

[54] **PHOTOTHERMOGRAPHIC ELEMENT,
COMPOSITION AND PROCESS**

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[22] Filed: **June 14, 1972**

[21] Appl. No.: **262,907**

[52] U.S. Cl. **96/114.1, 96/94 BF, 96/114.6**

[51] Int. Cl. **G03c 1/02, G03c 1/72**

[58] Field of Search **96/94 BF, 94 R, 114.1,
96/114.6**

[56] **References Cited**

UNITED STATES PATENTS

3,549,379 12/1970 Hellings et al. 96/114.1

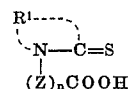
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[57] **ABSTRACT**

A photothermographic element comprising a support having thereon (a) a reducing agent, (b) a silver salt of a thione compound, the thione compound being represented by the formula:



wherein n is 1 to 10, R^1 represents atoms completing a 5-member heterocyclic nucleus, Z is alkylene, such as alkylene containing 1 to 10 carbon atoms, and (c) a photosensitive component consisting essentially of photosensitive silver halide, in the absence of an image stabilizer or stabilizer precursor, can provide a developed and stabilized image upon imagewise exposure and then overall heating of the element. The photothermographic element can, but need not, contain a binder for the described components. Other addenda employed in photothermographic materials can be employed with the photothermographic element.

31 Claims, No Drawings

PHOTOTHERMOGRAPHIC ELEMENT, COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photothermographic elements, compositions and processes for developing an image with processing with heat which can provide transparency in non-image areas. In one of its aspects it relates to photothermographic elements suitable for processing with heat containing a combination of certain reducing agents and thione complexes of silver with certain compounds which provide in the absence of image stabilizer or stabilizer precursor a stable image which is transparent in non-image areas. In another of its aspects it relates to photothermographic compositions having the described properties. It further relates to a process for developing the described image in the absence of processing solutions.

2. Description of the State of the Art

Photothermographic materials for developing an image in a photothermographic element with processing with heat are well known, as described, for example, in U.S. Pat. No. 3,457,075 of Morgan et al., issued July 22, 1969; U.S. Pat. No. 3,152,904 of Shepard et al., issued Oct. 13, 1964; U.S. Pat. No. 3,392,020 of Yutzy and Yackel, issued July 9, 1968 and Belgian Pat. No. 765,452 issued May 28, 1971. It has been desirable to provide a photothermographic element which provides transparency in the non-image areas in the absence of additional dye layers or components other than the photothermographic components.

Also, in order to provide a desired stable image, it has been often necessary to provide a separate image stabilizer or image stabilizer precursor in the photothermographic element or composition. This image stabilizer or stabilizer precursor, in most instances, provides a stable complex with one or more of the components of the photothermographic material, but increases the cost of the photothermographic material.

In this connection thione compounds have been used in photosensitive materials for different purposes. For example, silver complexes of thione compounds have been employed in photosensitive materials as a source of silver for physical development in solution processing such as described in Belgian Pat. No. 739,708 issued Dec. 15, 1969. Such complexes have been employed as a photosensitive component as described in Belgian Pat. No. 739,705 issued Dec. 15, 1969 or as antifoggants as described in Belgian Patent 739,709 issued Dec. 15, 1969. They have also been used with silver dye complexes as described, for example, in Belgian Pat. 765,452 issued May 28, 1971. They have been used for other purposes also such as described in East German Pat. No. 10,184 of VEB Film Fabrik, issued July 28, 1955 and U.S. Pat. No. 3,433,640 of Nishio et al., issued Mar. 18, 1969. Surprisingly, however, thione compounds as a class do not provide the desired properties in photosensitive materials for processing with heat in which transparency is desired in the non-image areas of a processed photothermographic element.

It has also been desirable to eliminate a binding agent in photothermographic materials. Photothermographic components have been combined in a polymeric binder and coated on a suitable support. It has surprisingly

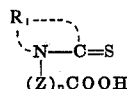
been found that with the photothermographic materials of the invention that such a binding agent can be eliminated. This is demonstrated in following Example 24.

It has further been desirable to provide a photothermographic material which employs photosensitive silver halide due to its high photosensitivity, which enables use of commonly employed silver halide technology. This eliminates the necessity for preparation of silver halide in situ in the photosensitive composition and enables easier control for the preparation.

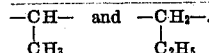
There has accordingly been a continuing need to provide a photothermographic element, composition and process which provides a photothermographic material which eliminates the need of a separate stabilizer or stabilizer precursor component, provides transparency in non-image areas upon processing with heat, eliminates the need for preparation of the silver halide commonly employed in the photosensitive component in situ in the photothermographic material, and provides ease of control of the preparation of the photothermographic material.

SUMMARY OF THE INVENTION

It has been found according to the invention that the described improvements are provided by a photothermographic element and/or composition comprising (a) a reducing agent, typically a polyhydroxybenzene reducing agent, (b) a silver salt of a thione compound, the thione compound being represented by the formula:



wherein n is 1 to 10, typically 1 to 3, R^1 represents atoms completing a 5 member heterocyclic nucleus, such as a thiazoline nucleus, Z is alkylene, such as alkylene containing 1 to 10 carbon atoms, (c) a photosensitive component consisting essentially of photosensitive silver halide, in the absence of an image stabilizer or stabilizer precursor, and, if desired, in the absence of a binder. A 5 member heterocyclic nucleus and alkylene as described include a 5 member heterocyclic nucleus and/or alkylene containing substituent groups which do not adversely affect the desired properties of the photothermographic element, such as alkyl containing 1 to 3 carbon atoms, e.g., methyl, ethyl or propyl, or phenyl. Examples of alkylene are methylene ($-\text{CH}_2-$), ethylene ($-\text{CH}_2\text{CH}_2-$), propylene ($-\text{CH}_2\text{CH}_2\text{CH}_2-$),



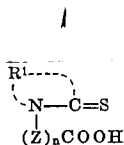
. After imagewise exposure of this photothermographic material, an image can be developed which has transparency in the non-image areas by merely heating the element to moderately elevated temperatures, such as about 100°C to about 250°C for a short time, such as for several seconds.

