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(54) **Method for preparing photosensitive image forming medium coating solution, and photothermographic elements**

(57) A photosensitive image forming medium coating solution is prepared by converting a water dispersion containing at least an organic silver salt, but substantially free of a photosensitive silver salt into a high pressure, high speed flow, causing a pressure drop of 900-3,000 kg/cm<sup>2</sup> to the flow, and then mixing the flow with a photosensitive silver salt. Using this aqueous coating solution, a photothermographic element having a low haze, low fog and high sensitivity can be produced with the advantages of environmental protection and low cost.

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## Description

This invention relates to a method for preparing a coating solution containing organic silver salt image forming media, and a photothermographic element comprising the image forming media. More particularly, it relates to a technique of finely dispersing a dispersion of an organic silver salt in water, and a photosensitive element for laser image setters and laser imagers (sometimes referred to as LI photosensitive element) prepared using the organic silver salt water dispersion.

## Related Art

There are known a number of photosensitive materials having a photosensitive layer on a support wherein images are formed by imagewise exposure. Of these, a thermographic technique of forming images by heat development is known as a system capable of environmental protection and simplification of image forming means.

From the contemporary standpoints of environmental protection and space saving, it is strongly desired in the medical imaging field to reduce the quantity of spent solution. Needed in this regard is a technology relating to photothermographic materials for use in medical diagnosis and general photography which can be effectively exposed by means of laser image setters and laser imagers and produce clear black images having a high resolution and sharpness. These photothermographic materials offer to the customer a simple thermographic system which eliminates a need for solution type chemical agents and is not detrimental to the environment.

The thermographic process of forming images by heat development are disclosed, for example, in USP 3,152,904 and 3,457,075, D. Morgan and B. Shely, "Thermally Processed Silver Systems" in "Imaging Processes and Materials," Neblette, 8th Ed., Sturge, V. Walworth and A. Shepp Ed., page 2, 1969.

These photosensitive materials generally contain a reducible non-photosensitive silver source (e.g., organic silver salt), a catalytic amount of a photocatalyst (e.g., silver halide), and a reducing agent for silver, typically dispersed in an organic binder matrix. Photosensitive materials are stable at room temperature. When they are heated at an elevated temperature (e.g., 80°C or higher) after exposure, redox reaction takes place between the reducible silver source (functioning as an oxidizing agent) and the reducing agent to form silver. This redox reaction is promoted by the catalysis of a latent image produced by exposure. Silver formed by reaction of the organic silver salt in exposed regions provides black images in contrast to unexposed regions, forming an image.

Photothermographic materials of this type are well known from the past. In most of these photothermographic image forming materials, photothermographic image forming layers are formed by applying coating solutions in organic solvents such as toluene, methyl ethyl ketone and methanol. Use of organic solvents is not only harmful to humans during the manufacturing process, but also economically disadvantageous because of a substantial cost for recovery.

It was thus envisaged to form photothermographic layers using coating solutions in water solvent free of such concerns. These photothermographic layers are referred to as aqueous photosensitive layers, hereinafter. For example, JP-A 52626/1974 and 116144/1978 disclose the use of gelatin as the binder. JP-A 151138/1975 discloses the use of polyvinyl alcohol as the binder. JP-A 61747/1985 discloses the combined use of gelatin and polyvinyl alcohol. Besides, JP-A 28737/1983 discloses a photosensitive layer using water-soluble polyvinyl acetal as the binder.

It is true that the use of such binders has environmental and economical advantages because photosensitive layers can be formed using coating solutions in water solvent.

Aqueous coating solutions containing organic silver salts and such polymers as gelatin, polyvinyl alcohol and water-soluble polyvinyl acetal as the binder, however, have several problems with respect to their preparation and application. On account of these problems, it was difficult to obtain practically acceptable photothermographic materials. One problem is the poor compatibility between the organic silver salt and water and between the organic silver salt and the binder. Agglomeration and sedimentation occur during preparation of a coating solution, which cannot be coated. Even when a coating solution with less agglomeration and sedimentation can be prepared and coated, coating and drying steps yield photothermographic materials having an extremely high haze and coating quality far from the practically acceptable level.

For solving these problems, it is desired to have a technique of forming finely dispersed organic silver salt fine crystals well compatible with water and binders.

Known techniques of finely dispersing organic silver salt fine crystals are by mechanical dispersion in the presence of dispersing agents using well-known fine graining means, for example, high-speed mixers, homogenizers, high-speed impact mills, Banbury mixers, homomixers, kneaders, ball mills, vibrating ball mills, planetary ball mills, attritors, sand mills, bead mills, colloid mills, jet mills, roller mills, trommels, and high-speed stone mills. In preparing water dispersions of organic silver salts, these techniques yield only polydisperse dispersions, failing to solve the problems of agglomeration/sedimentation and coating quality. From the photographic aspect, these techniques tend to increase the fog.

JP-B 119953/1995, JP-A 137044/1996 and JP-A 238848/1996 disclose methods of finely dispersing organic silver salts by pressure treatment. These methods, however, pertain to organic silver salt dispersions in organic solvents and

do not suggest any solution to the above-mentioned problems.

WO 97/104355 and WO 97/104356 refer to water dispersions of organic silver salts. In the former, a dispersion liquid in the co-presence of a photosensitive silver salt is dispersed by a dispersing apparatus. In the latter, after a water dispersion of an organic silver salt is prepared, a portion of this dispersion is converted into a photosensitive silver halide salt. The former suffers from a fog problem and the latter suffers from a sensitivity problem. These methods are far from the practical application to photothermographic materials.

A great deal of research efforts have been made to solve the above-mentioned problems, but no effective solutions have been discovered.

## SUMMARY OF THE INVENTION

Therefore, an object of the invention is to provide a method for preparing an aqueous photothermographic image forming medium coating solution of organic silver salt image forming media which are necessary to manufacture photothermographic elements which are improved in environmental protection and economy and have a low haze, low fog and high sensitivity.

Another object of the invention is to provide a photothermographic element comprising the organic silver salt image forming media. A further object of the invention is to provide a photothermographic element having improved coating quality and silver tone.

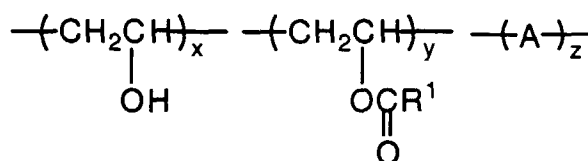
According to the invention, there is provided a method for preparing a photothermographic image forming medium coating solution for use in the manufacture of photothermographic elements. First, a water dispersion containing at least an organic silver salt, but substantially free of a photosensitive silver salt is converted into a high pressure, high speed flow. Then a pressure drop takes place in the flow or dispersion. Thereafter, the dispersion is mixed with a photosensitive silver salt.

Preferably, the pressure drop is in the range of 900 to 3,000 kg/cm<sup>2</sup> and especially, 1,500 to 3,000 kg/cm<sup>2</sup>.

In one preferred embodiment, a cooling step is included prior to the conversion step and/or after the pressure drop step whereby the water dispersion is maintained at a temperature in the range of 5 to 90°C.

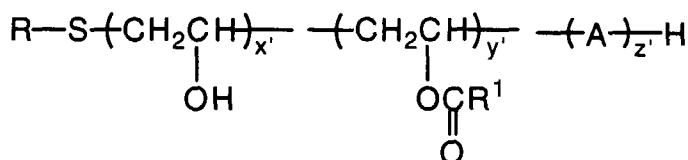
The water dispersion preferably contains as a dispersant a compound of the following formula (I) or (II).

(I)



In formula (I), R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, A represents recurring units of a copolymerizable ethylenically unsaturated monomer, and letters x, y and z represent the molar fractions of the respective components, x is 50 to 90 mol%, y is 0 to 50 mol%, z is 0 to 30 mol%, and x + y + z = 100 mol%.

(II)



In formula (II), R represents alkyl having at least 8 carbon atoms or aryl, R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, A represents recurring units of a copolymerizable ethylenically unsaturated monomer, and letters x', y' and z' represent the molar fractions of the respective components, x' is 50 to 99.9 mol%, y' is 0 to 50 mol%, z' is 0 to 30 mol%, and x' + y' + z' = 100 mol%.

Also contemplated herein is a photothermographic element comprising at least a photosensitive silver salt, an organic silver salt, a reducing agent, and a binder on a support. The element has been prepared using the photosensitive image forming medium coating solution defined above.

Preferably, the photosensitive image forming medium coating solution is based on a solvent containing at least 30%

by weight of water. Also preferably, a binder in a layer containing the organic silver salt is a polymer (polymer latex) having an equilibrium moisture content of up to 2% by weight at 25°C and RH 60%.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically illustrates one exemplary image recording apparatus.

FIG. 2 schematically illustrates an image exposure section of the image recording apparatus shown in FIG. 1.

## DETAILED DESCRIPTION OF THE INVENTION

For the purpose of obtaining a solid particle dispersion of an organic silver salt having a high S/N ratio and a small particle size and free of agglomeration, the present invention provides a dispersion method involving the steps of converting a water dispersion containing an organic silver salt as an image forming medium, but substantially free of a photosensitive silver salt into a high pressure, high speed flow, and causing a pressure drop to the flow. Thereafter, the dispersion is mixed with a photosensitive silver salt, thereby preparing a photosensitive image forming medium coating solution.

When a photothermographic element is prepared using this coating solution, the resulting photothermographic element has a low haze, low fog and high sensitivity. In contrast, if a photosensitive silver salt is co-present when an organic silver salt is dispersed in water by converting into a high pressure, high speed flow, then there result a fog increase and a substantial sensitivity drop. If an organic solvent is used instead of water as the dispersing medium, then there result a haze increase, a fog increase and a sensitivity drop. If dispersion is carried out without a pressure change, then there result a haze increase, a fog increase and a sensitivity drop. If a conversion technique of converting a portion of an organic silver salt in a dispersion into a photosensitive silver salt is employed instead of mixing a photosensitive silver salt, then there results a sensitivity drop.

The water dispersion which is dispersed by converting into a high pressure, high speed flow should be substantially free of a photosensitive silver salt. The content of photosensitive silver salt is less than 0.1 mol% based on the non-photosensitive organic silver salt. The positive addition of photosensitive silver salt is avoided.

With respect to the solid dispersing technology and apparatus employed in carrying out the above-described dispersion method of the invention, reference should be made to Kajiuchi and Usui, "Dispersed System Rheology and Dispersing Technology," Shinzansha Publishing K.K., 1991, pp. 357-403; and Tokai Department of the Chemical Engineering Society Ed., "Progress of Chemical Engineering, Volume 24," Maki Publishing K.K., 1990, pp. 184-185. According to the dispersion method of the invention, a water dispersion liquid containing at least an organic silver salt is pressurized by a high pressure pump or the like, fed into a pipe, and passed through a narrow slit in the pipe whereupon the dispersion liquid is allowed to experience an abrupt pressure drop, thereby accomplishing fine dispersion.

Such a high pressure homogenizer which is used in the practice of the invention is generally believed to achieve dispersion into finer particles under the impetus of dispersing forces including (a) "shear forces" exerted when the dispersed phase is passed through a narrow gap under high pressure and at a high speed and (b) "cavitation forces" exerted when the dispersed phase under high pressure is released to atmospheric pressure. As the dispersing apparatus of this type, Gaulin homogenizers are known from the past. In the Gaulin homogenizer, a liquid to be dispersed fed under high pressure is converted into a high-speed flow through a narrow slit on a cylindrical surface and under that impetus, impinged against the surrounding wall surface, achieving emulsification and dispersion by the impact forces. The pressure used is generally 100 to 600 kg/cm<sup>2</sup> and the flow velocity is from several meters per second to about 30 m/sec. To increase the dispersion efficiency, improvements are made on the homogenizer as by modifying a high-flow-velocity section into a saw-shape for increasing the number of impingements. Apart from this, apparatus capable of dispersion at a higher pressure and a higher flow velocity were recently developed. Typical examples of the advanced dispersing apparatus are available under the trade name of Micro-Fluidizer (Microfluidex International Corp.) and Nanomizer (Tokushu Kika Kogyo K.K.).

