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Ericson

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[54] PHOTOTHERMOGRAPHIC ELEMENT, COMPOSITION AND PROCESS

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[58] **Field of Search**.... 96/48 HD, 109, 114.1, 66 R, 96/114.6

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

768,071 6/1971 Belgium

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[57] ABSTRACT

A stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor in a photothermographic element or composition provides improved post-processing stability upon heat processing of the element or composition. This stabilizer precursor combination is useful in photothermographic materials, for example, comprising photosensitive silver salt and an oxidation-reduction image-forming combination comprising a heavy metal salt oxidizing agent with a reducing agent.

25 Claims, No Drawings

PHOTOTHERMOGRAPHIC ELEMENT, COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to certain stabilizer precursor combinations in photothermographic elements, compositions and processes to provide improved stable images. In one of its aspects it relates to a heat stabilizable photothermographic element comprising photosensitive silver halide and a stabilizer precursor combination as described. In another of its aspects it relates to a photothermographic composition comprising the described stabilizer precursor combination. A further aspect relates to a method of stabilizing an image in a photothermographic element comprising photosensitive silver halide and a stabilizer precursor combination as described by overall heating the exposed photothermographic element.

2. Description of the State of the Art

It is known to obtain an image in a photosensitive element by so-called dry processing with heat. The photothermographic element employed for providing such an image can contain a reducing agent, a light-insensitive silver salt of an organic acid, such as silver behenate, as an oxidizing agent and a low concentration of photographic silver halide. Such photothermographic elements are 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 Sorensen, et al., issued Oct. 13, 1964; British Specification No. 1,161,777 published Aug. 20, 1969; U.S. Pat. No. 3,707,377 of Tiers, et al., issued Dec. 26, 1972 and in *Research Disclosure*, January, 1973, pages 16–21.

In a photothermographic material one of the main difficulties involves post-processing stability. Because heat developable photographic elements are suitable for so-called dry processing with heat and are designed to eliminate a fixing step which normally would remove undeveloped silver, it is necessary that a means be provided for post-processing stabilization to enable roomlight handling.

Several means have been proposed to answer the need for post-processing stability of photothermographic elements, such as (1) washing with water to remove undeveloped silver salts, (2) heating to release Bronstead or Lewis acid such as HCl, fluoride or HF from incorporated compounds such as m-nitrobenzenesulfonylchloride, para-toluene sulfonic acid urea addition complex of p-acetamidobenzenediazonium fluoroborate and (3) chelation of the oxidizing agent with, for example, salicylaldoxime or benzotriazole as described in U.S. Pat. No. 3,152,904 of Sorensen, et al., issued Oct. 13, 1964. Another method proposed for solving the problem of post-processing instability is to provide a photothermographic combination is on one sheet of material and the latent image forming photographic silver halide is on a separate sheet. The sheets are separated after exposure such as described in U.S. Pat. No. 3,152,904. A further means proposed for stabilization involves swabbing a 1 percent solution of phenylmercaptotetrazole onto the surface of the overall heated photothermographic material or rubbing benzotriazole into the surface of the coating. These proposed means for stabilization are not useful for large volume handling of heat developable photographic materials.

It has also been proposed to provide stabilized images in heat developable materials by treating the developed image with a solution containing certain thiol or thione compound stabilizers. This is described, for example, in U.S. Pat. No. 3,617,289 of Ohkubo, et al., issued Nov. 2, 1971. One of the compounds proposed for this solution stabilization is 1-phenyl-5-mercaptotetrazole. Unfortunately, the addition of this compound to photographic silver compositions provides undesired desensitization at concentrations which produce stabilization and toning of a developed image.

Another means of stabilization of an image in a photothermographic material is described in copending U.S. application Ser. No. 249,260 of Hiller, filed May 1, 1972, which is a continuation-in-part application of U.S. Ser. No. 43,171 of Hiller, filed June 3, 1970, now abandoned. This subject matter is also described in corresponding Belgian Pat. No. 768,071 published July 30, 1971. Certain stabilizer precursors which are azole thioethers or blocked azolinethiones are employed in photothermographic materials according to the description in these applications and patent. An example of a stabilizer precursor proposed in photothermographic materials is 5-methoxycarbonylthio-1-phenyltetrazole. Unfortunately, this compound does not always provide the desired increased stability of a heat developed image.

Another means for post-processing stabilization of certain photothermographic materials is described in U.S. Pat. No. 3,707,377 of Tiers, et al., issued Dec. 26, 1972. Certain polyhalogenated organic oxidizing agents, such as tetrabromobutane, are described in certain heat developable photographic materials to provide post-processing stabilization. As illustrated in the following comparative examples, certain combinations of compounds can provide surprisingly improved stabilization without the adverse sensitometric effects which may be observed with certain polyhalogenated organic oxidizing agents.