DETAILED DESCRIPTION OF THE INVENTION

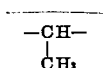
Various reducing agents can be employed in the described photothermographic materials of the invention. These are typically silver halide developing agents and

include, for example, polyhydroxybenzenes such as hydroquinone developing agents including, for instance, hydroquinone, alkyl substituted hydroquinones, exemplified by tertiary butyl hydroquinone, methyl hydroquinone, 2,5-dimethyl hydroquinone and 2,6-di-methyl hydroquinone; catechols and pyrogallol; halo-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinones such as methoxy hydroquinone or ethoxy hydroquinone and the like. Other reducing agents which can be employed include reductone developing agents such as anhydro dihydro piperidino hexose reductone; hydroxy tetronic acid reducing agents and hydroxy tetronimide developing agents; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and those described in British Pat. 930,572 published July 3, 1963; certain hydroxyl amine developing agents; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals, and other ascorbic acid derivatives; phenylenediamine developing agents; certain aminophenol developing agents and the like. Combinations of reducing agents can also be employed. One test which can be employed for a suitable reducing agent is set out in following Example 1. In this example a suitable reducing agent is one which provides a developed image within about 90 seconds at a temperature of about 100° to 250°C upon heating the photothermographic element containing the reducing agent.

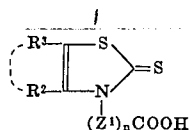
A silver salt of a thione compound is also employed in the photothermographic materials of the invention. The silver salt of the thione can be prepared in situ in the photothermographic materials by combining a source of silver, such as silver trifluoroacetate, with the thione compound in the composition. The thione compound is a compound represented by the formula:



wherein R¹ and Z are as described. Examples of suitable 5 member heterocyclic nuclei are thiazoline-2-thione, benzothiazoline-2-thione, imidazoline thione or similar heterocyclic thione nucleus. The heterocyclic nucleus can contain substituent groups which do not adversely affect the described photothermographic materials such as alkyl containing 1 to 3 carbon atoms, or phenyl. Alkylene as employed herein includes so called branched chain alkylene such as

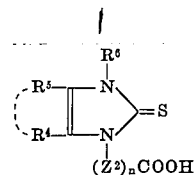


An especially suitable thione compound is a thiazoline-2-thione represented by the formula:



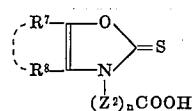
wherein n is 1 to 10, typically 1 to 4; Z¹ is alkylene containing 1 to 4 carbon atoms, typically methylene; R² and R³ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group. The alkyl, aryl and benzo groups which do not adversely affect the described photothermographic materials, include groups such as alkyl containing 1 to 4 carbon atoms or phenyl.

Another suitable thione compound is an imidazoline-2-thione represented by the formula:



wherein n is 1 to 10, typically 1 to 3; Z² is alkylene containing 1 to 4 carbon atoms, typically methylene; R⁶ is alkyl, typically alkyl containing 1 to 3 carbon atoms, such as methyl, ethyl or propyl, aryl containing 6 to 10 carbon atoms, such as phenyl, or a carboxyalkyl, such as carboxyethyl and carboxymethyl; R⁴ and R⁵ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl and propyl, aryl containing 6 to 10 carbon atoms, such as phenyl or tolyl, or R⁴ and R⁵ taken together are atoms completing a benzo group.

A further suitable thione compound is an oxazoline-2-thione represented by the formula:



wherein n is 1 to 10, typically 1 to 3; Z² is as described; R⁷ and R⁸ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl and propyl, aryl containing 6 to 10 carbon atoms, such as phenyl or tolyl, or R⁷ and R⁸ taken together are atoms completing a benzo group.

Examples of suitable thione compounds within the described formulas include:

3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)benzothiazoline-2-thione,

3-(2-carboxyethyl)-5-phenyl-1,3,4-oxadiazoline-2-thione,

3-(2-carboxyethyl)-5-phenyl-1,3,4-thiadiazoline-2-thione,

3-carboxymethyl-4-methyl-4-thiazoline-2-thione,

3-(2-carboxyethyl)-1-phenyl-1,3,4-triazoline-2-thione,

1,3-bis(2-carboxyethyl)imidazoline-2-thione,

1,3-bis(2-carboxyethyl)benzimidazoline-2-thione,

3-(2-carboxyethyl)-1-methylimidazoline-2-thione,

3-(2-carboxyethyl)benzoxazoline-2-thione, and

3-(1-carboxyethyl)-4-methyl-4-thiazoline-2-thione.

The described thione compounds can be prepared employing processes known in the art. The described

silver complexes of the thione compounds can be prepared in situ, as described, or the silver complexes can be isolated. The described 4-thiazoline-2-thiones, for instance, can be prepared from amino acids. Preparation of the described thione compounds can be carried out employing procedures described, for example, in an article of R. W. Lamon and W. J. Humphlett, *Journal of Heterocyclic Chemistry*, Volume 4, pages 605-609, 1967. 4-thiazoline-2-thiones bearing a carboxy alkyl group in the three position can, for instance, be prepared by treating a dithiocarbamic acid derived from an amino acid and carbon disulfide with an alpha halogenated ketone. In this process the use of methyl alcohol as a solvent can improve the solubility of the reactants.