Examples of appropriate dispersing apparatus which are used in the practice of the invention include Micro-Fluidizer M-110S-EH (with G10Z interaction chamber), M-110Y (with H10Z interaction chamber), M-140K (with G10Z interaction chamber), HC-2000 (with T50Z or M250Z interaction chamber), HC-5000 (with L30Z or H230Z interaction chamber), and HC-8000 (with E230Z or L30Z interaction chamber), all available from Microfluidex International Corp.

Using such apparatus, a water dispersion liquid containing at least an organic silver salt is pressurized by a high pressure pump or the like, fed into a pipe, and passed through a narrow slit in the pipe for applying a desired pressure to the liquid and thereafter, the pressure within the pipe is quickly released to atmospheric pressure whereby the dispersion liquid experiences an abrupt pressure drop, thereby accomplishing the fine dispersion effect of the invention.

According to the invention, the organic silver salt dispersion can be dispersed to a desired particle size by adjusting a flow velocity, a differential pressure upon pressure drop, and the number of dispersing cycles. From the standpoints of photographic properties and particle size, it is preferable to use a flow velocity of 200 to 600 m/sec and a differential

pressure upon pressure drop of 900 to 3,000 kg/cm<sup>2</sup>, and especially a flow velocity of 300 to 600 m/sec and a differential pressure upon pressure drop of 1,500 to 3,000 kg/cm<sup>2</sup>. The number of dispersing cycles may be selected as appropriate although it is usually 1 to 10. From the productivity standpoint, the number of dispersing cycles is 1 to about 3. It is not recommended from the standpoints of dispersibility and photographic properties to elevate the temperature of the water dispersion under high pressure. High temperatures above 90°C tend to increase the particle size and the fog due to poor dispersion. Accordingly, in the preferred embodiment of the invention, a cooling step is provided prior to the conversion step and/or after the pressure drop step whereby the water dispersion is maintained at a temperature in the range of 5 to 90°C, more preferably 5 to 80°C and most preferably 5 to 65°C. It is effective to use the cooling step particularly when dispersion is effected under a high pressure of 1,500 to 3,000 kg/cm<sup>2</sup>. The cooling means used in the cooling step may be selected from various coolers, for example, double tube type heat exchangers, static mixer-built-in double tube type heat exchangers, multi-tube type heat exchangers, and serpentine heat exchangers, depending on the necessary quantity of heat exchange. For increasing the efficiency of heat exchange, the diameter, gage and material of the tube are selected as appropriate in consideration of the pressure applied thereto. Depending on the necessary quantity of heat exchange, the refrigerant used in the heat exchanger may be selected from well water at 20°C, cold water at 5 to 10°C cooled by refrigerators, and if necessary, ethylene glycol/water at -30°C.

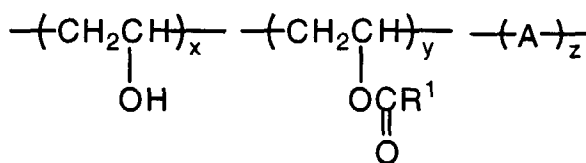
Prior to the dispersing operation according to the invention, the starting liquid is preferably pre-dispersed. For such pre-dispersion, there may be used any of well-known dispersing means, for example, high-speed mixers, homogenizers, high-speed impact mills, Banbury mixers, homomixers, kneaders, ball mills, vibrating ball mills, planetary ball mills, attritors, sand mills, bead mills, colloid mills, jet mills, roller mills, trommels, and high-speed stone mills. Rather than such mechanical dispersion, the pre-dispersion may be carried out by controlling the pH of the starting liquid for roughly dispersing particles in a solvent, and then changing the pH in the presence of dispersing agents for fine graining. The solvent used in the rough dispersing step may be an organic solvent although the organic solvent is usually removed after the completion of fine graining.

In the dispersing operation according to the invention, the organic silver salt is preferably dispersed in the presence of dispersants or dispersing agents soluble in an aqueous medium. The dispersing agents used herein include synthetic anionic polymers such as polyacrylic acid, acrylic acid copolymers, maleic acid copolymers, maleic acid monoester copolymers, and acryloylmethylpropanesulfonic acid copolymers; 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; compounds as described in Japanese Patent Application No. 350753/1995; well-known anionic, nonionic and cationic surfactants; well-known polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose and hydroxypropylmethyl cellulose; and naturally occurring polymers such as gelatin. Of these, polyvinyl alcohol and water-soluble cellulose derivatives are especially preferred.

The water-soluble cellulose derivatives include substituted celluloses having various substituents, for example, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, carboxymethyl cellulose and alkali metal salts thereof, carboxymethylethyl cellulose, and ethylhydroxyethyl cellulose.

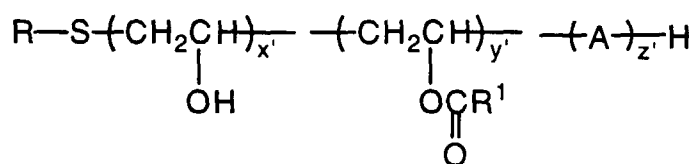
The polyvinyl alcohol derivatives include polymers of the following general formula (I) or (II).

(I)



In formula (I), R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, A represents recurring units of a copolymerizable ethylenically unsaturated monomer, and letters x, y and z represent the molar fractions of the respective components, x is 50 to 90 mol%, y is 0 to 50 mol%, z is 0 to 30 mol%, and x + y + z = 100 mol%.

(II)



In formula (II), R represents alkyl having at least 8 carbon atoms or aryl, R<sup>1</sup> and A are as defined above, and letters x', y' and z' represent the molar fractions of the respective components, x' is 50 to 99.9 mol%, y' is 0 to 50 mol%, z' is 0 to 30 mol%, and x' + y' + z' = 100 mol%.

These preferred vinyl alcohol polymers are described in more detail.

In formula (I), R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, which may have substituents, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, isobutyl, t-butyl, chloromethyl, and 2-chloroethyl, with the methyl being especially preferred. Letters x, y and z represent the molar fractions of the respective components, x is 50 to 90 mol%, preferably 60 to 90 mol%, and more preferably 65 to 85 mol%, y is 0 to 50 mol%, preferably 5 to 40 mol%, and more preferably 10 to 35 mol%, z is 0 to 30 mol%, preferably 0 to 25 mol%, and more preferably 0 to 20 mol%, and x + y + z = 100 mol%.

The ethylenically unsaturated monomer represented by A is selected from such monomers of various structures by taking into account the compositional ratio, solubility in solvent, and dispersibility of the copolymer. Examples of the monomer which can be used herein are given below.

Acrylic acid esters, for example, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, amyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, 2-chloroethyl acrylate, 2-acetoxyethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, cyclohexyl acrylate, and phenyl acrylate.

Methacrylic acid esters, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, glycidyl methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, and 2-hydroxyethyl methacrylate.

Acrylamides, for example, acrylamide, methylacrylamide, ethylacrylamide, propylacrylamide, butylacrylamide, tert-butylacrylamide, cyclohexylacrylamide, benzylacrylamide, phenylacrylamide, dimethylacrylamide, diethylacrylamide, and diacetoneacrylamide.

Methacrylamides, for example, methacrylamide, methylmethacrylamide, ethylmethacrylamide, butylmethacrylamide, tert-butylmethacrylamide, and benzylmethacrylamide.

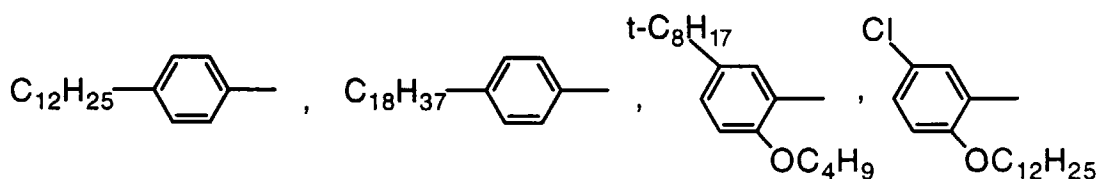
Olefins, for example, dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, isoprene, chloroprene, butadiene, and 2,3-dimethylbutadiene; styrenes, for example, styrene, methylstyrene, dimethylstyrene, ethylstyrene, isopropylstyrene, chloromethylstyrene, methoxystyrene, acetoxystyrene, chlorostyrene, bromostyrene, and methyl vinylbenzoate.

Vinyl ethers, for example, methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, and methoxyethyl vinyl ether.

Monomers containing dissociable groups, for example, acrylic acid, methacrylic acid, itaconic acid, vinylbenzoic acid, crotonic acid, 2-acrylamidopropionic acid, 4-acrylamidobenzoic acid, styrenesulfonic acid, vinylsulfonic acid, acryloyloxyethylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, and salts thereof.

Others, for example, butyl crotonate, dimethyl itaconate, diethyl fumarate, methyl vinyl ketone, acrylonitrile, and methacrylonitrile.

In formula (II), R represents alkyl having at least 8 carbon atoms, preferably 8 to 50 carbon atoms, which may have substituents, or aryl, preferably phenyl. Illustrative examples of R include C<sub>8</sub>H<sub>17</sub>-, n-C<sub>12</sub>H<sub>25</sub>-, t-C<sub>12</sub>H<sub>25</sub>-, C<sub>16</sub>H<sub>33</sub>-, C<sub>18</sub>H<sub>37</sub>-, C<sub>31</sub>H<sub>63</sub>-, C<sub>8</sub>H<sub>17</sub>OCOCH<sub>2</sub>-, C<sub>12</sub>H<sub>25</sub>OCOCH<sub>2</sub>-, C<sub>18</sub>H<sub>37</sub>OCOCH<sub>2</sub>-, C<sub>12</sub>H<sub>25</sub>OCOCH<sub>2</sub>CH<sub>2</sub>-, C<sub>16</sub>H<sub>33</sub>SO<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>-, and groups shown below.



Of these, unsubstituted alkyl groups of at least 10 carbon atoms are especially preferred. R<sup>1</sup> is as defined in formula (I).

Letters x', y' and z' represent the molar fractions of the respective components, x' is 50 to 99.9 mol%, preferably 60 to 99.9 mol%, and more preferably 65 to 90 mol%, y' is 0 to 50 mol%, preferably 0.1 to 40 mol%, and more preferably 5 to 35 mol%, z' is 0 to 30 mol%, preferably 0 to 25 mol%, and more preferably 0 to 20 mol%, and x' + y' + z' = 100 mol%.

Preferred, non-limiting, examples of the vinyl alcohol polymers which can be used herein are illustrated below.