Halogenated organic compounds have been employed in photographic materials for various purposes, such as antifoggants. Monohalogenated organic antifoggants for photographic emulsions are described, for example, in U.S. Pat. No. 3,128,187 of Sagal, et al., issued Apr. 7, 1964; U.S. Pat. No. 3,232,762 of Ford, et al., issued Feb. 1, 1966; U.S. Pat. No. 2,732,303 of Morgan, et al., issued Jan. 24, 1956; U.S. Pat. No. 2,835,581 of Tinker, et al., issued May 20, 1958 and U.S. Pat. No. 3,271,154 of Dersch, issued Sept. 6, 1966. None of these patents, however, indicate that certain combinations of stabilizer precursors can be employed in photothermographic materials to provide improved post-processing stability.

Also, while various 5-mercaptotetrazole compounds are known in photographic materials for various purposes, such as described in British Pat. No. 1,238,928 published July 14, 1971, and other of the described patents, none of the art suggests a useful solution to the continuing need for improved heat-developable, thione compound containing, photographic materials providing improved post-processing stability.

Accordingly, there has been a continuing need for heat-developable photographic materials, especially photothermographic materials comprising an image-forming combination containing a silver salt oxidizing agent, such as silver behenate, with a reducing agent, and photosensitive silver halide, which have improved post-processing image stability, that is reduced background density and more desired image tone, when employing a combination of stabilizer precursors.

SUMMARY OF THE INVENTION

The described improvements are provided in a photothermographic element or composition by employing as a stabilizer percursor, a stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor. This stabilizer precursor combination is especially useful in a photothermographic material comprising photosensitive silver halide and an oxidation-reduction image-forming combination comprising (i) a heavy metal silver salt oxidizing agent, such as silver behenate and silver stearate, with (ii) a reducing agent.

The described improvements are provided, for example, in a photothermographic element comprising a support having thereon a layer comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) a silver salt of a long-chain fatty acid, such as silver behenate and silver stearate with, (ii) an organic reducing agent, such as a sulfonamidophenol reducing agent, (C) a polymeric binder for the described layer, such as poly(vinyl butyral) and (D) a stabilizer precursor combination of (a) a blocked thione stabilizer precursor as described herein with (b) a halogen containing stabilizer precursor, also as described herein.

DETAILED DESCRIPTION OF THE INVENTION

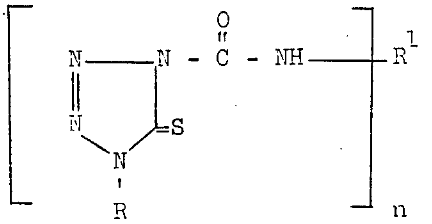
A variety of blocked thione stabilizer precursors can be employed in the practice of the invention to provide improved post-processing stability without adversely affecting desired properties of the heat-developable photograhpic material.

A blocked thione stabilizer precursor as employed herein is intended to mean a thione compound which contains a group or moiety which blocks or prevents the thione compound from reacting with silver ions in the photothermographic material prior to heating the photothermographic material. While the exact mechanism of stabilization according to the invention is not fully understood, it is believed that the blocked thione as described remains in a state which does not adversely affect the photothermographic material containing the blocked thione prior to heating. Upon heating, it is believed the thione compound is changed from its blocked state to a state which enables reaction with silver ions in the unexposed areas of the photothermographic material to form a stable silver mercaptide in the unexposed areas. This is believed to prevent undesired decreased stability to room-light exposure.

A test can be used to determine whether or not a thione compound is a useful blocked thione image stabilizer precursor as described. While different tests can be employed to determine useful image stabilizer precursors depending upon the particular photothermographic element and composition, desired image, processing conditions and the like, one test which can be employed for certain photothermographic elements is described in following Example 4. The compound tested in the described combination, after incorporation with the described halogen containing compound in the photothermographic element and after imagewise exposure and overall heating of the element as described in Example 1, should prevent the buildup of background density or minimum density above 0.10 density unit more than the original minimum density without undesired stain and without significantly adversely affecting maximum density.

One class of especially useful blocked thione stabilizer precursors is a 4-aryl-1-carbamoyl-2-tetrazoline-5-thione represented by the formula:

(I)



wherein R is aryl, such as aryl containing 6 to 12 carbon atoms, including phenyl and naphthyl; and R^1 is alkyl containing 1 to 12 carbon atoms, such as methyl, propyl, butyl and hexyl, aryl, such as aryl containing 6 to 12 carbon atoms, including phenyl and naphthyl, cycloalkyl containing 3 to 8 carbon atoms, such as cyclohexyl and cyclopropyl, when *n* is 1; or alkylene containing 1 to 10 carbon atoms when *n* is 2, such as alkylene containing 1 to 6 carbon atoms including methylene and ethylene; and *n* is 1 or 2. These blocked thione stabilizer precursors are described in copending U.S. application Ser. No. 435,806 of Burness, et al., filed January 23, 1974.