The photothermographic materials of the invention contain photosensitive silver halide as a photosensitive component. An advantage of the photothermographic materials is that the concentration of photosensitive silver halide which is needed can be very low compared to photographic materials which contain photographic silver halide in the absence of other of the photothermographic components of the invention. For example, the concentration of photosensitive silver halide which is suitable in a photothermographic composition of the invention can be about 0.0025 to about 0.3 moles of photosensitive silver halide per mole of silver as the described complex. In a photothermographic element of the invention the concentration of photosensitive silver halide is typically about 0.02×10^{-3} to about 0.12×10^{-3} moles of silver halide per square foot of support. This is a surprisingly low concentration of photosensitive silver halide in a photographic element. Suitable photosensitive silver halides include, for example, silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide, or mixtures thereof. For the purposes of the invention, silver iodide is also included as a photosensitive silver halide. While the photosensitive silver halide can be prepared in situ in the photothermographic material, this is not necessary according to the invention. The photosensitive silver halide can be coarse or fine-grain, very fine-grain photosensitive silver halide being especially useful. The photosensitive silver halide can be prepared by any of the well-known procedures employed in the photographic art. The silver halide can be prepared, for example, employing single-jet preparation techniques, double-jet preparation techniques, such as techniques employed in preparing Lippmann emulsions and the like. Surface image silver halide materials can be used. If desired, mixtures of surface and internal image silver halide materials can be used. Negative type silver halide is typically employed. The silver halide materials can be regular grain such as described in Klein and Moisar, *Journal of Photographic Science*, Volume 12, No. 5, September-October (1964), pages 242-251.

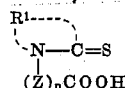
The photosensitive silver halide can be chemically sensitized employing techniques known in the photographic arts.

In preparing the photothermographic material of the invention, one suitable procedure includes preparation of the silver salt of the described thione compound in situ with the photosensitive silver halide. It is desirable to avoid preparation of the silver salt in the presence of compounds which could cause undesired reduction. The preparation of the silver salt in situ can typically include mixing of a source of silver, such as silver tri-

fluoroacetate, with the thione compound as described in following Example 1.

Although a binder is not essential with the photothermographic materials described, a binder can be employed, if desired. The binders which can be employed with the described photothermographic materials include various colloids employed alone or in combination as vehicles and/or binding agents which do not adversely affect the desired photothermographic properties of the described compositions and in various layers of a photothermographic element. Suitable materials can be hydrophilic or hydrophobic. The binders which are suitable are transparent or translucent and include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds such as in latex form and particularly those which increase dimensional stability of photothermographic materials. Suitable binders include polymers such as water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and those which have cross-linking sites which facilitate hardening or curing as well as those having recurring sulfobetaine units. Especially suitable binding agents include high molecular weight materials and resins such as poly(vinyl butyral), cellulose acetate butyrate, poly(methyl methacrylate), poly(vinylpyrrolidone), ethyl cellulose, poly(styrene), poly(vinylchloride), chlorinated rubber, poly(isobutylene), butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid, poly(vinyl alcohol), and high molecular weight ethylene oxide polymers. One test for a suitable binder or vehicle is set out in following Example 1.

Employing a binder, one embodiment of the invention is a photothermographic element comprising a support having thereon (a) a reducing agent, as described, (b) a silver salt of a thione compound, the thione compound being represented by the formula:



wherein n is 1 to 10, R¹ represents atoms completing a 5 member heterocyclic nucleus, typically a thiazoline-2-thione nucleus, Z is alkylene, such as alkylene containing 1 to 10 carbon atoms, as described, (c) a photosensitive component consisting essentially of photosensitive silver halide, and (d) a binder, in the absence of an image stabilizer or stabilizer precursor.

The photothermographic layers and other layers of a photothermographic element according to the invention can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically a flexible support is employed, especially a paper support which can be partially acetylated or coated with baryta and/or an

alpha olefin polymer, particularly a polymer of an alpha olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

Hardenable layers of a photothermographic element, as described, can be hardened by various organic or inorganic hardeners alone or in combination, such as aldehydes, ketones, and the like which do not adversely affect the sensitometric properties of the photothermographic materials. Hardeners which cause adverse reduction of the described composition should be avoided.

The photothermographic elements and materials according to the invention can contain addenda commonly employed in photothermographic elements, such as antistatic and/or conducting layers, plasticizers and/or lubricants, surfactants, matting agents, brightening agents, light-absorbing materials, filter dyes, anti-halation dyes and absorbing dyes, and the like.

The various components of the photothermographic materials of the invention can be added from water solutions or suitable organic solvent solutions can be used. The components can be added using various procedures known in the photographic art.

The photothermographic layer and/or other layers of a photothermographic element according to the invention can be coated by various coating procedures including dip coating, airknife coating, curtain coating or extrusion coating using hoppers of the type described in U.S. Pat. No. 2,681,294 of Beguin, issued June 15, 1954. If desired, two or more layers can be coated simultaneously by procedures known in the art.

A range of concentrations of each component in the described photothermographic material can be employed. Typically, a photothermographic element according to the invention can comprise a support having thereon (a) about 0.2×10^{-3} to about 1.0×10^{-3} moles of said reducing agent, (b) about 0.23×10^{-3} to about 2×10^{-3} moles of silver as the described complex and (c) about 0.02×10^{-3} to about 0.12×10^{-3} moles of the described photosensitive silver halide per square foot of support. An optimum concentration of each component will depend upon the particular components, the desired image, processing temperature and the like.