B-1 poly(vinyl alcohol/vinyl acetate) (molar ratio 88/12)

B-2 poly(vinyl alcohol/vinyl acetate) (molar ratio 82/18)

B-3 poly(vinyl alcohol/vinyl acetate) (molar ratio 79/21)

B-4 poly(vinyl alcohol/vinyl acetate) (molar ratio 71/29)

B-5 poly(vinyl alcohol/vinyl acetate) (molar ratio 65/35)

B-6 poly(vinyl alcohol/vinyl acetate/methacrylic acid) (molar ratio 83/12/5)

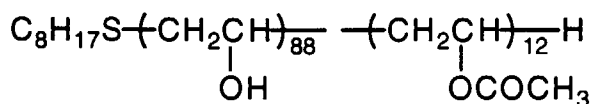
B-7 poly(vinyl alcohol/vinyl acetate/itaconic acid) (molar ratio 75/20/5)

B-8 poly(vinyl alcohol/vinyl propionate) (molar ratio 80/20)

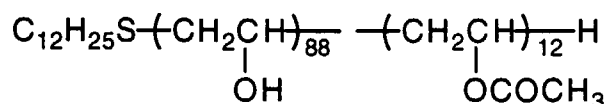
B-9 poly(vinyl alcohol/vinyl pivalate) (molar ratio 88/12)

B-10 poly(vinyl alcohol/vinyl butyrate) (molar ratio 88/12)

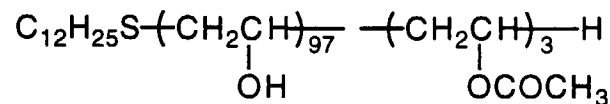
B-11



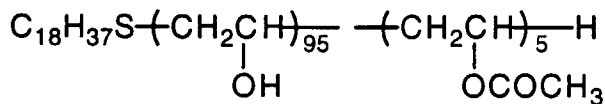
B-12



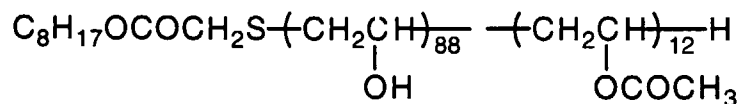
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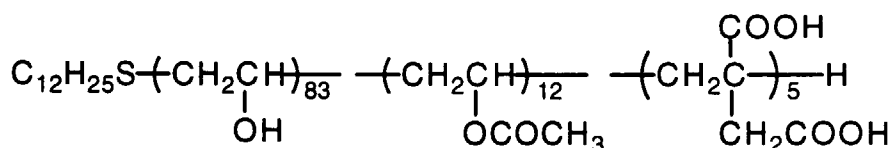
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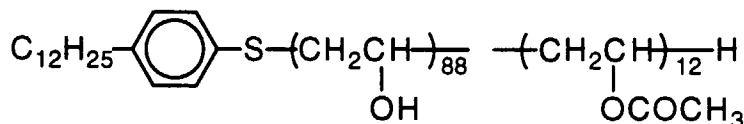
B-15



B-16



B-17



Note that the suffixes attached to parentheses represent molar ratios.

The water-soluble cellulose derivatives and polyvinyl alcohol derivatives mentioned above are commercially available and such commercially products are utilizable. Examples of the water-soluble cellulose derivatives include Metrose SM, Metrose 60SH, and Metrose 6SH (Shin-Etsu Chemical K.K.), and Celogen 5A, Celogen 6A, Celogen PR and Celogen WS-A (Nisso K.K.). Examples of the polyvinyl alcohol derivatives include PVA-203, PVA-205, PVA-217, PVA-224, MP-102, MP-202, and MP-203 (Kurare K.K.).

The molecular weight of the polymers used herein is not critical. An appropriate molecular weight range varies with the structure of polymer. Preferably the polymers have a weight average molecular weight (Mw) of 1,000 to 1,000,000, more preferably 3,000 to 300,000.

The polymers used herein may be prepared by any of well-known polymerization techniques such as solution polymerization, suspension polymerization, emulsion polymerization, and precipitation polymerization. Reference is made to Murahashi et al. Ed., "Synthetic Polymers," Vol. 1, pp. 246-290 and Vol. 3, pp. 1-108, for example. Also, polymers having polyvinyl alcohol units in a molecule may be prepared by effecting homo- or co-polymerization of vinyl esters by the above technique, followed by hydrolysis to form vinyl alcohol units. Polymers of formula (II) may be synthesized by effecting polymerization in the co-presence of mercaptan compounds represented by R-SH and hydrolyzing the resulting polymers.

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 perform pH control with a suitable pH adjusting agent before, during or after dispersion.

The dispersion liquid used herein is composed of at least the organic silver salt and water. It is preferred that the water dispersing medium consists solely of water although an organic solvent which is miscible with water may be contained insofar as its content is up to 30% by weight. The ratio of the organic silver salt to water is not critical although it is preferred that the organic silver salt accounts for 5 to 50% by weight, especially 10 to 30% by weight, of the entire system. It is preferred to use the dispersing agent as mentioned above and more preferably, in a minimum amount necessary to minimize the particle size. The dispersing agent is preferably used in an amount of 1 to 30% by weight, especially 3 to 15% by weight of the organic silver salt. When the water dispersion of the organic silver salt which has been converted into a high pressure, high speed flow and subjected to a pressure drop is mixed with a water dispersion of a photosensitive silver salt, their mixing ratio is determined in accordance with the ratio of the organic silver salt to the photosensitive silver salt. The proportion of the photosensitive silver salt is preferably 1 to 30 mol%, more preferably 3 to 20 mol% and most preferably 5 to 15 mol%, based on the moles of the organic silver salt. With respect to this mixing, a method of mixing two or more organic silver salt water dispersion with two or more photosensitive silver salt water dispersion is preferably employed for the purpose of adjusting photographic properties. It is preferred that the water solvent in the photosensitive silver salt water dispersion consists solely of water, although a water-miscible organic solvent may be contained insofar as its content is up to 30% by weight.

The grain size (volume weighed mean diameter) of the solid particle dispersion of the organic silver salt obtained by the present invention 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. Preferably, the solid particle dispersion has a mean grain size of 0.05  $\mu\text{m}$  to 10.0  $\mu\text{m}$ , more preferably 0.1  $\mu\text{m}$  to 5.0  $\mu\text{m}$ , and most preferably 0.1  $\mu\text{m}$  to 2.0  $\mu\text{m}$ .



The grain size distribution of the organic silver salt is desirably monodisperse. Illustratively, the standard deviation of a volume weighed mean diameter divided by the volume weighed mean diameter, expressed in percent, which is a coefficient of variation, is preferably up to 80%, more preferably up to 50%, most preferably up to 30%.

The shape of the organic silver salt may be determined by observing a dispersion of the organic silver salt under a transmission electron microscope (TEM).

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.

#### Organic silver salt

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 photo-sensitive silver halide) and a reducing agent. The organic silver salt may be of any desired organic compound containing a source capable of reducing silver ion. Preferred are silver salts of organic acids, typically long chain aliphatic carboxylic acids having 10 to 30 carbon atoms, especially 15 to 28 carbon atoms. Also preferred are complexes of organic or inorganic silver salts with ligands having a stability constant in the range of 4.0 to 10.0. A silver-providing substance is preferably used in an amount of about 5 to 70% by weight of an image forming layer. Preferred organic silver salts include silver salts of organic compounds having a carboxyl group. Examples include silver salts of aliphatic carboxylic acids and silver salts of aromatic carboxylic acids though not limited thereto. Preferred examples of the silver salt of aliphatic carboxylic acid include silver behenate, silver 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.

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-mercapto-benzimidazole, 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.

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.

#### Silver halide

The photosensitive silver salt used herein is typically a photosensitive silver halide.

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.

The photosensitive silver halide should preferably have a smaller mean grain size for the purpose of minimizing white turbidity after image formation. Specifically, the grain size is preferably up to 0.20  $\mu\text{m}$  more preferably 0.01  $\mu\text{m}$  to 0.15  $\mu\text{m}$  most preferably 0.02  $\mu\text{m}$  to 0.12  $\mu\text{m}$ . 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.

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 indi-

ces) of an outer surface of photosensitive silver halide grains. Preferably silver halide grains have a high proportion of a face featuring high spectral sensitization efficiency upon adsorption of a spectral sensitizing dye. The proportion of that face is preferably at least 50%, more preferably at least 65%, most preferably at least 80%. Note that the proportion of a certain Miller index 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.

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.

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  $1 \times 10^{-9}$  to  $1 \times 10^{-2}$  mol, more preferably  $1 \times 10^{-8}$  to  $1 \times 10^{-3}$  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.

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.

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, aminoiminomethanesulfinic 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.

According to the invention, the photosensitive silver halide is preferably used in an amount of 0.01 to 0.5 mol, more preferably 0.02 to 0.3 mol, most preferably 0.03 to 0.25 mol per mol of the organic silver salt.

The photothermographic element according to the invention contains a photosensitive silver salt, an organic silver salt, a reducing agent and a binder on at least one surface of a support and is prepared using a coating solution containing an organic silver salt dispersion according to the invention.

More benefits of the invention are obtained when the organic silver salt-containing layer is formed by coating a coating solution in which at least 30% by weight of the solvent is water and drying the coating, and especially when a latex of a polymer soluble or dispersible in an aqueous solvent, typically water solvent and having an equilibrium moisture content of up to 2% by weight at 25°C and RH 60% (referred to as inventive polymer, hereinafter) is used as the binder of the organic silver salt-containing layer. As compared with the coating of organic solvent systems, more benefits of environmental protection and economy are obtained when the organic silver salt-containing layer is formed by coating a coating solution using a polymer latex and an aqueous solvent containing at least 30% by weight of water. In contrast, conventional binders customarily used for aqueous solvent coating such as gelatin and polyvinyl alcohol (PVA) tend to degrade the coating quality and silver tone.

The "aqueous" solvent in which the inventive polymer is soluble or dispersible is water or a mixture of water and less than 70% by weight of a water-miscible organic solvent. Examples of the water-miscible organic solvent include alcohols such as methanol, ethanol, and propanol, cellosolves such as methyl cellosolve, ethyl cellosolve, and butyl cellosolve, and ethyl acetate and dimethylformamide. The term "aqueous solvent" is also applied to a system wherein a

polymer is not thermodynamically dissolved, but dispersed.

The equilibrium moisture content (Weq) of a polymer at 25°C and RH 60% is calculated according to the following expression:

$$\text{Weq} = (W1 - W0)/W0 \times 100\%$$

using the weight (W1) of the polymer conditioned in an atmosphere of 25°C and RH 60% until equilibrium is reached and the weight (W0) of the polymer in an absolute dry condition at 25°C. With respect to the definition and measurement of an equilibrium moisture content, reference is made to Kobunshi Gakkai Ed., "Polymer Engineering Series 14 - Polymeric Material Tests," Chijin Shokan K.K.

No further limits are imposed on the polymers used herein insofar as they are soluble or dispersible in the aqueous solvent and have an equilibrium moisture content of up to 2% by weight at 25°C and RH 60%. Of these polymers, polymers dispersible in aqueous solvents are especially preferred.

With respect to the dispersed state, latexes in which fine particles of a solid polymer are dispersed and dispersions in which polymer molecules are dispersed in a molecular or micelle state are included.

While the polymers used herein should preferably have an equilibrium moisture content of up to 2% by weight at 25°C and RH 60%, the more preferred equilibrium moisture content is from 0.01 to 1.5% by weight, especially 0.02 to 1% by weight at 25°C and RH 60%.

One preferred embodiment of the invention uses hydrophobic polymers such as acrylic resins, polyester resins, rubbery resins (e.g., SBR resins), polyurethane resins, vinyl chloride resins, vinyl acetate resins, vinylidene chloride resins, and polyolefin resins. The polymers may be linear or branched or crosslinked. The polymers may be either homopolymers or copolymers having two or more monomers polymerized together. The copolymers may be either random copolymers or block copolymers. The polymers preferably have a number average molecule weight Mn of about 5,000 to about 1,000,000, more preferably about 10,000 to about 200,000. Polymers with a too lower molecular weight would generally provide emulsion layers with a low strength whereas polymers with a too higher molecular weight are difficult to form films.