Useful blocked thione stabilizer precursors within the described formula (I) include, for instance:

4-phenyl-1-phenylcarbamoyl-2-tetrazoline-5-thione,
1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione,'
1-methylcarbamoyl-4-phenyl-2-tetrazoline-5-thione,
4-hexylcarbamoyl-1-phenyl-2-tetrazoline-5-thione,
N,N-hexamethylenebis(1-carbamoyl-4-phenyl-2-tetrazoline-5-thione),
4-butylcarbamoyl-1-phenyl-2-tetrazoline-5-thione, and
di-2-(1-phenyl-5-thione-2-tetrazolin-4-ylcarbonylaminoethyl fumarate

Other useful classes of blocked stabilizer precursors are described, for example, in copending U.S. application Ser. No. 249,260 of Hiller, filed May 1, 1972 and corresponding Belgian Pat. No. 768,071 published July 30, 1971. Useful blocked thione and blocked thiol stabilizer precursors within these classes are:

5-Acetyl-2-benzoylthio-4-methylthiazole,
4-Benzoylmethyl-2-benzoylthiothiazole,
2-(2-Furoylthio)-4-hydroxymethylthiazole,
2-Benzoylthio-4-hydroxymethylthiazole,
2-Benzoylthio-4-tert.-butylthiazole,
5-Carbethoxy-4-methyl-2-(3-oxobutylthio)thiazole,
5-Acetyl-2-(2-benzoylethylthio)-4-methylthiazole,
2-(3-Oxobutylthio)thiazole,
4,5-Dimethyl-2-(3-oxobutylthio)thiazole,
2-(3-Oxobutylthio)-4-phenylthiazole,
4-Carboxy-2-(3-oxobutylthio)thiazole,
4-Carboethoxy-2-(3-oxobutylthio)thiazole,
4-(4-Methoxyphenyl)-2-(3-oxobutylthio)thiazole,
4-(4-Nitrophenyl)-2-(3-oxobutylthio)thiazole,
4-Tert.-butyl-2-(3-oxobutylthio)thiazole,
5-Acetyl-4-methyl-2-(3-oxobutylthio)thiazole,

5-Acetyl-2-furoylthio-4-methylthiazole,
4-Furoyl-3-(3-oxobutylthio)1,2,4-thiadiazoline-5-thione,
3-Methylthio-4-benzoyl-1,2,4-thiadiazoline-5-thione,
4-Acetyl-3-methylthio-1,2,4-thiadiazoline-5-thione,
4-Acetyl-3-furoylethylthio-1,2,4-thiadiazoline-5-thione,
4-Furoyl-3-methylthio-1,2,4-thiadiazoline-5-thione,
5-(2-Benzoylethylthio)-1-phenyltetrazole,
5-(2-Acetylethylthio)-1-phenyltetrazole,
5-Methoxycarbonylthio-1-phenyltetrazole,
5-(4-Nitrobenzyloxycarbonylthio)phenyltetrazole,
5-(Ethoxycarbonylthio)-1-phenyltetrazole
5-Benzoylthio-1-phenyltetrazole,
5-Acetyl-3-benzoyl-4-methylthiazoline-2-thione,
4-Benzoylmethyl-3-benzoylthiazoline-2-thione
3-Furoyl-4-hydroxymethylthiazoline-2-thione,
3-Benzoyl-4-hydroxymethylthiazoline-2-thione,
3-Benzoyl-4-tert.-butylthiazoline-2-thione, and
5-Carboethoxy-4-methyl-3-(3-oxobutyl)-thiazoline-2-thione

The listed compounds have also in some cases been known as azole thioethers and blocked azolinethiones. These compounds can be prepared by methods known in the art. For example, they can be prepared by the Michael addition of alpha, beta-unsaturated ketones such as methyl vinyl ketone to 4-thiazoline-2-thione. This is described in the *Journal of Heterocyclic Chemistry*, 6, pages 397–401 (1969) by Humphlett.

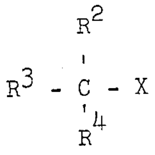
The blocked thione stabilizer precursors which are tetrazoline-5-thione compounds can be prepared by reacting 1-phenyl-2-tetrazoline-5-thione in a suitable solvent in the presence of a catalyst such as heptamethylisobiguanide, with a suitable isocyanate compound. The preparation of 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione is typical of a useful preparation. It is preferred that the resulting product be purified such as by treatment with solvents and other typical purification means.

A variety of halogen containing stabilizer precursor can be employed according to the invention to provide improved post-processing stability without adversely affecting desired properties of the photothermographic material.

A test can be employed to determine useful halogen containing compounds or materials such as described in the following Example 4. In this test, the halogen compound, after incorporation with the described blocked thione compound in the photothermographic element and after imagewise exposure and overall heating of the element as described in Example 4, should prevent buildup of background density or minimum density above 0.10 density unit more than the original minimum density without undesired stain and without significantly adversely affecting maximum density.

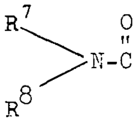
It is believed that the described halogen containing stabilizer precursors are precursors to the moiety, compound or material which, is formed upon heating and combines with silver ions or atoms to prevent undesired instability due to room-light exposure. However, the exact mechanism of stabilization is not fully understood. The stabilizer precursors according to the invention are compounds which do not prevent a redox reaction upon imagewise exposure of the described photothermographic materials.