An especially suitable embodiment of the invention is a photothermographic element comprising a support having thereon (a) a hydroquinone reducing agent, (b) a silver salt selected from the group consisting of silver salts of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione, 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione, 3-(2-carboxyethyl)-benzothiazoline-2-thione, 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof (c) silver iodide, and, if desired, (d) a gelatino binder, in the absence of an image stabilizer or stabilizer precursor.

If desired, an agent, sometimes referred to as an activator toning agent, can be employed with the photothermographic materials of the invention to provide an increase in density at certain processing temperatures. Suitable toning agents, also known as activator-toning agents, include cyclic imide toning agents such as phthalimide, N-hydroxyphthalimide, succinimide, and N-hydroxy succinimide, and the like. These are described, for instance, in Belgian Pat. No. 766,590, issued June 15, 1971. Sulfolane in some instances can provide improved results in the described photother-

mographic compositions. Some photothermographic elements and compositions described according to the invention do not need a toning agent.

If it is desired to provide added silver ion to the described photothermographic compositions of the invention one source of silver ion can be a silver salt of an organic acid can be employed in the described photothermographic materials. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of the developed image. When a silver salt of an organic acid is employed, transparency in the non-image areas of the photothermographic element is often not observed. Therefore, it is often advantageous to avoid the use of silver salts of organic acids. However, if silver salts of organic acids are employed in the described photothermographic materials, suitable silver salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxy stearate, silver caprate, silver myristate, and/or silver palmitate. Other silver compounds which can be employed in the described photothermographic materials include, for instance, silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, and the like. If desired, oxidizing agents which are not silver salts can be employed in the described photothermographic materials.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide employed according to the invention. For instance, additional spectral sensitization can be obtained by treating the silver halide with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion. Spectral sensitizers which can be used include the cyanines, merocyanines, complex(trinuclear or tetranuclear) merocyanines, complex(trinuclear or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines, such as enamines, oxonols, and hemioxonols.

A visible image on a photothermographic element according to the invention can be produced after imagewise exposure within a short time by merely moderately overall heating the photothermographic element. For instance, a visible image on a photothermographic element according to the invention can typically be produced within a few seconds, e.g., about 1 to about 60 seconds after exposure by heating the element to about 100°C. to about 250°C., typically about 130°C. to about 180°C. Usually, the time of heating is less than about 20 seconds, such as about 2 to 5 seconds at a temperature of about 180°C. Optimum time of heating and optimum temperature of heating can be determined employing test procedures well known in the art.

One embodiment of the invention accordingly is a method of developing and stabilizing an image in an exposed photothermographic element comprising a support having thereon (a) a reducing agent, as described, (b) a silver salt of a thione compound, also as described, (c) a photosensitive component consisting essentially of photosensitive silver halide, and, if desired, (d) a binder, in the absence of an image stabilizer or stabilizer precursor, comprising heating the photothermographic element to about 100°C. to about 250°C.

In developing an image in a photothermographic element according to the invention, increasing or decreasing the length of time of heating can enable use of a

higher or lower temperature within the described range.

Heating of the photothermographic element can be carried out employing various heating means. These include any suitable means which provides the desired temperature within the desired time, such as a hot metal block, heated roller, plate or the like.

Processing is usually carried out under ambient conditions of pressure and humidity. Pressures and humidity outside normal atmospheric conditions can be employed if desired, however, normal atmospheric conditions are preferred.

Various exposure means can be employed for providing a latent image in the described photothermographic materials. While the photothermographic materials are typically sensitive to the ultraviolet and blue regions of the spectrum, various exposure means can be employed for providing exposure not only in this range of sensitivity but other ranges of the spectrum. Typically, the photothermographic element is exposed employing a visible light source.

The pH of a photothermographic composition employed according to the invention can vary. In an aqueous formulation it is typically less than about 7, such as about 2 to about 6.

While the exact mechanism by which an image is developed in a photothermographic material according to the invention is not fully understood, it is believed that the concentration of silver ion in equilibrium with silver complexing moieties in the photothermographic material is a significant factor. It is believed that those silver complexes, such as complexes of silver with the described thione compound, which exhibit a pAg decrease of 2.0 or more units over a temperature range of about 25 to about 80°C at a thione to silver ratio of 4:1 are especially useful. This is measured by potentiometric methods, typically in aqueous medium. This is believed to correspond to marked increase in silver ion concentration during processing.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

This illustrates the invention.

A photothermographic element is prepared as follows: A coating formulation is prepared by mixing the following components:

- 3-(2-Carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione — 350.0 mg
- Silver trifluoroacetate — 175.0 mg
- AgBr dispersed in acetone — 0.1 ml
- Poly(vinyl butyral) 2% by weight in 1:1:1 parts by volume acetone-toluene-methanol — 3.0 ml.
- Hydroquinone 5% in methanol — 2.0 ml.
- Methanol — 5.0 ml.

The coating formulation, which is designated as composition A, is coated at 25°C at a wet coating thickness of 0.004 inch on a polyethylene coated paper support. The concentration of silver bromide is about 0.04×10^{-3} moles of silver bromide per square foot of support. The resulting photothermographic element, after drying the coating, is exposed imagewise to a tungsten light source through a step tablet for 20 seconds. Processing is carried out by contacting the photothermographic element with a heated metal plate at 130°C. for 20 seconds.

A second photothermographic element is prepared in the same manner. Upon exposing and processing by overall heating for 10 seconds at 140°C., a dark image is developed in each instance having an off-white background. The image developed with 20 seconds heating at 130°C. has a maximum density of 0.58. The image developed employing 10 seconds heating at 140°C. has a maximum density of 0.52.