The polymers used herein are dispersed in an aqueous dispersing phase. The aqueous phase is a dispersing phase containing at least 30% by weight of water. 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 although polymer latexes are most preferred.

Illustrative preferred examples of the polymer are given below as P-1 to P-7, expressed by starting monomers, wherein numerical values in parentheses are % by weight and Mn is a number average molecular weight.

Designation	Units	Mn
P-1	-MMA(70)-EA(27)-MAA(3)- latex	37,000
P-2	-MMA(70)-2EHA(20)-St(5)-AA(5)- latex	40,000
P-3	-St(70)-Bu(25)-AA(5)- latex	60,000
P-4	-St(60)-Bu(35)-DVB(3)-MAA(2)- latex	150,000
P-5	-VC(50)-MMA(20)-EA(20)-AN(5)-AA(5)- latex	80,000
P-6	-VDC(85)-MMA(5)-EA(5)-MAA(5)- latex	67,000

(continued)

Designation	Units	Mn
P-7	-Et(90)-MAA(10)- latex	12,000
MMA: methyl methacrylate EA: ethyl acrylate MAA: methacrylic acid 2EHA: 2-ethylhexyl acrylate St: styrene Bu: butadiene AA: acrylic acid DVB: divinyl benzene VC: vinyl chloride AN: acrylonitrile VDC: vinylidene chloride Et: ethylene		

These polymers are commercially available. Useful examples of the polymer which can be used herein include acrylic resins such as Sebian A-4635, 46583 and 4601 (Daicell Chemical K.K.) and Nipol Lx811, 814, 821, 820 and 857 (Nippon Zeon K.K.); polyester resins such as FINETEX ES650, 611, 675 and 850 (Dai-Nippon Ink & Chemical K.K.) and WD-size and WMS (Eastman Chemical Products, Inc.); polyurethane resins such as HYDRAN AP10, 20, 30 and 40 (Dai-Nippon Ink & Chemical K.K.); rubbery resins such as LACSTAR 7310K, 3307B, 4700H and 7132C (Dai-Nippon Ink & Chemical K.K.) and Nipol Lx416, 410, 438C and 2507 (Nippon Zeon K.K.); vinyl chloride resins such as G351 and G576 (Nippon Zeon K.K.); vinylidene chloride resins such as L502 and L513 (Asahi Chemicals K.K.); and olefin resins such as Chemipearl S120 and SA100 (Mitsui Petro-Chemical K.K.)

These polymers may be used in polymer latex form alone or in admixture of two or more.

The polymer latex used herein is preferably a latex of a styrene-butadiene copolymer. The styrene-butadiene copolymer preferably contains styrene monomer units and butadiene monomer units in a weight ratio of from 40:60 to 95:5. Also preferably the styrene-butadiene copolymer contains 60 to 99% by weight of styrene and butadiene monomer units combined. Other components are acrylic acid, methacrylic acid, acrylonitrile, and divinyl benzene, with the acrylic acid and methacrylic acid being preferred. The preferred molecular weight range is as previously described.

Preferred examples of the styrene-butadiene copolymer latex which is used herein are P-3, P-4, LACSTAR 3307B and 7132C, and Nipol Lx416.

In the preferred embodiment wherein a polymer latex is used in the organic silver salt-containing layer according to the invention, a hydrophilic polymer is added to the organic silver salt-containing layer if desired. Such hydrophilic polymers include gelatin, polyvinyl alcohol, methyl cellulose, and hydroxypropyl cellulose. The amount of the hydrophilic polymer added is more preferably up to 30%, especially up to 20% by weight of the entire binder in the organic silver salt-containing layer.

While the organic silver salt-containing layer according to the invention is preferably formed using the polymer latex as mentioned above, the content of the binder in the organic silver salt-containing layer is such that the weight ratio of entire binder to organic silver salt may range from 1/10 to 10/1, and especially from 1/5 to 4/1.

The organic silver salt-containing layer is typically a photosensitive layer (or emulsion layer) containing a photosensitive silver halide as the photosensitive silver salt. In this case, the weight ratio of the entire binder to silver halide ranges from 400/1 to 5/1 and especially from 200/1 to 10/1.

The solvent of the coating solution from which the organic silver salt-containing layer of the photosensitive material according to the invention is formed (for simplicity's sake, the term solvent is used as a mixture of a solvent and a dispersing medium) is an aqueous solvent containing at least 30% by weight of water. The component other than water may be any of water-miscible organic solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide and ethyl acetate. The solvent of the coating solution should more preferably contain at least 50%, further preferably at least 70% by weight of water. Exemplary solvent mixtures are a 90/10 or 70/30 mixture of water/methyl alcohol, a 80/15/5 mixture of water/methyl alcohol/dimethylformamide, a 85/10/5 mixture of water/methyl alcohol/ethyl cellosolve, and a 85/10/5 mixture of water/methyl alcohol/isopropyl alcohol, all expressed in a weight ratio.

The photothermographic element according to the invention contains a photosensitive silver halide (as a typical photosensitive silver salt), an organic silver salt, a reducing agent and a binder on a support while the photosensitive silver halide and the organic silver salt are contained in a common layer so that the organic silver salt-containing layer is a photosensitive layer. Further, the reducing agent may be contained in the same layer.

In the photosensitive element according to the invention, the organic silver salt-containing layer may be a single layer or two or more layers. The organic silver salt-containing layer is preferably formed on one surface of the support although it may be formed on each surface. Where more than one organic silver salt-containing layer are present, it suffices that at least one layer is an organic silver salt-containing layer which is formed by coating a solid particle dispersion of the organic silver salt and preferably a polymer latex, and further preferably an aqueous solvent as the coating solvent according to the invention. Preferably all the layers are organic silver salt-containing layers according to the invention.

In the photosensitive element according to the invention, the organic silver salt-containing layer which is a photosensitive layer desirably has a thickness of 0.2 to 30  $\mu\text{m}$ , more desirably 1 to 20  $\mu\text{m}$  per layer.

The organic silver salt-containing layer is formed using a coating solution containing components corresponding to the composition of the organic silver salt-containing layer and a coating solvent, preferably an aqueous solvent. In the coating solution, the weight ratio of the components (solids) to the aqueous solvent is usually from about 1/99 to about 40/60. After application, the coating is dried at about 30 to 200°C for about 30 seconds to 30 minutes. This layer may be applied separately from other layers such as a surface protective layer or simultaneously with other layers in an overlapping manner. Such two or more layers may be dried at the same time. Also, prior to drying, the coating(s) may be held at a temperature of about 0 to 20°C for about 5 seconds to 10 minutes.

In the photothermographic element according to the invention, the organic silver salt may be used in any desired amount although an appropriate coverage of the organic silver salt per square meters of the photosensitive element is 0.1 to 20  $\text{g/m}^2$ , and especially 1 to 12  $\text{g/m}^2$ .

### Reducing Agent

In the photosensitive element according to the invention, the reducing agent may be added to any layer.

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<sup>®</sup>, hydroquinone and catechol are useful although hindered phenols are preferred reducing agents. The reducing agent should preferably be contained in an amount of 6 to 60 mol% of the organic silver salt. In a multi-layer construction wherein the reducing agent is added to a layer other than the emulsion layer, the reducing agent is preferably added in a slightly larger amount of about 8 to 80 mol% of the organic silver salt.

For photothermographic materials using organic silver salts, a wide range of reducing agents are disclosed. Exemplary reducing agents include amidoximes such as phenylamidoxime, 2-thienylamidoxime, and p-phenoxyphenylamidoxime; azines such as 4-hydroxy-3,5-dimethoxybenzaldehydeazine; combinations of aliphatic carboxylic acid arylhydrazides with ascorbic acid such as a combination of 2,2-bis(hydroxymethyl)propionyl- $\beta$ -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  $\beta$ -anilinehydroxamic acid; combinations of azines with sulfonamidophenols such as a combination of phenothiazine with 2,6-dichloro-4-benzenesulfonamidephenol;  $\alpha$ -cyanophenyl acetic acid derivatives such as ethyl- $\alpha$ -cyano-2-methylphenyl acetate and ethyl- $\alpha$ -cyanophenyl acetate; bis- $\beta$ -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- $\beta$ -naphthols with 1,3-dihydroxybenzene derivatives such as 2,4-dihydroxybenzophenone and 2,4-dihydroxyacetophenone; 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones such as dimethylaminohexosereductone, anhydrodihydroaminohexosereductone and anhydrodihydropiperidonehexosereductone; sulfonamidephenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidephenol and p-benzenesulfonamidephenol; 2-phenylindane-1,3-dione, etc.; chromans such as 2,2-dimethyl-7-t-butyl-6-hydroxychroman; 1,4-dihydropyridines such as 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine; bisphenols such as bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-ethylidene-bis(2-t-butyl-6-methylphenol), 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.

### Toner

Better results are sometimes achieved when an additive known as a "toner" for improving images is contained in addition to the aforementioned components. The toner is preferably present in an amount of 0.1 to 10% by weight of the entire silver-carrying components. The toner is well known in the photographic art as disclosed in USP 3,080,254, 3,847,612 and 4,123,282.

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; naphthalim-

ides such as N-hydroxy-1,8-naphthalimide; cobalt complexes such as cobaltic hexamine trifluoroacetate; mercaptans as exemplified by 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole, and 2,5-dimercapto-1,3,4-thiadiazole; N-(aminomethyl)aryldicarboxyimides such as (N,N-dimethylaminomethyl)phthalimide and N,N-(dimethylaminomethyl)naphthalene-2,3-dicarboxyimide; blocked pyrazoles, isothiuronium derivatives and certain photo-bleach agents such as N,N'-hexamethylenebis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoc-  
 5 tane)bis(isothiuroniumtrifluoroacetate) and 2-tribromomethylsulfonyl-benzothiazole; 3-ethyl-5-((3-ethyl-2-benzothiazolinyli-  
 10 denylidene)-1-methyl-ethylidene)-2-thio-2,4-oxazolidinedione; phthalazinone, phthalazinone derivatives or metal salts, or derivatives such as 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinedione; combinations of phthalazinones with phthalic acid derivatives (e.g., phthalic  
 10 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; rho-  
 15 dium 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 hexachlororhodate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodate (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.  
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### Antifoggant

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.  
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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.  
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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.

Still further, the photothermographic imaging 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 recording 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  $\mu$ mol to 2 mol, more preferably 1 mmol to 0.5 mol per mol of silver.  
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In the practice of the invention, addenda necessary to construct the photosensitive element such as reducing agents, toners and antifoggants may be added by any desired technique. Like the organic silver salt, these addenda are preferably added as a solid particle dispersion using a dispersing agent. Fine graining techniques are the same as the techniques for forming a solid particle dispersion of the organic silver salt, whereby the desired solid particle dispersion can be obtained. The solid particle dispersion of such an addendum should preferably have a mean particle size of 0.005 to 10  $\mu$ m, more preferably 0.01 to 3  $\mu$ m, and most preferably 0.05 to 0.5  $\mu$ m.  
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Sensitizing dye

A sensitizing dye may be used in the practice of the invention. 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 printing plate-forming cameras.

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.

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 or imidazole nucleus. Preferred examples of the useful merocyanine dye contain an acidic nucleus such as a thiohydantoin, rhodanine, oxazolidinedione, thiazolidinedione, barbituric acid, thiazolinone, malononitrile or 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.

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.

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.

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.

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.

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.

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.

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.

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.

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, bensotellurazole, imidazole, oxazole, pyrazole, 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-mercaptimidazole, 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.