One class of useful halogen containing stabilizer precursors according to the invention comprises a compound represented by the formula:



$$R^3-\overset{\overset{\textstyle R^2}{|}}{\underset{\underset{\textstyle R^4}{|}}{C}}-X$$

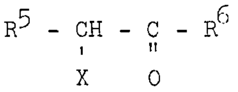
wherein X is chloro, bromo or iodo; R^2, R^3 and R^4 are individually selected from the group consisting of hydrogen; alkyl, such as alkyl containing 1 to 10 carbon atoms including methyl, ethyl, propyl or octyl; hydroxyalkyl, such as hydroxyalkyl containing 1 to 10 carbon atoms, including hydroxymethyl, hydroxyethyl and hydroxyhexyl; acyloxyalkyl, such as acyloxyalkyl containing 2 to 10 carbon atoms; nitro; nitroalkyl, such as nitroalkyl containing 1 to 10 carbon atoms, including nitromethyl, nitroethyl and nitropropyl; aryl, such as aryl containing 6 to 12 carbon atoms, including phenyl and naphthyl; acyl, such as acyl of the formula R″—CO— wherein R″ is alkyl containing 1 to 5 carbon atoms including methyl, ethyl, propyl and butyl, or aryl containing 6 to 12 carbon atoms, such as phenyl and naphthyl; amido, such as amido represented by the formula



$$\begin{matrix}R^7\\R^8\end{matrix}\Big\rangle N-\overset{\overset{\textstyle O}{\|}}{C}$$

wherein R^7 and R^8 individually selected from the group consisting of hydrogen, alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl and propyl, phenyl and naphthyl; sulfonyl represented by the formula R^9 — SO_2 — wherein R^9 is alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl and propyl or aryl, such as aryl containing 6 to 12 carbon atoms, such as phenyl, naphthyl or tolyl; bromo; chloro; and iodo; and wherein at least one of R^2, R^3 and R^4 is hydroxyalkyl, acyloxyalkyl, acyl, amido or sulfonyl as defined. Alkyl, aryl, hydroxyalkyl, acyloxyalkyl, acyl, amido and sulfonyl as employed herein include substituents on the defined groups which do not adversely affect stabilization or desired properties of photothermographic materials according to the invention. Suitable substituents include, for example, chloro, bromo, methoxy, phenyl, hydroxy, nitro and the like.

Another class of useful stabilizer precursors according to the invention comprises a monohalogenated organic compound having at least one carbonyl or sulfonyl group bonded to the carbon atom having the halogen substituent, such as an alpha-monohaloketone represented by the formula:



$$R^5-\underset{\underset{\textstyle X}{|}}{CH}-\underset{\underset{\textstyle O}{\|}}{C}-R^6$$

wherein X is chloro, bromo or iodo; R^5 is hydrogen, alkyl containing 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl or octyl, acyl containing 1 to 5 carbon atoms, such as acetyl and CH_3CH_2CO—, sulfamyl and aryl containing 6 to 12 carbon atoms, such as phenyl and naphthyl; R^6 is amino, alkyl containing 1 to 10 carbon atoms, as described, and aryl containing 6 to 12 carbon atoms, such as phenyl and naphthyl. The described substituent groups on the alpha-monohaloketone compounds can contain substituents which do not adversely affect the stabilizing action of the alpha-monohaloketone, such as methyl, ethyl and the like.

Useful halogenated organic compound stabilizer precursors within the described classes include the following compounds:

α-bromo-2,5-dimethoxyacetophenone
α-bromo-γ-nitro-β-phenylbutyrophenone
2-bromo-2-p-tolylsulfonylacetamide
α-iodo-γ-nitro-β-phenylbutyrophenone α-bromo-p-nitrotoluene
2-bromo-4'-phenylacetophenone
2-chloro-4'-phenylacetophenone
α-bromo-m-nitrotoluene
2-bromo-2-nitro-1,3-propanediol
1,3-dibenzoyloxy-2-bromo-2-nitropropane
2,2-dibromo-2-phenylsulfonylacetamide
2-bromo-2-p-tolylsulfonylacetamide
2-bromoacetophenone
α-chloro-p-nitrotoluene
2-bromo-2phenylacetophenone
2-bromo-1,3-diphenyl-1,3-propanedione
tetrabromobutane
hexabromocyclohexane
hexabromoethane
2-tribromomethylsulfonylbenzothiazole
2-bromo-2-nitro-1,3-di-(4-nitrobenzoyloxy)propane
2-bromo-1,3-di-(4-methoxybenzoyloxy)-2-nitropropane

The described halogen containing organic stabilizer precursors can be prepared by methods known in the art. For example, the parent organic compound can be halogenated employing, for example, bromine or chlorine. The resulting halogenated compounds can be purified employing purification procedures known in the art. Some organic compound impurities can be present in the resulting composition. In some cases it is necessary to separate the organic compound impurities before mixing the halogenated organic stabilizer precursors with the described photothermographic materials.

The useful concentration of the combination of stabilizer precursors according to the invention will depend upon different factors such as the particular photothermographic element, processing temperatures, particular components of the photographic element, desired image and the like.