EXAMPLE 2

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the coating formulation designated as composition A has the following composition:

- AgBr dispersed in acetone — 0.1 ml.
- Hydroquinone, 5 percent by weight in methanol — 2.0 ml.
- Poly(vinyl butyral), 2% by weight in 1:1:1 parts by volume acetone-toluene-methanol — 3.0 ml.
- Methanol — 5.0 ml.

Upon exposure and processing as described in Example 1, no discernible image is observed.

EXAMPLE 3

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the coating formulation designated as composition A contains 0.1 milliliters of acetone in place of 0.1 milliliters of silver bromide dispersed in acetone. Exposure and processing are the same as in Example 1. No visible image or reduction of silver is observed. Prolonged exposure to fluorescent light of the photothermographic element produces only a slight yellow coloration.

EXAMPLE 4

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the thiazoline-2-thione compound is omitted from the coating composition. Reduction of silver ion is observed during coating. No satisfactory image is produced.

This example demonstrates the thiazoline-2-thione and not the trifluoroacetate is the silver complexing agent in the described composition.

EXAMPLE 5

The following components are ball-milled for 12 hours:

- 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione — 3.5 g.
- silver trifluoroacetate — 1.75 g.
- sodium bromide — 100 ml.
- polyvinyl butyral, 2% by weight in 1:1:1 parts by volume acetone-toluene-methanol — 50 ml.

The resulting composition is combined with 30 milliliters of 1:1 parts by volume acetone-methanol.

8 milliliters of the resulting dispersion is mixed with 2 milliliters of a solution containing 5 percent by weight hydroquinone in methanol.

After mixing, the formulation is coated on a polyethylene coated paper support at a wet thickness of 0.004 inch. The resulting photothermographic element after drying is exposed sensitometrically using a tungsten light source through a step tablet. The exposed photothermographic element is then processed by overall heating at 130°C. to 170°C. for 90 to 15 seconds. A

brownish image on an off-white background results. The resulting image has a maximum density of 0.44.

EXAMPLE 6

The dispersion of Example 5 before adding the hydroquinone solution is designated as composition B.

8 milliliters of composition B is mixed with 1.0 milliliters of 5 percent by weight hydroquinone and 1.0 milliliters of 10 percent by weight sulfolane in acetone. The resulting composition is coated on a polyethylene coated paper support as described in Example 1 and exposed sensitometrically to tungsten light through a step wedge, also as described in Example 1. The resulting image is developed by overall heating the photothermographic element from 130°C. to 170°C. for 60 to 15 seconds. A range of images is produced having from brown to deep purple color at the higher processing temperatures. The maximum density of the resulting image is 0.81.

EXAMPLE 7

8 milliliters of composition B as described in Example 1 is mixed with 1 milliliter of 5 percent by weight hydroquinone and 1 milliliter of 2 percent by weight succinimide in methanol. The resulting composition is coated and exposed as described in Example 1. Development of the resulting image in the photothermographic element is carried out by processing as described in Example 6. This provides images similar to those resulting from the process of Example 6. Maximum density of the resulting image is 0.71.

EXAMPLE 8

The procedure set out in Example 7 is repeated with the exception that the 1 milliliter of 2 percent by weight succinimide is replaced with 1 milliliter of 1 percent by weight phthalimide. Results similar to those of Example 7 are produced. Maximum density of the resulting image is 0.88.

EXAMPLE 9

The following components are mixed:

gelatin, 4 percent by weight in water — 4 ml.

silver trifluoroacetate — 175 mg.

3-(2-carboxyethyl)-4-hydroxy-methyl-4-thiazoline-2-thione — 350 mg.

ammonium bromide, 80 mg. per milliliter of methanol — 0.2 ml.

hydroquinone, 5% by weight in water — 2 ml.

saponin — 0.1 ml.

water — 3 ml.

The formulation is dispersed with an ultrasonic probe and coated at about 38°C. at a wet thickness of 0.004 inch on a polyethylene coated paper support. The coating is chill set at about 4°C. and air dried.

The resulting photothermographic element is exposed sensitometrically to tungsten light through a step tablet for 40 seconds. The image is developed by overall heating the element for 10 seconds at 150°C. A second element prepared in the same manner is heated for 10 seconds at 170°C. A warm tone low contrast image of moderate density, i.e., a maximum density of 0.76, results at 170°C. More neutral tone is observed employing the higher processing temperature.

EXAMPLE 10

The following components are ball-milled for about 12 hours:

3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione — 4.0 g.

silver trifluoroacetate — 1.75 g.

water — 30 ml.

The dispersion is combined with 30 ml. of an aqueous solution containing 2 percent by weight gelatin. This is designated as composition C.

A coating melt is prepared by mixing the following components:

Composition C — 7 ml.

Hydroquinone, 5 percent weight in water — 2.0 ml.

Silver iodide gelatino emulsion, 3 to 6 milligrams of silver — 0.2 ml.

Surfactant, 0.5 percent by weight in water — 0.2 ml.

The composition is coated on a polyethylene coated paper support at a thickness of 0.004 inches and air dried. The photothermographic element resulting is exposed sensitometrically to tungsten light through a step tablet and processed by overall heating at 150°C. to 180°C. for 30 to 5 seconds. This produces a brown to nearly neutral tone image with the tone depending upon processing temperature. The higher processing temperatures provide more neutral tone images. The background of the image is off-white. The image has a maximum density of 0.98. The processed areas exhibit virtually no post processing print up.

EXAMPLE 11

The procedure set out in Example 10 is repeated with the exception that silver iodide is replaced with silver bromide. Exposure and processing is carried out as described in Example 10 to provide a developed image having neutral tone with a maximum density of 0.51 and low contrast. The processed areas exhibit virtually no post processing print up.