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.

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.

In the imaging 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.

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.

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

A surface protective layer may be provided in the photosensitive element according to the present invention for the purpose of preventing sticking of the image forming layer. The binder in the surface protective layer is not critical although natural or synthetic resins and synthetic polymers which can be used in the image forming layer are preferably used. In the surface protective layer, any desired anti-sticking material may be used. Examples of the anti-sticking mate-



rial 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.

In the emulsion layer serving as 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 filter 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.

In the photosensitive layer of the photothermographic element according to the invention, 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.

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.

The back layer preferably exhibits a maximum absorbance of about 0.3 to 2.0 in the predetermined wavelength range. Where the predetermined wavelength range is 750 to 1,400 nm, the back layer preferably has an absorbance of 0.005 to less than 0.5 in the visible range. More preferably the back layer is an antihalation layer having an optical density of 0.001 to less than 0.3. Where the predetermined wavelength range is up to 750 nm, the back layer is preferably an antihalation layer having a maximum absorbance of 0.3 to 2.0 before image formation and an optical density of 0.005 to less than 0.3 after image formation. The means for reducing the optical density after image formation to the above-mentioned range is not critical although the density is preferably reduced by thermal decolorization of a dyestuff as disclosed in Belgian Patent No. 733,706 or by decolorization of a dyestuff upon light irradiation as disclosed in JP-A 17833/1979.

Where antihalation dyestuffs are used in the back layer according to the invention, such a dyestuff may be any compound which has desired absorption in a predetermined wavelength range and provides the back layer with a preferred absorbance spectrum profile.

In the practice of the invention, the binder used in the back layer is preferably transparent or translucent and generally colorless. Exemplary binders are naturally occurring polymers, synthetic resins, polymers and copolymers, and other film-forming media, for example, gelatin, gum arabic, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), 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.

In the one-side photosensitive material according to the invention, a matte agent may be added to the surface protective layer for the photosensitive emulsion layer and/or the back layer for improving feed efficiency. The matte agents used herein are generally microparticulate water-insoluble organic or inorganic compounds. There may be used any desired one of matte agents, for example, well-known matte agents including organic matte agents as described in USP 1,939,213, 2,701,245, 2,322,037, 3,262,782, 3,539,344, and 3,767,448 and inorganic matte agents as described in USP 1,260,772, 2,192,241, 3,257,206, 3,370,951, 3,523,022, and 3,769,020. Illustrative examples of the organic compound which can be used as the matte agent are given below; exemplary water-dispersible vinyl polymers include polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, acrylonitrile- $\alpha$ -methylstyrene copolymers, polystyrene, styrene-divinylbenzene 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 coacervation 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 it is preferred in the practice of the invention to use a matte agent having a particle size of 0.1  $\mu\text{m}$  to 30  $\mu\text{m}$ . 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.

In one preferred embodiment of the invention, a matte agent is added to the back layer. 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.

In the photosensitive material of the invention, the matte agent is preferably contained in an outermost surface layer, a layer functioning as an outermost surface layer, a layer close to the outer surface or a layer functioning as a so-called protective layer. The emulsion surface protective layer may have any degree of matte insofar as no star dust failures occur although a Bekk smoothness of 1,000 to 10,000 seconds, especially up to 2,000 seconds is preferred.

The thermographic photographic emulsion used in one preferred embodiment of the invention is contained in one or more layers on a support. In the event of single layer construction, it should contain an organic silver salt, silver halide, reducing agent, and binder, and other optional additives such as a toner, coating aid and other auxiliary agents. In the event of two-layer construction, a first emulsion layer which is generally a layer disposed adjacent to the support should contain an organic silver salt and silver halide and a second emulsion layer or both the layers contain other components. Also envisioned herein is a two-layer construction consisting of a single emulsion layer containing all the components and a protective topcoat. In the case of multi-color sensitive photothermographic material, a combination of such two layers 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, emulsion (or photosensitive) layers are distinctly supported by providing a functional or non-functional barrier layer therebetween as described in USP 4,460,681.

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

According to the invention, the photothermographic 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  $\alpha$ -olefin polymers, especially polymers of  $\alpha$ -olefins having 2 to 10 carbon atoms such as polyethylene, polypropylene, and ethylene-butene copolymers. The supports are either transparent or opaque, preferably transparent. Among others, biaxially oriented polyethylene terephthalate (PET) film of about 100 to 200  $\mu\text{m}$  thick is especially preferred.

For antistatic purposes, the photosensitive material of the invention may have an electroconductive layer, for example, a layer containing soluble salts (e.g., chlorides and nitrates), an evaporated metal layer, and layers containing ionic polymers as described in USP 2,861,056 and 3,206,312, insoluble inorganic salts as described in USP 3,428,451, and tin oxide microparticulates as described in JP-A 252349/1985 and 104931/1982. The support is tinted if desired.

A method for producing color images using the photothermographic material 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.

In the practice of the invention, the photothermographic emulsion can be coated by various coating procedures including dip coating, air knife coating, flow coating, and extrusion coating using a hopper of the type described in USP 2,681,294. If desired, two or more layers (for example, a combination of the emulsion layer and the surface protective layer) may be concurrently coated by the methods described in USP 2,761,791 and BP 837,095.

In the photothermographic material 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 thermographic photographic 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.

The photosensitive material 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 and the preferred developing time is about 1 to 180 seconds, more preferably about 10 to 90 seconds.

Any desired technique may be used for the exposure of the photothermographic material of the invention. A choice may be made of well-known exposure techniques using tungsten lamps, mercury lamps, lasers, CRT light sources, xenon lamps, and iodide lamps. Among these, exposure techniques using lasers are preferred.

Upon exposure, the photothermographic material of the invention tends to generate interference fringes due to low

haze. 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.

Upon exposure of the photothermographic material 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.

#### Recording apparatus

The photothermographic element according to the invention is processed by means of an image recording apparatus.

FIG. 1 schematically illustrates one exemplary image recording apparatus for use in the processing of the photothermographic element according to the invention.

The image recording apparatus designated at 10 in FIG. 1 is designed to process a photothermographic element A which requires no wet development process. More particularly, the apparatus 10 is to record images by carrying out scanning exposure with a light beam L for imagewise exposure of photothermographic element A, thereby forming a latent image, and effecting heat development to form a visible image. Basically, the apparatus 10 includes a recording element supply 12, a widthwise alignment section 14, an image exposure section 16, and a heat developing section 18, arranged in series in the feed direction of the element A.

The photothermographic element is a recording material in which an image is recorded with at least one light beam, typically a laser beam and then heat development is effected to visualize the latent image. The photothermographic element A is in sheet form. A predetermined number of sheets (for example, 100 sheets) are stacked into a pile which is packed in a bag or with a band into a package.

The image exposure section 16 is to perform scanning exposure with a light beam for the imagewise exposure of the photothermographic element A. The exposure section 16 includes an exposure unit 46 and a sub-scanning feed means 48.

The exposure section 16 is schematically illustrated in FIG. 2. The exposure unit 46 is a well-known light beam scanning apparatus adapted to deflect a light beam L, which has been modulated in accordance with an image to be recorded, in a main scanning direction (perpendicular to the plane of sheet in FIGS. 1 and 2) so that the light beam reaches the sheet at the predetermined record position X. The exposure unit 46 includes a light source 50 for emitting a light beam L in a narrow wavelength band appropriate to the spectral sensitivity properties of the photothermographic element A, a record control device 52 for driving the light source, a polygon mirror 54 serving as a light deflector, a  $f\theta$  lens 56, and a down mirror 58. If desired, the exposure unit 46 further includes various members used in well-known light beam scanners, for example, a collimator lens for shaping the light beam L from the light source, a beam expander, a figuring optical system, and an optical path adjusting mirror.

Since the image recording method used herein is to record an image by pulse width modulation, the recording apparatus 10 is to record an image by pulse width modulation. The record control device 52 is to drive the light source 50 by pulse width modulation in accordance with an image to be recorded for thereby emitting a light beam L which has been modulated in accordance with an image to be recorded.

The light beam L emitted from the light source 50 is deflected in the main scanning direction by the polygon mirror 54, adjusted by the  $f\theta$  lens 56 so as to focus at the record position X, and redirected to the record position X by the down mirror 58.

Since the recording apparatus 10 of the illustrated embodiment is for recording monochromatic images, the exposure unit 46 has only one light source 50. When it is desired to use the recording apparatus for recording color images, use may be made of an exposure unit having three light sources emitting three light beams of wavelengths complying with the spectral sensitivity characteristics of red (R), green (G) and blue (B) of color photosensitive elements.

The sub-scanning feed means 48 includes two pairs of feed rollers 60 and 62 disposed on opposite sides of the record position X (scanning line) for feeding the photothermographic element A in a sub-scanning direction (shown by arrow  $\underline{a}$  in FIG. 2) perpendicular to the main scanning direction while holding it at the record position X.

At this point, the photothermographic element A is subject to two-dimensional scanning exposure with the light beam L since the light beam L has been modulated in accordance with an image to be recorded and deflected in the main scanning direction. A latent image is recorded in the element A.

Although the recording apparatus 10 is described in the illustrated embodiment as effecting pulse width modulation by directly modulating the light source 50, an apparatus adapted to effect pulse number modulation can also be used. An apparatus of the indirect modulation type using an external modulator such as an acoustooptic modulator (AOM) is also useful insofar as the apparatus is capable of pulse modulation. Although the recording apparatus 10 is described in the illustrated embodiment as carrying out image recording by pulse width modulation, image recording can also be carried out by analog intensity modulation.

After the photothermographic element A is fed from the recording material supply 12, transported through the widthwise alignment section 14, and exposed in the exposure section 16 where a latent image is recorded as shown in FIG. 1, it is further transported by pairs of feed rollers 64 and 66 to the heat developing section 18.

The heating developing section 18 is to heat the photothermographic element A for heat development to convert the latent image into a visible image. This section includes a heating drum 68, an endless belt 70, and a peeling claw 72.

The heating drum 68 is a drum having built therein a heat source, for example, a heating light source such as a halogen lamp or an electric heater. The drum surface is heated to and maintained at a temperature corresponding to the heat developing temperature of the photothermographic element A. The drum 68 rotates about a shaft 68a and cooperates with the endless belt 70 for clamping and feeding the photothermographic element A. The temperature of the heating drum 68 is typically 100 to 140°C for the photothermographic element A as previously described. The heat developing time is typically about 10 to 90 seconds. The heat developing time may be adjusted by altering the feed rate depending on the type of photothermographic element A.

The endless belt 70 is trained around four rollers 74a, 74b, 74c and 74d, and a portion thereof is pressed against and wrapped around the heating drum 68. The peeling claw 72 is removably set in light contact with the heating drum 68 for peeling the photothermographic element A from the heating drum 68 as the element A is fed forward by the drum 68.

The photothermographic element A which has been carried into the heat developing section 18 by the pair of feed rollers 66 is clamped and carried forward by the endless belt 70 and rollers 76 and 78, carried between the endless belt 70 and the heating drum 68, and carried further forward with the rotation of the heating drum 68 where it is heat developed for converting the latent image recorded by exposure into a visible image.

When the leading edge of the photothermographic element A reaches the peeling claw 72, the peeling claw 72 in light contact with the heating drum 68 penetrates between the heating drum 68 and the photothermographic element A for peeling the element A from the drum 68.

After the photothermographic element A is heat developed and peeled from the heating drum 68 by the claw 68, it is delivered into a tray 79 outside the apparatus.