A useful concentration of the combination of stabilizer precursors according to the invention is (a) about 0.005 to about 0.035 mole of the described blocked thione stabilizer precursor per mole of total silver with (b) about 0.001 to about 1.0 mole of the described halogen containing stabilizer precursor per mole of total silver in the described photothermographic material. The optimum concentration useful can be determined based on the described factors.

The described halogen stabilizer precursors are also observed to provide desired, incubation antifoggant activity in photothermographic materials according to the invention at a cencentration within the range of about 0.001 mole to about 0.025 mole of the described halogen stabilizer precursor per mole of total silver in the photothermographic material. The optimum concentration of the halogen stabilizer precursor for incubation antifoggant activity will depend upon such factors as the particular halogen compound, the particular photothermographic material, desired image and the like.

Typical photothermographic elements in which the stabilizer precursor combination of the invention is useful are 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 Sorensen, et al., issued Oct. 13, 1964; U.S. Pat. No. 3,429,706 of Shepard, et al, issued Feb. 25, 1969; U.S. Pat. No. 3,672,904 of deMauriac, issued June 27, 1972 and *Research Disclosure*, January, 1973, pages 16–21.

The stabilizer precursor combination of the invention is especially useful in photothermographic materials comprising photosensitive silver halide in association with an oxidation-reduction image-forming combination comprising (i) silver behenate, with (ii) a phenolic reducing agent, such as a sulfonamidophenol reducing agent, a poly(vinyl butyral) binder, a spectral sensitizing dye, and a toning agent (also known as an activator-toning agent) comprising succinimide, N-hydroxynaphthalimide or phthalazinone. Such a photothermographic material is described, for example, in *Research Disclosure*, January, 1973, pages 16–21.

An especially useful embodiment of the invention is a photothermographic element comprising a support having thereon a layer comprising (a) photosensitive silver halide in association with (b) an oxidation-reduction image-forming combination comprising (i) silver behenate, with (ii) a phenolic reducing agent, such as a sulfonamidophenol reducing agent, (c) a poly(vinyl butyral) binder, (d) a spectral sensitizing dye, (e) a toning agent, such as succinimide or N-hydroxy-1,8-naphthalimide, and a stabilizer precursor combination comprising (f) 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione with (g) a halogen containing stabilizer precursor selected from tetrabromobutane, α-bromo-gamma-nitro-β-phenylbutyrophenone, 2-bromo-2-p-tolylsulfonylacetamide, 2-tribromomethylsulfonylbenzothiazole, 2,2-dibromo-2-phenylsulfonylacetamide, 1,3-dibenzoyloxy-2-bromo-2-nitropropane, 2-bromo-2-nitro-1,3-propanediol and combinations thereof.

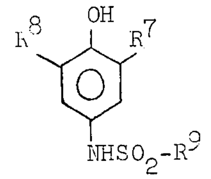
The described photographic materials according to the invention comprise a photosensitive component which comprises photosensitive silver halide. In the photothermographic materials comprising the described oxidation-reduction image-forming combination, it is believed that the photosensitive silver halide or a component resulting from the photosensitive silver halide acts as a catalyst for the described oxidation-reduction image-forming combination. A typical concentration range of photosensitive silver halide is from about 0.01 mole to about 20.0 moles of photosensitive silver halide per mole of heavy metal salt oxidizing agent, for example, per mole of silver salt oxidizing agent. Other photosensitive components can be useful in combination with photosensitive silver halide. Useful photosensitive silver salts include silver-dye complexes and other photosensitive silver salts. Preferred photosensitive silver halides are silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. Very fine-grain photosensitive silver halide is especially useful although coarse or fine-grain photosensitive silver halide can be employed if desired.

The photosensitive silver halide can be prepared by any of the procedures known in the photographic art. Such procedures and forms of photosensitive silver halide are described, for example, in the *Product Licensing Index*, Volume 92, December, 1971, publication 9232 at page 107, paragraph I. The photosensitive silver halide according to the invention can be unwashed or washed, can be chemically sensitized, can be protected against the production of fog and stabilized against loss of sensitivity during keeping, as described in the *Product Licensing Index*, Volume 92, December, 1971, publication 9232, pages 107–110.

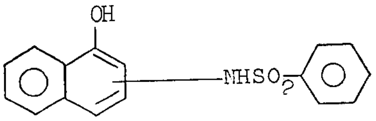
The photothermographic elements and compositions according to the invention typically comprise an oxidation-reduction image-forming combination which contains an oxidizing agent, preferably a heavy metal salt oxidizing agent. The heavy metal salt oxidizing agent can be a heavy metal salt of an organic acid such as a fatty acid which is resistant to darkening upon illumination. An especially useful class of heavy metal salts of organic acids is represented by the water insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable silver salt oxidizing agents include: silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate and silver palmitate. Silver salts can be employed as the heavy metal salt oxidizing agent which are not silver salts of long-chain fatty acids. Such silver salt oxidizing agents which are useful include, for example, silver benzoate, silver benzotriazole, silver terephthalate, silver phthalate and the like.

