye Precursor



Acidic Substance

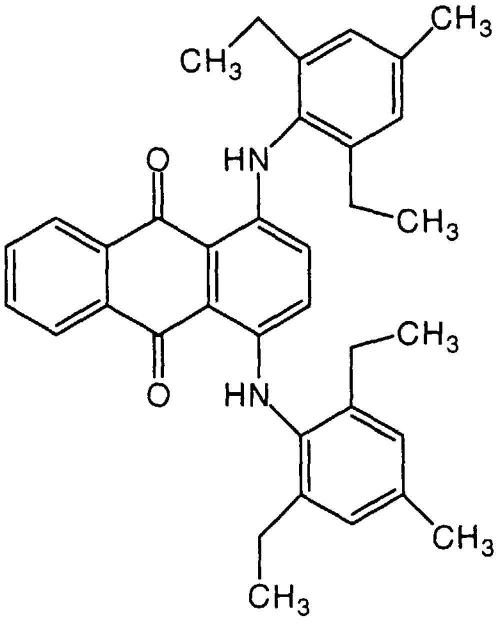


Surfactant A



n≒8.5

Blue Dyestuff



<u>Measurement of index of refraction</u>

[0129] A solution or dispersion of a binder was applied to a glass plate and dried at 50°C for one hour, forming a polymer film of about 100 µm thick. The film was peeled from the glass plate. The film was measured for an index of refraction with respect to the D line of a sodium lamp using an Abbe refractometer Type IT (Atago K.K.).

Examination of interference fringes

[0130] Using a laser diode of 660 nm (maximum output 30 mW), a photographic sample was exposed to light at an angle θ of 90° in FIG. 2. It was developed by heating at 120°C for 15 seconds so as to finish to an image density of 1.0. It was visually evaluated for wood grain-like interference fringes. The criterion for evaluating interference fringes is as follows.

○: no interference fringes
△: some interference fringes
X: unacceptable interference fringes

Examination of folding brittleness

[0131] The photosensitive element prepared above was cut into a strip of 3.5 cm x 25 cm in size, which was conditioned for more than 3 hours at 25°C and RH 10%. The strip was set in a brittleness tester with a wedge set at an angle of 5° by longitudinally extending it through the tester with its emulsion layer-coated side faced upward and securing one end of the strip by a clip. The other end was manually pulled through the slit in the tester. The strip was set in the tester such that as the strip was pulled, the strip was increased in curvature and finally folded. The position at which cracks generated at the surface of the strip was ascertained and the distance of the cracked position from the clipped position was read. Shorter distances are desirable. When necessary for further evaluation, the crazed portion was examined for adhesion by attaching an adhesive tape to the crazed portion and peeling it therefrom.

[0132] The criterion for evaluating folding brittleness is as follows.

○: no crazing
△: some crazing
X: noticeable crazing

[0133] The results are shown in Table 1.

Table 1

Sample No.	Coating mode	Intermediate layer's index of refraction	**	Interference fringe	Brittleness
1*	sequential	1.54	0.24	X	○
2*	sequential	1.59	0.19	X	△
3*	sequential	1.64	0.14	X	X
4*	sequential	1.70	0.08	△	X
5*	sequential	1.75	0.03	○	X
6	concurrent	1.54	0.24	○	○
7	concurrent	1.59	0.19	○	○
8	concurrent	1.64	0.14	○	○
9*	concurrent	1.70	0.08	○	X
10*	concurrent	1.75	0.03	○	X

* comparison
** difference in index of refraction between emulsion layer and intermediate layer

[0134] It is evident from Table 1 that the samples within the scope of the invention are improved in both interference fringe and folding brittleness.

Example 2

[0135] Photosensitive element samples were prepared as in Example 1 except that the intermediate layer was omitted and an emulsion surface protective layer-1 having an index of refraction as reported in Table 2 was prepared and coated. In the column of coating mode in Table 2, concurrent coating means that the three layers on the emulsion side were concurrently coated in an overlapping manner, and sequential coating means that the emulsion layer was first coated and dried before the remaining two layers were concurrently coated and dried.

[0136] These samples were tested as in Example 1, with the results shown in Table 2.

Table 2

Sample No.	Coating mode	Emulsion surface protective layer's index of refraction	**	Interference fringe	Brittleness
11*	sequential	1.50	0.28	X	○
12*	sequential	1.57	0.21	X	△
13*	sequential	1.64	0.14	X	X
14*	sequential	1.71	0.07	○	X
15*	sequential	1.76	0.02	○	X
16	concurrent	1.50	0.28	○	○
17	concurrent	1.57	0.21	○	○
18	concurrent	1.64	0.14	○	○
19*	concurrent	1.71	0.07	○	X
20*	concurrent	1.76	0.02	○	X

* comparison

** difference in index of refraction between emulsion layer and emulsion surface protective layer

[0137] It is evident from Table 2 that the samples within the scope of the invention are improved in both interference fringe and folding brittleness.