The image recording apparatus for the photothermographic element according to the invention is not limited to the illustrated example. Any of image recording apparatus of various constructions may be used as long as they are adapted for photothermographic elements.

### EXAMPLE

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

#### Example 1

Organic silver salt dispersions A to J were prepared as follows. Using these dispersions, coated samples were prepared for confirming the benefits of the invention.

#### Organic silver salt dispersion A

After 40 grams of behenic acid, 7.3 grams of stearic acid, and 500 ml of water were stirred for 15 minutes at 90°C, 187 ml of 1N NaOH aqueous solution was added over 15 minutes. With 61 ml of 1N nitric acid aqueous solution added, the mixture was cooled to 50°C. Then 124 ml of 1N silver nitrate aqueous solution was added over 2 minutes and the solution combined was agitated for a further 30 minutes. Thereafter, the solids were separated by suction filtration and washed with water until the water filtrate reached a conductivity of 30  $\mu$ S/cm.

The thus obtained solids were handled as a wet cake without drying. To 100 grams as dry solids of the wet cake were added 10 grams of polyvinyl alcohol (trade name: PVA-205) and water. This was further diluted with water to a total weight of 500 g and pre-dispersed by a homomixer.

The pre-dispersed liquid was processed three times by a dispersing machine Micro-Fluidizer M-110S-EH (with G10Z interaction chamber, manufactured by Microfluidex International Corporation) which was operated under a pressure of 1,750 kg/cm<sup>2</sup>. There was obtained a dispersion of organic acid silver microcrystalline grains having a volume weighed mean diameter of 0.93  $\mu$ m as measured by Master Sizer X (Malvern Instruments Ltd.). The desired dispersion temperature was set by mounting serpentine heat exchangers at the front and rear sides of the interaction chamber and adjusting the temperature of refrigerant.

Organic silver salt dispersion B

An organic silver salt dispersion B was prepared by the same procedure as the preparation of organic silver salt dispersion A except that silver halide A to be described later was added to the pre-dispersed liquid in an amount to give 10 mol% of silver halide based on the organic silver salt, the resulting liquid was thoroughly agitated and then processed by the dispersing machine. It is understood that the procedure after the addition of silver halide A was carried out in light-shielded conditions.

Organic silver salt dispersions C to I

Organic silver salt dispersions C to I were prepared by the same procedure as the preparation of organic silver salt dispersion A except that the amount of water added during pre-dispersion, the pressure during dispersing operation, the number of dispersing cycles, and the cooling procedure during dispersing operation were changed. See Tables 1 and 2.

Organic silver salt dispersion J

The pre-dispersed liquid obtained in the preparation of organic silver salt dispersion A was admitted into a vessel together with 1,400 g of zirconia beads having a mean diameter of 0.5 mm and dispersed for 5 hours in a dispersing machine 1/4G Sand Grinder Mill (by Imex K.K.). There was obtained a dispersion of organic silver salt grains having a volume weighed mean diameter of 1.65  $\mu\text{m}$ .

Organic silver salt dispersion K

Following the preparation of organic silver salt dispersion A, this dispersion was heated at 72°C and with stirring, a calcium bromide aqueous solution was added in an amount to give 10 mol% of calcium bromide based on the organic silver salt. After the completion of addition, the mixture was agitated for a further 30 minute while maintaining it at a temperature of 72°C, obtaining an organic silver salt/silver bromide mixed composition. To this, 6  $\mu\text{mol}$  of dipotassium hexachloroiridate, 8.5  $\mu\text{mol}$  of sodium thiosulfate, 1.1  $\mu\text{mol}$  of 2,3,4,5,6-pentafluorophenyldiphenylphosphine selenide, 0.2  $\mu\text{mol}$  of Tellurium Compound 1, 0.33  $\mu\text{mol}$  of chloroauric acid, and 23  $\mu\text{mol}$  of thiocyanic acid were added per mol of organic silver salt/silver bromide mixed composition. The mixture was ripened for 120 minutes. Thereafter, with stirring, Sensitizing Dye A was added in an amount of  $3.5 \times 10^{-5}$  mol per mol of organic silver salt/silver bromide mixed composition, and after 5 minutes of stirring, Compound A was added in an amount of  $4.6 \times 10^{-4}$  mol. After 5 minutes of stirring, there was obtained an organic silver salt dispersion K.

The volume weighed mean diameters of the organic silver salt dispersions thus obtained are shown in Table 2.

Silver halide grains A

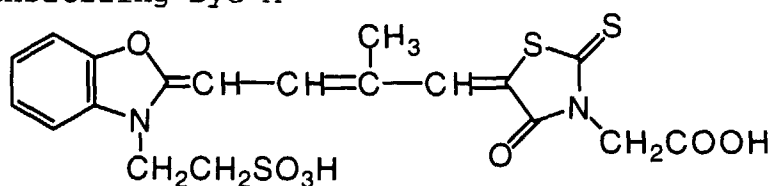
In 700 ml of water were dissolved 22 grams of phthalated gelatin and 30 mg of potassium bromide. The solution was adjusted to pH 5.0 at a temperature of 40°C. To the solution, 159 ml of an aqueous solution containing 18.6 grams of silver nitrate and an aqueous solution containing potassium bromide were 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 an aqueous solution containing 8  $\mu\text{mol/liter}$  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. Desalting was then carried out by lowering the pH to cause agglomeration and sedimentation. With 0.1 gram of phenoxyethanol added, the emulsion was adjusted to pH 5.9 and pAg 8.0. There were obtained cubic grains having a mean grain size of 0.07  $\mu\text{m}$ , a coefficient of variation of the projected area diameter of 8%, and a (100) face proportion of 86%.

The thus obtained silver halide grains A were heated at 60°C, to which 85  $\mu\text{mol}$  of sodium thiosulfate, 11  $\mu\text{mol}$  of 2,3,4,5,6-pentafluorophenyldiphenylphosphine selenide, 2  $\mu\text{mol}$  of Tellurium Compound 1, 3.3  $\mu\text{mol}$  of chloroauric acid, and 230  $\mu\text{mol}$  of thiocyanic acid were added per mol of silver. The emulsion was ripened for 120 minutes.

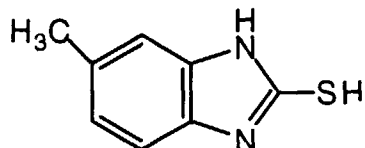
Thereafter the temperature was lowered to 40°C. With stirring,  $3.5 \times 10^{-4}$  mol of Sensitizing Dye A was added per mol of silver halide. After 5 minutes of stirring,  $4.6 \times 10^{-3}$  mol of Compound A was added per mol of silver halide. After 5 minutes of stirring, the emulsion was quenched to 25°C, completing the preparation of silver halide grains A.

Note that Sensitizing Dye A, Compound A and Tellurium Compound 1 used herein have the following chemical structures.

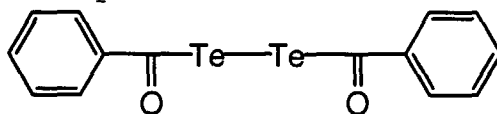
Sensitizing Dye A



Compound A



Tellurium Compound 1



#### Solid particle dispersions of chemical addenda

Solid particle dispersions of tetrachlorophthalic acid, 4-methylphthalic acid, 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, phthalazine, and tribromomethylphenylsulfone were prepared.

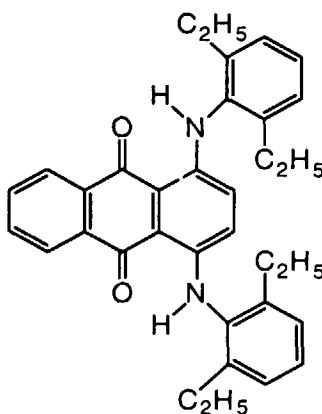
To tetrachlorophthalic acid were added 0.81 gram of hydroxypropyl methyl cellulose and 94.2 ml of water. They were thoroughly agitated to form a slurry, which was allowed to stand for 10 hours. A vessel was charged with the slurry together with 100 ml of zirconia beads having a mean diameter of 0.5 mm. A dispersing machine as used above in the preparation of the organic acid silver grain dispersion was operated for 5 hours for dispersion, obtaining a solid particle dispersion of tetrachlorophthalic acid in which particles with a diameter of up to 1.0  $\mu\text{m}$  accounted for 70% by weight.

Solid particle dispersions of the remaining chemical addenda were similarly prepared by properly changing the amount of the dispersing agent and the dispersion time to achieve a desired mean particle size.

#### Dyed polymer particle dispersion

A mixture of 2 grams of Dye A, 6 grams of a methyl methacrylate-methacrylic acid (85/15) copolymer and 40 ml of ethyl acetate was heated at 60°C for dissolution. This solution was added to 100 ml of an aqueous solution containing 5 grams of polyvinyl alcohol. The mixture was finely dispersed by a high-speed homogenizer (Nippon Seiki Mfg. K.K.) at 12,000 rpm for 5 minutes, obtaining an emulsified dispersion P of polymer particles having a mean particle size of 0.3  $\mu\text{m}$ .

Dye A

Emulsion layer coating solution 1

To the above-prepared organic silver salt grain dispersion A (corresponding to 1 mol of silver), the above-prepared silver halide grains A in an amount of 10 mol% of silver halide based on the organic acid silver and the binder and developing addenda described below were added, obtaining an emulsion layer coating solution 1.

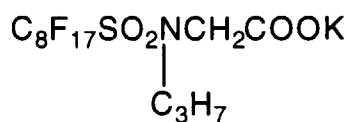
Binder:	
LACSTAR 3307B SBR latex	430 g
Developing addenda:	
Tetrachlorophthalic acid	5 g
1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane	98 g
Phthalazine	9.2 g
Tribromomethylphenylsulfone	12 g
4-methylphthalic acid	7 g
Dye:	
Dye A (as dyed polymer particle dispersion)	4 g

It is noted that LACSTAR 3307B is a styrene-butadiene rubber (SBR) latex commercially available from Dai-Nippon Ink & Chemicals K.K. wherein the polymer has an equilibrium moisture content of 0.6 wt% at 25°C and RH 60% and the dispersed particles have a mean particle diameter of about 0.1 to 0.15  $\mu\text{m}$ .

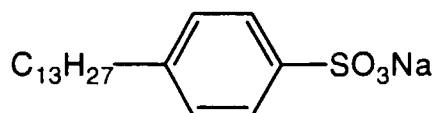
Emulsion surface protective layer coating solution

A surface protective layer coating solution was prepared by adding 0.26 gram of Surfactant A, 0.09 gram of Surfactant B, 0.9 gram of silica microparticulates having a mean particle size of 2.5  $\mu\text{m}$ , 0.3 gram of 1,2-bis(vinylsulfonylacetamide)ethane, and 64 grams of water to 10 grams of inert gelatin.