The described photothermographic elements and compositions can comprise various reducing agents. Suitable reducing agents which can be employed with the described stabilizer precursors include substituted phenols and naphthols, for example, bis-beta-naphthols. Suitable bis-beta-naphthols include, for example, 2,2′-dihydroxy-1,1′-binaphthyl, 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl, 6,6′-dinitro-2,2′-dihydroxy-1,1′-binaphthyl and bis-(2-hydroxy-1-naphthyl) methane. Other reducing agents which can be employed in photothermographic elements, according to the invention, include polyhydroxybenzenes such as hydroquinone, alkyl-substituted hydroquinones such as tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone and 2,6-dimethylhydroquinone; catechols and pyrogallols, chloro-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy-substituted hydroquinone such as methoxyhydroquinone or ethoxyhydroquinone; aminophenol developing agents, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives; hydroxylamine developing agents; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and the like. Combinations of reducing agents can be employed if desired.

Especially useful reducing agents which can be employed in the photothermographic materials according to the invention are sulfonamidophenol reducing agents as described in *Research Disclosure*, January, 1973, pages 16–21. One especially useful class of sulfonamidophenol reducing agents is represented by the formula:



wherein R^9 is phenyl, naphthyl, methylphenyl, thienyl, quinolinyl, thiazyl, or alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl; R^7 is hydrogen, R^9SO_2NH—, alkoxy containing 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy and butoxy, bromo or chloro; R^8 is hydrogen, bromo, chloro, alkyl containing 1 to 4 carbon atoms, as described, or alkoxy containing 1 to 4 carbon atoms, such as methoxy, ethoxy and propoxy. R^7, R^8 and/or R^9 can contain substituent groups which do not adversely affect the reducing properties of the described sulfonamidophenol reducing agents or the desired sensitometric properties of the photothermographic elements and materials of the invention. Examples of substituent groups which can be present are alkyl containing 1 to 3 carbon atoms such as methyl, ethyl and propyl, chloro, bromo and phenyl. In some cases, it is desirable to avoid an amino group as a substituent. The amino group, in some cases, provides an overly active reducing agent. Sulfonamidophenol reducing agents, as described, include sulfonamidonaphthols. A sulfonamidonaphthol which is useful is represented by the formula:



The sulfonamido group in the described sulfonamidonaphthols can be in the two, three, or four position. The sulfonamidonaphthols and sulfonamidophenols which contain two sulfonamido groups are more active compounds within the sulfonamido reducing agent class. The sulfonamidophenols containing two or more sulfonamido groups are employed for shorter developing times or with heavy metal salt oxidizing agents which are less active than silver behenate. In some cases, image discrimination provided by photothermographic materials containing the sulfonamidonaphthols and trifunctional sulfonamidophenols is less than that provided by other of the described sulfonamidophenols.

It is desirable, in some cases, to employ a so-called toning agent, also known as an accelerator-toning agent or activator-toning agent, in the photothermographic materials of the invention. Useful toning agents are described, for example, in Belgian Pat. No. 766,590 issued June 15, 1971 and in *Research Disclosure*, January, 1973, pages 16–21. Combinations of toning agents can be employed in the photothermographic materials according to the invention if desired. Typical toning agents include, for example, phthalimide, 2,3-naphthalimide, N-hydroxyphthalimide, N-potassium phthalimide, succinimide, N-hydroxy-1,8-naphthalimide and/or N-hydroxysuccinimide. In some cases, other toning agents can be employed such as 1-(2H)-phthalazinone and 2-acetylphthalazinone and the like.

A photothermographic element or composition as described according to the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable materials can be hydrophobic or hydrophilic. They 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 photographic materials. Effective polymers include water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates, methacrylates and those which have crosslinking sites which facilitate hardening or curing as well as those have recurring sulfobetaine units as described in Canadian Pat. No. 774,054. Especially useful high molecular weight materials and resins include poly(vinyl butyral), cellulose acetate butyrate, poly(methyl methacrylate), poly(vinylpyrrolidone), ethylcellulose, polystyrene, poly(vinyl chloride), chlorinated rubber, polyisobutylene, butadienestyrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid and poly(vinyl alcohol).

The useful concentration of reducing agent according to the invention will vary depending upon the particular photographic element, desired image, processing conditions, particular stabilizer precursor combination employed and the like. A useful concentration of reducing agent is typically from about 0.2 mole to about 2.0 moles of reducing agent per mole of photosensitive silver halide. A useful concentration of reducing agent in relationship to oxidizing agent, such as silver behenate or silver stearate, is typically from about 0.01 mole to about 20 moles of reducing agent per mole of oxidizing agent such as per mole of silver behenate in the photothermographic material. Combinations of reducing agents can be employed if desired. When combinations are employed, the total concentration of reducing agent is typically within the described concentration range.

Photothermographic materials according to the invention can contain development modifiers that function as speed-increasing compounds, hardeners, antistatic layers, plasticizers and lubricants, coating aids, brighteners, spectral sensitizing dyes, absorbing and filter dyes, also as described in the *Product Licensing Index*, Volume 92, December, 1971, publication 9232, pages 107–110.