EXAMPLE 12

The procedure set out in Example 10 is repeated with the exception that the 4-thiazoline-2-thione is replaced by 3-(3-carboxypropyl)-4-hydroxymethyl-4-thiazoline-2-thione. Also, 4.24 grams of this thione compound is employed in place of the thione compound of Example 10. Upon exposure and processing, as described in Example 10, a developed image is produced having a maximum density and tone similar to that of the image developed according to Example 10.

EXAMPLE 13

The procedure set out in Example 10 is repeated with the exception that the described coating composition is coated on a gel subbed polyethylene terephthalate film support. Upon exposure and processing as described in Example 10, a developed image results. The film support is transparent and upon processing with heat, the emulsion layer becomes transparent in the non-image areas such that minimum transmission densities as low as 0.1 are observed.

EXAMPLES 14-19

In each of Examples 14-19, the procedure set out in Example 10 is repeated with the exception that the fol-

lowing thione compounds are employed in place of the thione compound described in Example 10. Processing conditions and the properties of the resulting developed image are set out in the following Table I.

Example No.	Compound
14	3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione
15	3-(2-carboxyethyl)benzothiazoline-2-thione
16	3-(2-carboxyethyl)-5-phenyl-1,3,4-oxadiazoline-2-thione
17	3-(2-carboxyethyl)-5-phenyl-1,3,4-thiadiazoline-2-thione
18	3-carboxymethyl-4-methyl-4-thiazoline-2-thione
19	3-(2-carboxyethyl)-1-phenyl-1,3,4-triazoline-2-thione

In each instance a developed image is provided which is stable. The processing temperature and time and properties of the resulting image are given in following Table II.

Example No.	Compound
20	3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione
21	3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione
22	3-carboxymethyl-4-methyl-4-thiazoline-2-thione
23	3-(2-carboxyethyl)benzothiazoline-2-thione

EXAMPLE 24

This illustrates preparation of a photothermographic element according to the invention in the absence of a binder.

Table II

Example	Processing Temp. °C.	Time Sec.	Dmax	Dmin	Dmin (print-up) 24 hrs. 100 fc*	D(unprocessed print-up) 24 hrs. 100 fc*
20	170	15	0.45	0.07	0.10	0.27
21	130	5	1.18	0.09	0.18	0.86
	140	5	1.12	0.13	0.20	0.84
22	160	5	0.75	0.10	0.15	—
	180	5	0.83	0.14	0.21	—
23	140	10	1.09	0.11	0.25	0.69
	160	15	1.27	0.13	0.25	0.73

*fc represents footcandles

Table I

Example	Processing Temp. (°C)	Time (Sec.)	Dmax	Dmin	Dmin (print-up) 24 hrs. 100 fc*	D(unprocessed print-up) 24 hrs. 100 fc*
14	150	30	.54	.14	.14	.35
	180	5	.65	.22	.22	.36
15	170	15	1.07	.15	.26	.33
	180	5	1.17	.13	.18	.31
16	170	5	.38	.15	.19	.23
17	125	5	.55	.36	.48	.62
18	170	15	.68	.14	.18	.23
	180	5	.78	.17	.22	.22
19	160	15	.22	.10	.11	.21

*fc represents footcandles.

EXAMPLES 20-23

Silver complexes are prepared by mixing a solution of the following thione compounds with a solution of a silver salt which is either silver nitrate or silver trifluoroacetate. The silver salt and thione compound are mixed in about stoichiometric proportions. Solvents which are employed are determined by the solubility properties of the thione compound. A solution ratio of a thione compound to silver ion is maintained at about 2:1. The resulting finally divided precipitates are isolated by filtration and either used directly in the composition described in Example 10 in place of the thione compound described in Example 10 or ball-milled for a short time before mixing with the processing composition of Example 10. The resulting silver complexes are mixed with the processing composition described in Example 10 using various organic solvent mixtures before coating on the described support. Exposure and processing are carried out as described in Example 10.

The following components are ball-milled together for 18 hours:

3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione — 16 g.
silver trifluoroacetate — 7 g.
water — 90 ml. This is designated as Composition D.

The following components are mixed:

Composition D — 3.5 ml.
water — 3.5 ml.
hydroquinone, 5 percent by weight in methanol — 2 ml.
surfactant, 0.5 percent by weight in water — 0.4 ml.

silver iodide gelatino emulsion — 0.4 ml. The resulting composition is coated on a polyethylene coated paper support at a wet thickness of 0.004 inches. The resulting coating contains 200 milligrams of silver as complex per square foot and about 10 milligrams silver as silver halide. After the coating is

chill set and dried at room temperature, it is sensitometrically exposed to tungsten light and processed by overall heating to a temperature of 170°C for about 15 seconds. The resulting image has a maximum density of 0.84 and has properties similar to a control coating which is prepared and processed in the same manner but containing gelatin as a binder.

EXAMPLES 25 - 28

Similar results are obtained employing the procedure of Example 5 and the following compounds in place of the described thiazoline-2-thione:

Example No.	Compound
25	1,3-bis(2-carboxyethyl)-imidazoline-2-thione
26	1,3-bis(2-carboxyethyl)-benzimidazoline-2-thione
27	3-(2-carboxyethyl)-1-methyl-imidazoline-2-thione
28	3-(2-carboxyethyl)-benzoxazoline-2-thione

EXAMPLES 29-32

Similar results are obtained employing the procedure of Example 24 and the compounds listed in Examples 25-28 in place of the described thiazoline-2-thione compound.

EXAMPLE 33

The procedure set out in Example 5 is repeated with the exception that a concentration of about 10 milligrams of silver as silver bromiodide is used in place of the silver iodide.