## Surfactant A

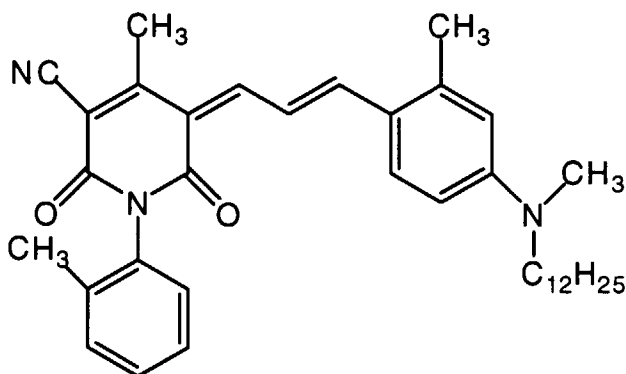


## Surfactant B

Dye dispersion

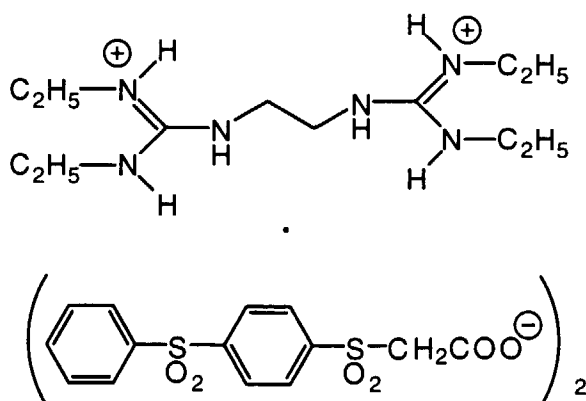
In 35 grams of ethyl acetate was dissolved 0.8 gram of Dye B shown below. To this solution, 85 grams of an aqueous solution of 6% by weight polyvinyl alcohol (PVA-217) was added. The mixture was agitated for 5 minutes by a homogenizer. Thereafter, the ethyl acetate was volatilized off for solvent removal. The residue was diluted with water, obtaining a dye dispersion.

## Dye B

Solid base particle dispersion

To 26 grams of a solid base shown below was added 234 grams of an aqueous solution of 2% by weight polyvinyl alcohol (PVA-217). The mixture was thoroughly agitated into a slurry, which was left to stand for 10 hours. The slurry was admitted into a vessel together with 100 ml of zirconia beads having a mean diameter of 0.5 mm and dispersed for 5 hours in a dispersing machine 1/4G Sand Grinder Mill (by Imex K.K.). There was obtained a solid base particle dispersion.





## Haze

Using a separately assembled haze meter, the proportion of light diffused by a sample relative to the entire transmitted light was determined. This proportion expressed in % is a haze value.

## Fog

Using the image recording apparatus shown in FIG. 1, an unexposed coated sample was developed at 120°C for 15 seconds. The image density of the developed sample was measured by means of a densitometer. The density measurement is reported as a fog value.

## Sensitivity

Using the image recording apparatus shown in FIG. 1, a coated sample was exposed to light in the exposure unit including a 660-nm diode as the light source (FIG. 2), and developed at 120°C for 15 seconds. The density of the thus obtained image was measured by means of a densitometer. The sensitivity is calculated from the measurements as the reciprocal of a ratio of an exposure providing a density of the minimum density ( $D_{min}$ ) plus 1.0 and expressed based on a sensitivity of 100 for sample No. 101.

The results are shown in Table 2. In Table 1, concentrations are expressed in % by weight.

Table 1

Dispersion composition								
Designation of organic salt dispersion	Organic silver salt concentration	Addition of photosensitive silver salt (mol% based on organic silver)			Dispersing agent			
		Organic silver salt concentration	Silver halide A added (10 mol%)	NO	PVA-205	2.0 %	Water	
								Type
Dispersion A	20 %			NO	PVA-205	2.0 %	Water	
Dispersion B	20 %			Silver halide A added (10 mol%)	PVA-205	2.0 %	Water	
Dispersion C	20 %			NO	PVA-205	2.0 %	xylene/n-butanol=2/1	
Dispersion D	20 %			NO	PVA-205	2.0 %		Water
Dispersion E	20 %			NO	PVA-205	2.0 %		Water
Dispersion F	20 %			NO	PVA-205	2.0 %		Water
Dispersion G	20 %			NO	PVA-205	2.0 %		Water
Dispersion H	20 %			NO	PVA-205	2.0 %		Water
Dispersion I	20 %			NO	PVA-205	2.0 %		Water
Dispersion J	20 %			NO	PVA-205	2.0 %		Water
Dispersion K	20 %			NO	PVA-205	2.0 %		Water

Table 1 (cont'd)

Designation of organic or silver salt dispersion	Dispersing conditions				Sand Grinder			Mill dispersion	
	Microfluidizer dispersion		Dispersion temperature		Dispersing time	RPM	Dispersion temperature immediately after dispersion	Dispersing time	RPM
	Differential pressure drop	Number of dispersing cycles	Cooling step	immediately after pressure drop					
Dispersion A	1750kg/cm <sup>2</sup>	3 cycles	YES	45°C	-	-	-	-	-
Dispersion B	1750kg/cm <sup>2</sup>	3 cycles	YES	45°C	-	-	-	-	-
Dispersion C	1750kg/cm <sup>2</sup>	3 cycles	YES	47°C	-	-	-	-	-
Dispersion D	2500kg/cm <sup>2</sup>	3 cycles	YES	48°C	-	-	-	-	-
Dispersion E	1200kg/cm <sup>2</sup>	5 cycles	YES	43°C	-	-	-	-	-
Dispersion F	900kg/cm <sup>2</sup>	7 cycles	YES	41°C	-	-	-	-	-
Dispersion G	600kg/cm <sup>2</sup>	10 cycles	YES	41°C	-	-	-	-	-
Dispersion H	2000kg/cm <sup>2</sup>	3 cycles	NO	72°C	-	-	-	-	-
Dispersion I	2200kg/cm <sup>2</sup>	3 cycles	NO	93°C	-	-	-	-	-
Dispersion J	-	-	-	-	5hr.	1000	35°C	-	-
Dispersion K	1750kg/cm <sup>2</sup>	3 cycles	YES	45°C	-	-	-	-	-

Table 2

Sample No.	Organic silver salt dispersion prepared and its grain size		Coated sample using organic silver salt dispersion and its characteristics			
	Designation of dispersion	Grain size	Addition of photosensitive silver salt (mol% based on organic silver)	Haze	Fog	Sensitivity
101	Dispersion A	0.93 $\mu\text{m}$	Silver halide A added (10 mol%)	10.0	0.11	100
102*	Dispersion B	0.98 $\mu\text{m}$	NO	12.0	0.90	10
103*	Dispersion C	1.25 $\mu\text{m}$	Silver halide A added (10 mol%)	38.0	1.00	70
104	Dispersion D	0.82 $\mu\text{m}$	Silver halide A added (10 mol%)	10.0	0.13	105
105	Dispersion E	1.20 $\mu\text{m}$	Silver halide A added (10 mol%)	15.0	0.11	98
106	Dispersion F	1.22 $\mu\text{m}$	Silver halide A added (10 mol%)	15.0	0.10	95
107	Dispersion G	1.60 $\mu\text{m}$	Silver halide A added (10 mol%)	19.0	0.10	90
108	Dispersion H	1.05 $\mu\text{m}$	Silver halide A added (10 mol%)	12.0	0.13	97
109	Dispersion I	1.12 $\mu\text{m}$	Silver halide A added (10 mol%)	13.0	0.14	95
110*	Dispersion J	1.65 $\mu\text{m}$	Silver halide A added (10 mol%)	20.0	1.10	85
111*	Dispersion K	0.93 $\mu\text{m}$	Organic silver salt partially converted into silver halide (10 mol%)	11.0	0.12	50

\* comparison

It is seen from the results of sample Nos. 101 and 110 that the dispersion method using a sand grinder mill yields a sample which is practically unacceptable because of high haze and fog values. The dispersion method of the invention involving converting a water dispersion containing an organic silver salt, but substantially free of a photosensitive silver salt into a high speed flow, and causing a pressure drop to the flow yields a sample which is practically acceptable because of low haze and fog values.

It is seen from the results of sample Nos. 101, 102 and 111 that a method of dispersing a dispersion containing both an organic silver salt and a photosensitive silver salt by means of a dispersing apparatus yields a sample having a high fog value; and that a method of dispersing a dispersion containing an organic silver salt, but free of a photosensitive silver salt by means of a dispersing apparatus and thereafter, converting a part of the organic silver salt into a photosensitive silver salt by the halogen conversion method yields a sample having a low sensitivity.

It is seen from the results of sample Nos. 101 and 103 that no improvements are obtained when the dispersing solvent of the organic silver salt-containing dispersion is changed to a non-aqueous solvent.

It is seen from the results of sample Nos. 101 and 104 to 107 that better results are obtained when the differential pressure upon pressure drop is in the range of 900 to 3,000  $\text{kg/cm}^2$ , and especially 1,500 to 3,000  $\text{kg/cm}^2$ .

It is seen from the results of sample Nos. 101, 108 and 109 that better results are obtained when the step of quenching by 5 to 50°C to lower the temperature of water dispersion below 65°C is involved before and/or after the pressure drop step.

Example 2

Sample Nos. 201 to 211 were prepared by the same procedure as sample No. 101 of Example 1 except that the binder and coating solvent were changed as shown in Table 3. The samples were examined by the following tests.

Coating surface quality

Each coated sample was cut into a section of 10 cm x 10 cm where the number of agglomerated specks was counted. The surface quality was evaluated according to the following criterion.

Rating	Number of specks
⊙	0 to 5
○	6 to 20
△	20 to 100
X	more than 100

Silver tone after heat development

Each coated sample was exposed through a step wedge and heat developed at 120°C for 15 seconds. The developed sample was observed under white light. A degree of deviation from the black tone regarded practically favorable was evaluated by a sensory test according to the following criterion.

Rating	Perception
⊙	black
○	a slight tone change from black, but inoffensive
△	brown, yellow, red or otherwise at a certain exposure
X	brown, yellow, red or otherwise

The results are shown in Table 3. In Table 3, the equilibrium moisture content at 25°C and RH 60% of the binder in the photosensitive layer is also reported.

Table 3

Sample No.	Photosensitive layer binder		Organic silver salt dispersion	Coating solvent	Coating surface quality	Silver tone
	Type	Moisture content (wt%)				
101	LACSTAR 3307B	0.6	Dispersion A	Water	⊙	⊙
201	LACSTAR 3307B	0.6	Dispersion A	Water/methanol= 70/30	⊙	⊙
202	LACSTAR 3307B	0.6	Dispersion A	Water/methanol =40/60	○	⊙

Table 3 (continued)

Sample No.	Photosensitive layer binder		Organic silver salt dispersion	Coating solvent	Coating surface quality	Silver tone
	Type	Moisture content (wt%)				
203	LACSTAR 3307B	0.6	Dispersion A	Water/methanol =20/80	X	⊙
204	PVA-205	3.2	Dispersion A	Water	○	X
205	Gelatin	10.5	Dispersion A	Water	X	△
206	P-1	0.6	Dispersion A	Water	⊙	○
207	P-2	0.4	Dispersion A	Water	⊙	○
208	P-3	0.3	Dispersion A	Water	⊙	○
209	P-4	0.5	Dispersion A	Water	⊙	○
210	P-5	0.3	Dispersion A	Water	⊙	○
211	P-6	0.3	Dispersion A	Water	⊙	○

It is evident from Table 3 that when an organic silver salt dispersion according to the invention is used and an organic silver salt-containing layer is formed by coating a coating solution whose solvent contains at least 30% by weight of water, followed by drying, and when a polymer latex having an equilibrium moisture content of up to 2% by weight at 25°C and RH 60% is used as the binder of the organic silver salt-containing layer, photothermographic elements having good coating surface quality and good silver tone can be produced through the coating step using an aqueous solvent which is advantageous from the standpoints of environmental protection and economy. That is, the preferred embodiments of the invention achieve improvements in coating surface quality and silver tone.

According to the invention, a photothermographic element which has a low haze and high sensitivity and is further improved in coating surface quality and silver tone can be produced through the coating step using an aqueous solvent without resorting to organic solvents which are hazardous to humans and expensive.