The photothermographic elements according to the invention can comprise 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. The support chosen should withstand the processing temperatures employed according to the invention. Typically, a flexible support is employed.

The photothermographic compositions and other compositions according to the invention can be coated on a suitable support by various coating procedures including dip coating, air knife coating, curtain coating or extrusion coating using hoppers such as 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 such as described in U.S. Pat. No. 2,761,791 of Russell, issued Sept. 4, 1956 and British Pat. No. 837,095.

Spectral sensitizing dyes can be used in the described photothermographic elements and compositions of the invention to confer additional sensitivity to the elements and compositions of the invention. Useful sensitizing dyes are described, for example, in the *Product Licensing Index*, Volume 92, December, 1971, publication 9232, paragraph XV.

After imagewise exposure of the photographic element according to the invention, typically to visible light, the resulting latent image can be developed merely by overall heating the element to moderately elevated temperatures. This overall heating merely involves heating the described element overall in the range from about 80° to about 250°C. such as for about 0.5 to about 60 seconds. By increasing or decreasing the length of time of heating, a higher or lower temperature within the described range can be employed depending upon the desired image, particular stabilizer precursor, particular reducing agent, and the like. Typically, a lower processing temperature is desired. A preferred processing temperature range is from about 115° to about 175°C. A developed and stabilized image is typically produced within several seconds, such as from about 0.5 to about 60 seconds.

Any suitable means can be used for providing the desired processing temperature range. The heating means can be a simple hot plate, iron, roller or the like.

Processing is usually carried out under ambient conditions of pressure and humidity. Conditions outside normal atmospheric pressure and humidity can be employed if desired.

The described stabilizer precursors according to the invention can be in any suitable location in the photographic material according to the invention which provides the desired stabilized image. If desired, one or more of the components of the photothermographic element according to the invention can be in one or more layers of the element. For example, in some cases, it can be desirable to include certain percentages of the reducing agent, toner, image stabilizer precursors and/or other addenda in a protective layer over the photothermographic element. This in some cases can reduce migration of certain addenda in the layers of the photothermographic element.

Another embodiment of the invention comprises a photothermographic composition or element comprising (a) photosensitive silver halide in association with (b) a photosensitive silver halide developing agent, as described, (c) a stabilizer precursor combination, also as described, (d) a base-release agent, and (e) a polymeric binder for the composition or element.

A further embodiment of the invention comprises a photographic silver halide image stabilizer precursor composition comprising (a) a polymeric binder for said composition with (b) a blocked thione, silver halide image stabilizer precursor and (c) a halogen containing stabilizer precursor as described.

A variety of base-release agents can be employed in the photographic materials according to the invention depending upon the particular photographic component, the particular stabilizer precursor, the desired image, processing temperature range, and the like. A base-release agent as employed herein is intended to mean a compound which releases base upon heating to a desired temperature to provide activation of at least one of the components of the photographic material, such as activation of the reducing agent. Typical base-release agents include those described, for example, in U.S. Pat. No. 3,531,285 of Haist, et al., issued Sept. 29, 1970. Useful base-release agents include, for example, guanidinium salts, such as guanidinium trichloroacetate, quaternary ammonium malonates, certain amino acids, heat cleavable hydrazides, and oxazolidones, as described in U.S. Pat. No. 3,531,285.

When a base-release agent is employed in a photographic material according to the invention, a range of concentration can be employed as described. A useful concentration is typically about 0.25 to about 10 moles of the base-release agent per mole of the photosensitive silver salt in the photographic material. A photothermographic composition or element according to the invention can accordingly comprise (a) photosensitive silver halide in association with (b) about 1 to about 4 moles of a silver halide developing agent per mole of such silver halide, (c) a blocked thione stabilizer precursor, as described, (d) a halogen containing stabilizer precursor, also as described, (e) about 0.25 to about 10 moles of a base-release agent per mole of such silver halide, and (f) a polymeric binder for the composition or element.

If desired, the described stabilizer precursors, according to the invention, can be used in combination with other stabilizers or stabilizer precursors, such as with S-carbamoyl stabilizer precursors in photographic elements and compositions such as photothermographic materials. Useful S-carbamoyl stabilizer precursors are described in copending U.S. application Ser. No. 251,728 of Pierce, et al., filed May 8, 1972, now U.S. Pat. No. 3,824,103.

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

EXAMPLE 1

This is a comparative example.

A silver behenate-behenic acid dispersion (I) is prepared by ball-milling the following components for 64 hours:

silver behenate	168 g
behenic acid	64 g
lithium stearate	16.8 g
poly(vinylbutyral)	120 g
acetone-toluene (1:1 by volume)	2 liters

The following addenda are combined with 71 ml of the above-identified dispersion (I), mixed thoroughly and then coated on a suitable paper support at 0.86 g Ag/m² and 2.5 g poly(vinylbutyral)/m².