Example 3

[0138] When the matte agent (polymethyl methacrylate particles) was omitted from the emulsion surface protective layer-2 in Example 1, slight interference fringes were found in sample No. 6. This could be canceled by adjusting the angle θ of laser exposure to 84°.

[0139] There has been described a photothermographic element wherein a photosensitive layer and a contiguous non-photosensitive layer are formed by concurrent coating and drying so as to give a specific difference in index of refraction therebetween, thereby eliminating the occurrence of interference fringes and improving the brittleness of the element.

[0140] 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 adapted for laser exposure, comprising on a support at least one photosensitive layer containing a photosensitive silver halide and a binder and at least one non-photosensitive layer containing a binder, characterized in that

    the difference in index of refraction between said photosensitive layer and said non-photosensitive layer disposed contiguous thereto is 0.10 to 0.70, and
    said photosensitive layer and said non-photosensitive layer have been formed by concurrent coating in a multiple manner and drying.

2. The photothermographic element of claim 1 wherein said photosensitive silver halide has a mean grain size from 0.01 µm to less than 0.1 µm and is contained in a silver coverage of 0.01 to 0.3 g/m^2.

3. The photothermographic element of claim 1 or 2 wherein said photosensitive layer and said non-photosensitive layer disposed contiguous thereto have been formed from aqueous coating solutions.

4. The photothermographic element of any one of claims 1 to 3 wherein said photosensitive layer further contains an organic silver salt and a reducing agent for silver ion.

5. The photothermographic element of any one of claims 1 to 4 wherein the binder in said photosensitive layer comprises a polymer latex.

6. The photothermographic element of any one of claims 1 to 5 wherein the binder in said non-photosensitive layer comprises a water-soluble polymer.

7. The photothermographic element of any one of claims 1 to 6 wherein an uppermost layer on the side where said photosensitive layer is situated contains a matte agent.

8. The photothermographic element of claim 7 wherein the matte agent consists of particles having a mean particle size of 1 to 10 µm and is contained in the uppermost layer at a population of 200 to 10,000 particles/mm^2.

9. The photothermographic element of any one of claims 1 to 8 wherein the difference in index of refraction between said photosensitive layer and said non-photosensitive layer disposed contiguous thereto is 0.10 to 0.50.

10. The photothermographic element of claim 9 wherein the difference in index of refraction is 0.10 to 0.40.

11. The photothermographic element of any one of claims 1 to 10 wherein said photosensitive layer has an index of refraction of 1.50 to 2.60.

12. The photothermographic element of any one of claims 1 to 11 wherein said non-photosensitive layer has an index of refraction of 1.40 to 1.90.

13. A method for preparing a photothermographic element adapted for laser exposure, said element comprising on a support at least one photosensitive layer containing a photosensitive silver halide and a binder and at least one non-photosensitive layer containing a binder, characterized in that

a photosensitive layer-forming solution and a non-photosensitive layer-forming solution are concurrently coated in a multiple manner and dried to form the photosensitive layer and the non-photosensitive layer contiguous thereto such that the difference in index of refraction between said photosensitive layer and said non-photosensitive layer is 0.10 to 0.70.