### Claims

1. A method for preparing a photothermographic image forming medium coating solution, comprising the steps of:

converting a water dispersion containing at least an organic silver salt, but substantially free of a photosensitive silver salt into a high pressure, high speed flow,  
causing a pressure drop to the flow, and  
thereafter, mixing the flow with a photosensitive silver salt.

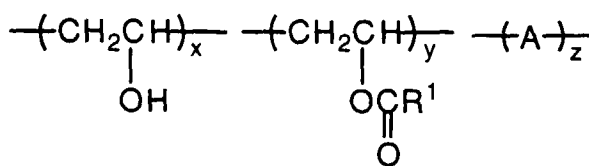
2. The method of claim 1 wherein the pressure drop is in the range of 900 to 3,000 kg/cm<sup>2</sup>.

3. The method of claim 1 wherein the pressure drop is in the range of 1,500 to 3,000 kg/cm<sup>2</sup>.

4. The method of claim 1 further comprising a cooling step prior to the conversion step and/or after the pressure drop step whereby said water dispersion is maintained at a temperature in the range of 5 to 90°C.

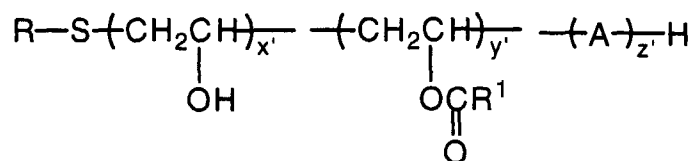
5. The method of claim 1 wherein said water dispersion contains as a dispersant a compound of the following formula (I) or (II):

(I)



wherein R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, A represents recurring units of a copolymerizable ethylenically unsaturated monomer, and letters x, y and z represent the molar fractions of the respective components, x is 50 to 90 mol%, y is 0 to 50 mol%, z is 0 to 30 mol%, and x + y + z = 100 mol%,

(II)



wherein R represents alkyl having at least 8 carbon atoms or aryl, R<sup>1</sup> represents alkyl of 1 to 4 carbon atoms, A represents recurring units of a copolymerizable ethylenically unsaturated monomer, and letters x', y' and z' represent the molar fractions of the respective components, x' is 50 to 99.9 mol%, y' is 0 to 50 mol%, z' is 0 to 30 mol%, and x' + y' + z' = 100 mol%.

6. The method of claim 1 wherein the conversion step uses a pressure of 100 to 600 kg/cm<sup>2</sup> and a flow velocity of from several meters per second to about 30 m/sec.
7. The method of claim 1 wherein the conversion and pressure drop steps include dispersing the flow at a flow velocity of 200 to 600 m/sec and a differential pressure upon pressure drop of 900 to 3,000 kg/cm<sup>2</sup>.
8. The method of claim 7 wherein the number of dispersing cycles is 1 to 10.
9. The method of claim 5 wherein the dispersant is contained in an amount of 1 to 30% by weight of the organic silver salt.
10. A method for preparing a photothermographic element, comprising the steps of:
  - converting a water dispersion containing at least a non-photosensitive organic silver salt, but substantially free of a photosensitive silver salt into a high pressure, high speed flow,
  - causing a pressure drop to the flow,
  - thereafter, mixing the flow with at least a photosensitive silver salt and a binder to form a coating solution, and
  - coating the coating solution onto a support.
11. The method of claim 10 wherein the coating solution further contains a reducing agent.
12. The method of claim 10 wherein the support has an undercoat layer on which the coating solution is coated.
13. A photothermographic element which has been prepared using the photosensitive image forming medium coating solution of any one of claims 1 to 9, said element comprising at least a photosensitive silver salt, an organic silver salt, a reducing agent, and a binder on a support.
14. The photothermographic element of claim 13 wherein said photosensitive image forming medium coating solution is based on a solvent containing at least 30% by weight of water.



- 15.** The photothermographic element of claim 13 wherein a binder in a layer containing the organic silver salt is a polymer latex having an equilibrium moisture content of up to 2% by weight at 25°C and RH 60%.

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FIG. 1

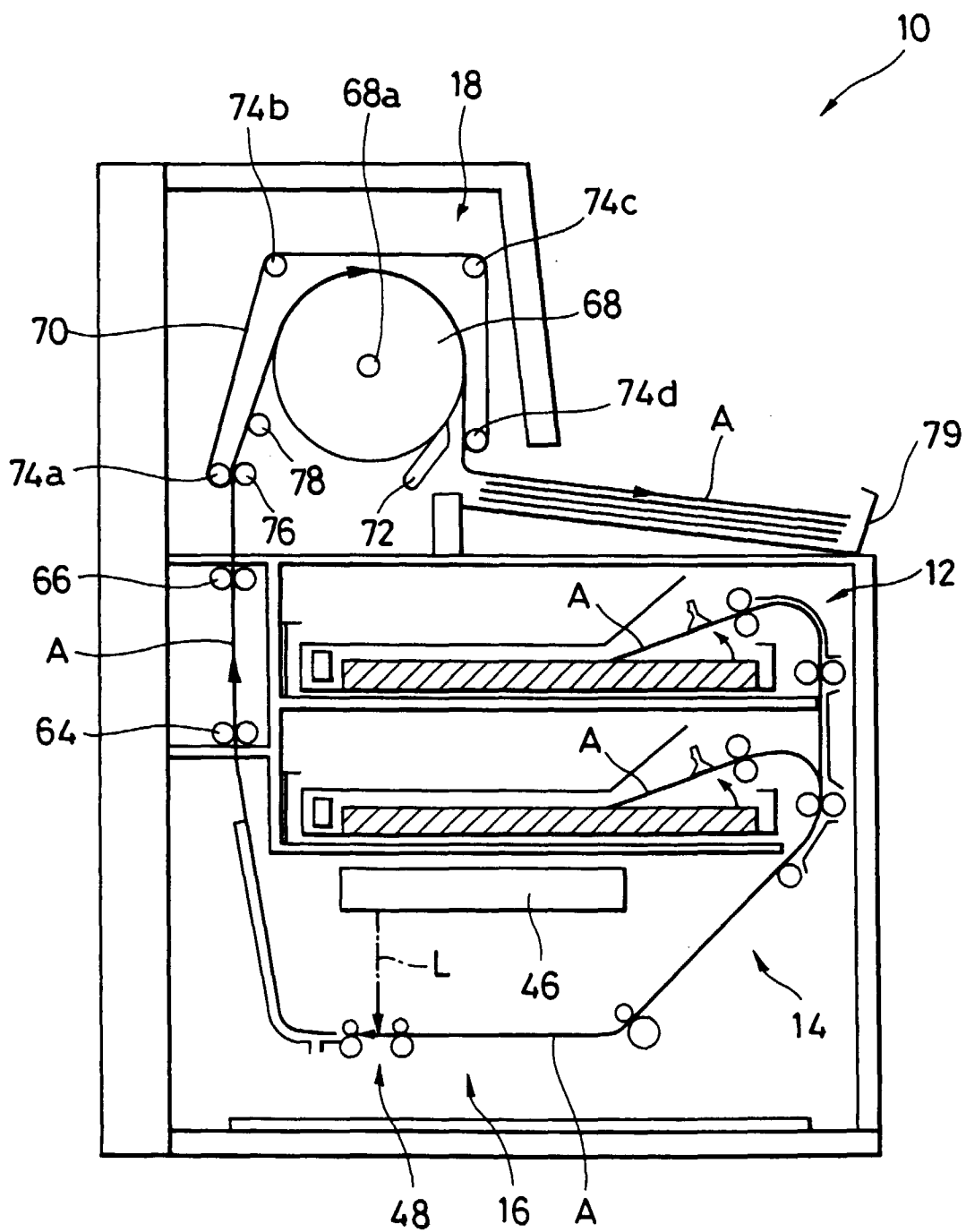
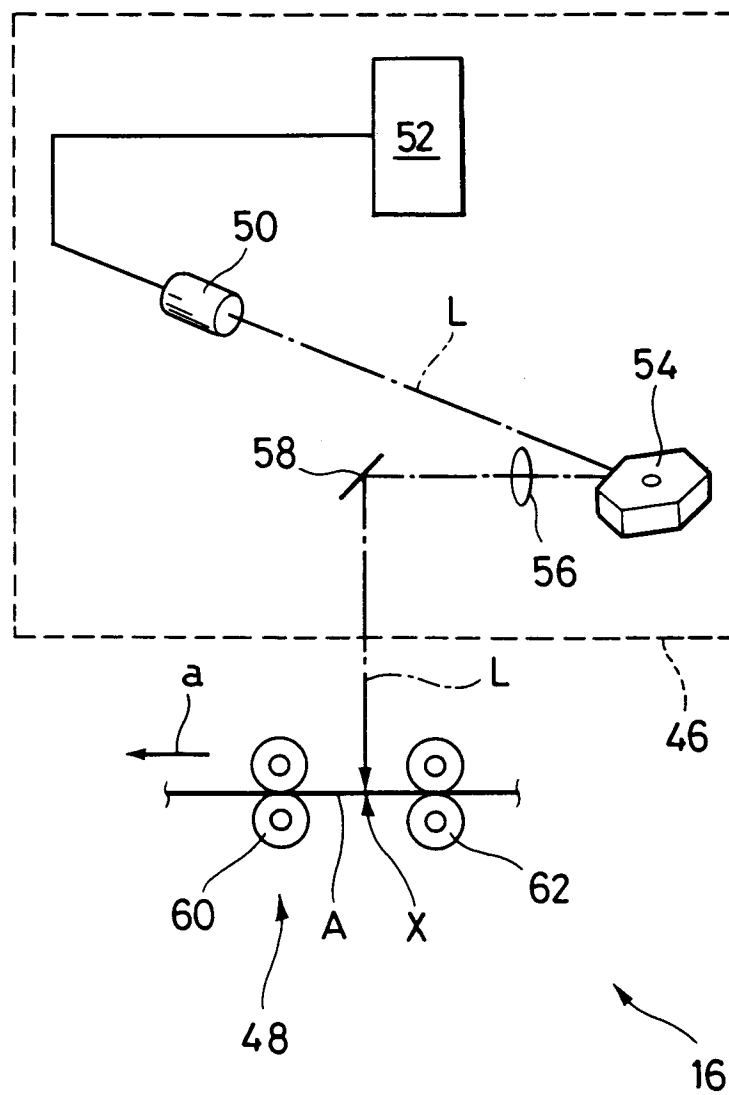


FIG. 2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 1438

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9632 Derwent Publications Ltd., London, GB; Class G06, AN 96-312982 XP002078175 & JP 08 137 044 A (CANON KK) * abstract *	1-3,6-8, 13	G03C1/498
D,A	WO 97 04355 A (AGFA GEVAERT NV ;UYTTERHOEVEN HERMAN (BE); GILLIAMS YVAN (BE)) 6 February 1997 * page 4, line 18 - page 6, line 22 * * page 7, line 7 - page 8, line 8 * * page 10, line 26 - line 34 * * page 12, line 4 - line 25 * * page 31, line 26 - line 32 * * page 11, line 20 - line 28 *	1-12	
X		13-15	
A	EP 0 736 799 A (FUJI PHOTO FILM CO LTD) 9 October 1996 * page 12, line 48 - page 13, line 2 *	1,5	
A		13-15	
A	US 5 424 182 A (MARGINEAN SR BARRY L ET AL) 13 June 1995 * column 5, line 19 - line 35 * * column 6, line 23 - line 36 * * examples 1,2,4 * * claims 1,4 *	1,5	
A	DE 44 40 337 A (DDS DRUG DELIVERY SERVICES GES) 15 May 1996 * page 2, line 25 - page 5, line 5 *	1	
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>21 September 1998</b>	Examiner <b>Lindner, T</b>
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