Upon sensitometric exposure and overall heating as described, a developed, stable image is provided at 170°C within 15 seconds.

EXAMPLE 34

The procedure set out in Example 5 is repeated with the exception that a concentration of about 10 mg. of silver as silver halide in the form of silver bromiodide is used in place of silver iodide. A spectral sensitizing dye which is 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)-isopropylidene]rhodanine is also added to composition C at a concentration of about 50 mg. to about 2.0 grams per mole of photosensitive silver.

Upon sensitometric exposure and overall heating, as described, a developed stable image is provided at 170°C within 15 seconds. The photographic speed of the photothermographic element is about 1.5 log E faster than the photographic speed of the photothermographic element of Example 33.

EXAMPLES 35-36

The procedure set out in Example 10 is repeated with the exception that 3-(1-carboxyethyl)-4-methyl-4-thiazoline-2-thione is employed in place of the thione compound described in Example 10. Processing conditions and the properties of the resulting developed image are set out in the following Table III:

Example No.	Processing Temp. °C	Time Sec.	Dmax	Dmin
35	170	15	0.75	0.14
36	160	15	0.64	0.09

When the exposed and processed photothermographic elements of Examples 35 and 36 are exposed to light (130 footcandles at 30°C) for a significant period of time (24 hours), minimum density increase is not significant.

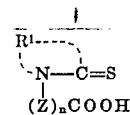
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A photothermographic element comprising a support having thereon

a. a reducing agent,

b. a silver salt of a thione compound, said thione compound being represented by the formula:



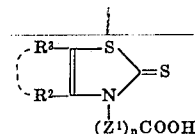
wherein n is 1 to 10, R^1 represents atoms completing a 5 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

c. a photosensitive component consisting essentially of photosensitive silver halide, and

d. a binder,

in the absence of an image stabilizer or stabilizer precursor.

2. The photothermographic element of claim 1 wherein said thione compound is a thiazoline-2-thione represented by the formula:



wherein n is 1 to 10; Z' is alkylene containing 1 to 4 carbon atoms; R^2 and R^3 are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group.

3. The photothermographic element of claim 1 wherein said reducing agent is a phenolic silver halide developing agent.

4. The photothermographic element of claim 1 wherein said photosensitive silver halide is silver iodide.

5. A photothermographic element comprising a support having thereon

a. a hydroquinone reducing agent,

b. a silver salt selected from the group consisting of silver salts of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione,

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- 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)-benzothiazoline-2-thione,
3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof,

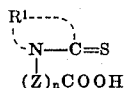
c. photosensitive silver halide, and
d. a binder, in the absence of an image stabilizer or stabilizer precursor.

6. The photothermographic element of claim 5 comprising a support having thereon per square foot of support

- a. about 0.25×10^{-3} to 1×10^{-3} moles of HQ
b. about 0.25×10^{-3} to 2×10^{-3} moles of silver as said silver salt of a thiazoline-2-thione compound, and
c. about 0.02×10^{-3} to 0.12×10^{-3} moles of said silver halide.

7. A photothermographic element comprising a support having thereon

- a. a reducing agent b. a silver salt of a thione compound, said thione compound being represented by the formula:

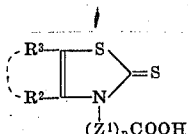


wherein n is 1 to 10, R¹ represents atoms completing a 5 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

- c. a photosensitive component consisting essentially of photosensitive silver halide,

in the absence of a binder and in the absence of an image stabilizer or stabilizer precursor.

8. The photothermographic element of claim 7 wherein said thione compound is a thiazoline-2-thione represented by the formula:



wherein n is 1 to 10; Z¹ is alkylene containing 1 to 4 carbon atoms; R² and R³ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group.

9. The photothermographic element of claim 7 wherein said reducing agent is a phenolic silver halide developing agent.

10. The photothermographic element of claim 7 wherein said photosensitive silver halide is silver iodide.

11. A photothermographic element comprising a support having thereon

- a. a hydroquinone reducing agent,
b. a silver salt selected from the group consisting of silver salts of
3-carboxymethyl-4-methyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)-benzothiazoline-2-thione,

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- 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof

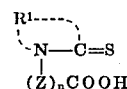
c. silver iodide in the absence of a binder and in the absence of an image stabilizer or stabilizer precursor.

12. The photothermographic element of claim 11 comprising a support having thereon per square foot of support

- a. about 0.25×10^{-3} to 1×10^{-3} moles of hydroquinone
b. about 0.25×10^{-3} to 2×10^{-3} moles of silver as said silver salt of a thiazoline-2-thione compound, and
c. about 0.02×10^{-3} to 0.12×10^{-3} moles of said silver halide.

13. A photothermographic composition comprising a. a reducing agent,

b. a silver salt of a thione compound, said thione compound being represented by the formula:



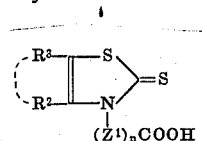
wherein n is 1 to 10, R¹ represents atoms completing a 5 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

- c. photosensitive silver halide, and

d. a binder,

in the absence of an image stabilizer or stabilizer precursor.

14. The photothermographic composition of claim 13 wherein said thione compound is a thiazoline-2-thione represented by the formula:



wherein n is 1 to 10; Z¹ is alkylene containing 1 to 4 carbon atoms, R² and R³ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group.

15. The photothermographic composition of claim 13 wherein said reducing agent is a phenolic silver halide developing agent.