FIG. 1

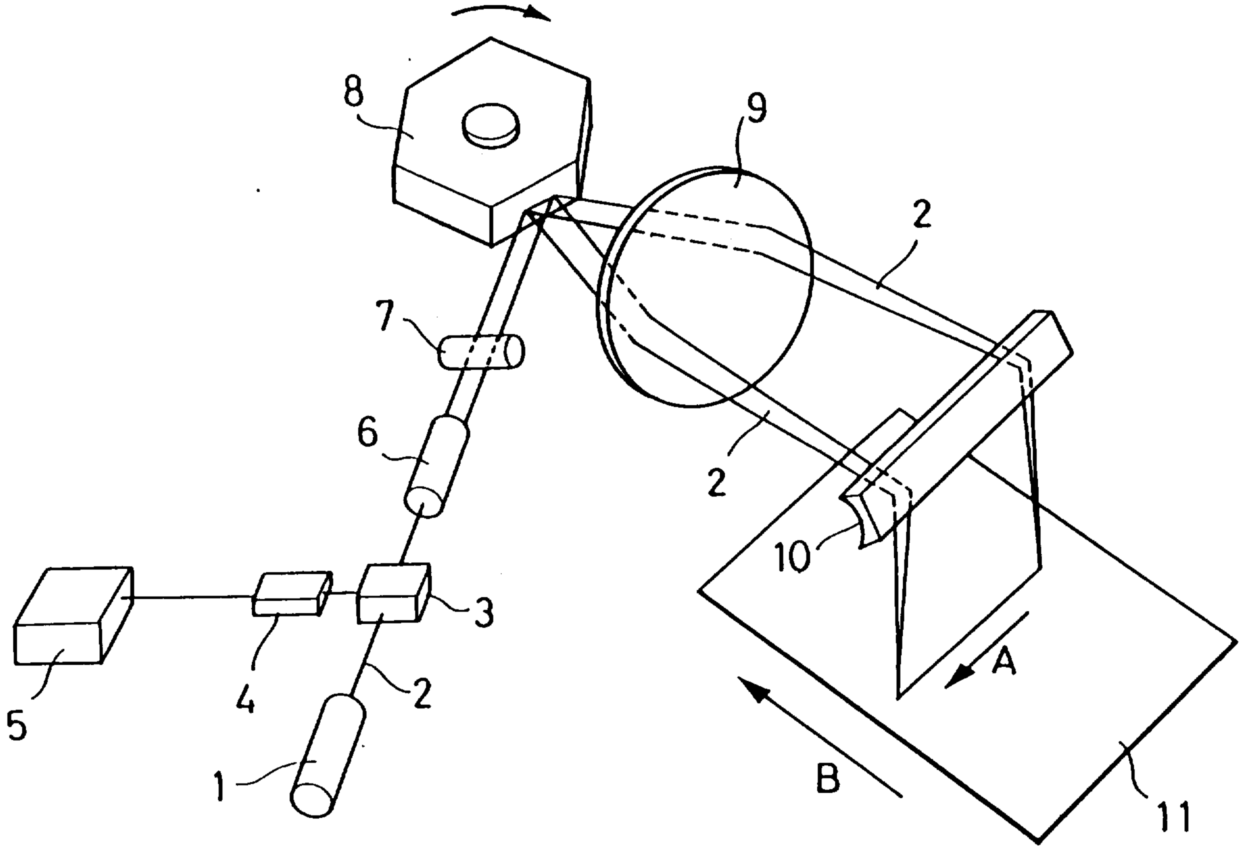


FIG. 2

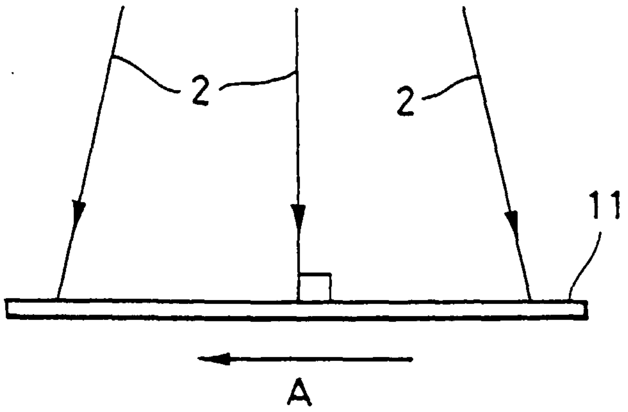
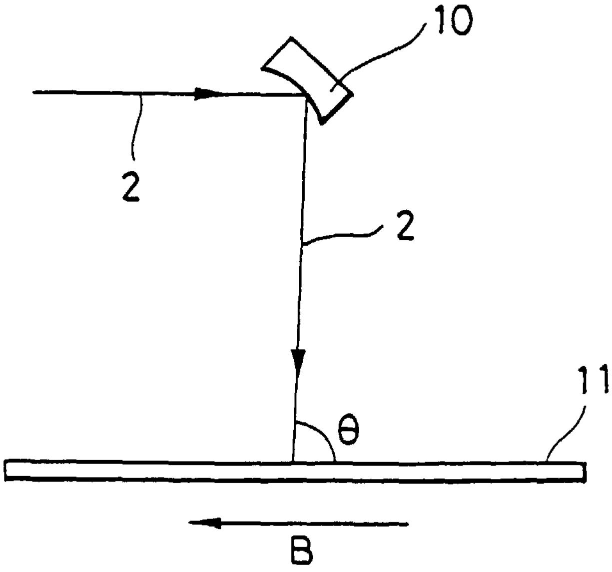


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number
EP 98 11 7757

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 504 575 A (LEE ROSS A) 12 March 1985 * examples 2,3 * -----	1-12	G03C1/498

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	1 March 1999	Buscha, A

CATEGORY OF CITED DOCUMENTS

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