16. The photothermographic composition of claim 13 wherein said photosensitive silver halide is silver iodide.

17. A photothermographic composition comprising a. a hydroquinone reducing agent,

b. a silver salt selected from the group consisting of silver salts of

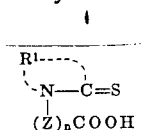
- 3-carboxymethyl-4-methyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,
3-(2-carboxyethyl)-benzothiazoline-2-thione,
3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof.

c. photosensitive silver halide

18. A photothermographic composition of claim 13 wherein said reducing agent is a hydroquinone.

19. A photothermographic composition comprising

- a. a reducing agent,
b. a silver salt of a thione compound, said compound containing the moiety



wherein n is 1 to 10, R¹ represents atoms completing a 5 or 6 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

c. a photosensitive component consisting essentially of photosensitive silver halide, in the absence of a binder and in the absence of an image stabilizer or stabilizer precursor.

20. A photothermographic composition comprising

a. a hydroquinone reducing agent,

b. a silver salt selected from the group consisting of silver salts of

3-carboxymethyl-4-methyl-4-thiazoline-2-thione,

3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,

3-(2-carboxyethyl)-benzothiazoline-2-thione,

3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof

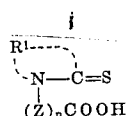
c. silver iodide,

in the absence of a binder and in the absence of an image stabilizer or stabilizer precursor.

21. A method of developing and stabilizing an image in a photothermographic element comprising a support having thereon

a. a reducing agent,

b. a silver salt of thione compound containing the unit:



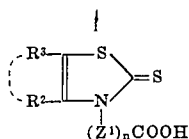
wherein n is 1 to 10, R¹ represents atoms completing a 5 or 6 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

c. a photosensitive component consisting essentially of photosensitive silver halide, and

d. a binder,

in the absence of an image stabilizer or stabilizer precursor, comprising heating said element to about 100°C. to about 250°C.

22. The method of claim 21 wherein said thione compound is a thiazoline-2-thione represented by the formula:



wherein n is 1 to 4; Z¹ is alkylene containing 1 to 4 carbon atoms, R² and R³ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group.

23. The method of claim 21 wherein said photothermographic element is heated for about 1 to 60 seconds.

24. The method of developing and stabilizing an image in a photothermographic element comprising a support having thereon

a. a hydroquinone reducing agent,

b. a silver salt selected from the group consisting of silver salts of

3-carboxymethyl-4-methyl-4-thiazoline-2-thione,

3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,

3-(2-carboxyethyl)-benzothiazoline-2-thione,

3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione,

and combinations thereof,

c. a photosensitive silver halide,

in the absence of an image stabilizer or stabilizer precursor, comprising heating said photothermographic element to about 100°C. to about 250°C. for about 1 to about 60 seconds.

25. The method of claim 24 wherein said element comprises a support having thereon

a. about 0.25×10^{-3} to 1×10^{-3} moles of HQ

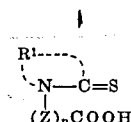
b. about 0.25×10^{-3} to 2×10^{-3} moles of silver as said silver salt of a thiazoline-2-thione compound, and

c. about 0.02×10^{-3} to 0.12×10^{-3} moles of said silver halide.

26. A method of developing and stabilizing an image in a photothermographic element comprising a support having thereon

a. a reducing agent

b. a silver salt of a thione compound, said compound containing the moiety

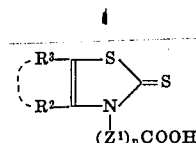


wherein n is 1 to 10, R¹ represents atoms completing a 5 or 6 member heterocyclic nucleus, Z is alkylene containing 1 to 10 carbon atoms,

c. a photosensitive component consisting essentially of photosensitive silver halide,

in the absence of a binder and in the absence of an image stabilizer or stabilizer precursor, comprising heating said photothermographic element to about 100°C. to about 250°C.

27. The method of claim 26 wherein said thione compound is a thiazoline-2-thione represented by the formula:



wherein n is 1 to 4; Z¹ is alkylene containing 1 to 4 carbon atoms; R² and R³ are each selected from the group consisting of hydrogen, alkyl containing 1 to 4 carbon atoms, and aryl containing 6 to 10 carbon atoms, or taken together are atoms completing a benzo group.

28. The method of claim 26 wherein said photothermographic element is heated for about 1 to about 60 seconds.

29. The method of developing and stabilizing an image in a photothermographic element comprising a support having thereon

- a. a hydroquinone reducing agent,
 - b. a silver salt selected from the group consisting of silver salts of
 - 3-carboxymethyl-4-methyl-4-thiazoline-2-thione,
 - 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,
 - 3-(2-carboxyethyl)-benzothiazoline-2-thione,
 - 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof
 - c. a photosensitive silver halide in the absence of an image stabilizer or stabilizer precursor, comprising heating said photothermographic element to about 100°C. to about 250°C. for about 60 seconds.
30. The method of claim 29 wherein said element comprises a support having thereon
- a. about 0.25×10^{-3} to 1×10^{-3} moles of HQ
 - b. about 0.25×10^{-3} to 2×10^{-3} moles of silver as said silver salt of a thiazoline-2-thione compound, and
 - c. about 0.02×10^{-3} to 0.12×10^{-3} moles of said sil-

- ver halide.
 - 31. The method of preparing a photographic transparency employing an imagewise exposed photothermographic element comprising a transparent support having thereon
 - a. a hydroquinone reducing agent,
 - b. a silver salt selected from the group consisting of silver salts of
 - 3-carboxymethyl-4-methyl-4-thiazoline-2-thione,
 - 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione,
 - 3-(2-carboxyethyl)-benzothiazoline-2-thione,
 - 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof,
 - c. a photosensitive silver halide
- in the absence of an image stabilizer or stabilizer precursor, comprising heating said photothermographic element to about 100°C. to about 250°C. for about 1 to about 60 seconds.

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