Poly(vinylbutyral)-silverbromoiodide emulsion (3 l./mole Ag, 100 g polymer/mole Ag, 6 mole % iodide)	11 ml
Acetone-methanol solution (33:1 by volume) containing 0.01% by weight 3-carboxymethyl-5-[(3-methyl-2-thiazolinylidene)-1-methylethylidene]-rhodanine and 0.03% by volume triethylamine	6 ml
Acetone solution containing 10% by weight 2,6-dichloro-4-benzenesulfonamidophenol	12 ml
Acetone-toluene-methanol solution (1:1:1 by volume) containing 0.5% by weight N-hydroxy-1,8-naphthalimide	11 ml
Acetone	12 ml

The material is also overcoated with the following composition at 0.95 g cellulose acetate/m².

cellulose acetate	20.0 g
acetone-dichloromethane (1:1 by volume)	800 ml

The dried element is exposed imagewise to tungsten light for 4 seconds and then heat-processed by contacting the element with a metal block heated to 140°C. for 2 seconds.

After a sensitometric curve is obtained of the freshly processed sample, the coating is subjected to roomlight (about 50–60 ft.-candles from a white fluorescent bulb) for 1, 2, 4, 24, 48, and 120 hours, respectively. After each time interval, a new sensitometric curve is plotted from the processed sample. The Dmin and Dmax values are listed in following Table I.

EXAMPLE 2

This is a comparative example.

This example is like Example 1 except that the composition now contains 2.5 ml of an acetone solution containing 3 percent by weight of 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione, designated Compound A, corresponding to 0.017 mole/mole Ag. The thione compound is added to the described photothermographic composition prior to coating on the paper support. The sample is exposed, heat processed and subjected to roomlight handling as described in Example 1. The results are given in following Table I.

EXAMPLE 3

This is a comparative example.

This example is like Example 1 except that the composition now contains 20 ml of an acetone solution containing 10 percent by weight of α-bromo-γ-nitro-β-phenylbutyrophenone, designated as Compound B, corresponding to 0.35 mole/mole Ag. The bromo compound is added to the described photothermographic composition prior to coating on the paper support. The sample is exposed, heat processed and subjected to the roomlight handling as described in Example 1. The results are given in following Table I.

EXAMPLE 4

The procedure in Example 1 is repeated except that the element contains the blocked thione and the α-haloketone of Examples 2 and 3 at the concentrations specified in Table I. The photothermographic element is exposed, heat processed and subjected to the roomlight handling as described in Example 1. The results are given in following Table I.

Table I

Example	Compound	Mole(s) Compound Per Mole Ag	Print-Out Time and Dmin							
			O hr.	1 hr.	2 hrs.	4 hrs.	24 hrs.	48 hrs.	120 hrs.	Dmax
1	—	0.000	0.36	0.51	0.52	0.51	0.52	0.51	0.51	1.47
2	A	0.017	0.29	0.32	0.34	0.34	0.36	0.38	0.40	1.42
3	B	0.35	0.48	0.58	0.56	0.55	0.44	0.38	0.39	1.40
4	A	0.017	0.28	0.30	0.32	0.30	0.26	0.23	0.20	1.32
	B	0.35								

EXAMPLE 5–19

Similar results are obtained when the following halogen containing stabilizer precursors are employed in the photothermographic element according to Example 4 in place of Compound B:

EXAMPLE 5

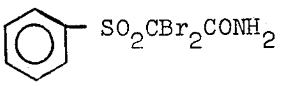
Tetrabromobutane

EXAMPLE 6

2-tribromomethylsulfonylbenzothiazole

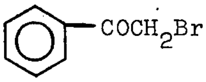
EXAMPLE 7

2,2-dibromo-2-phenylsulfonylacetamide



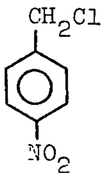
EXAMPLE 8

2-bromoacetophenone



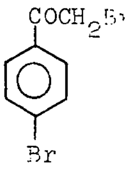
EXAMPLE 9

α-chloro-p-nitrotoluene



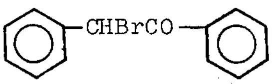
EXAMPLE 10

2,4′-dibromoacetophenone



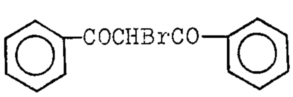
EXAMPLE 11

2-bromo-2-phenylacetophenone



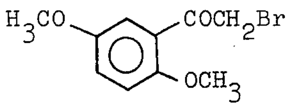
EXAMPLE 12

2-bromo-1,3-diphenyl-1,3-propanedione



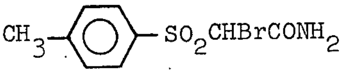
EXAMPLE 13

α-bromo-2,5-dimethoxyacetophenone



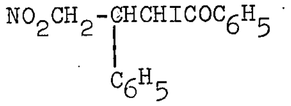
EXAMPLE 14

2-bromo-2-p-tolylsulfonylacetamide



EXAMPLE 15

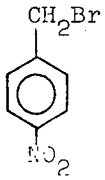
α-iodo-γ-nitro-β-phenylbutyrophenone



$$NO_2CH_2\text{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCHICOC_6H_5$$

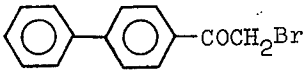
EXAMPLE 16

α-bromo-p-nitrotoluene



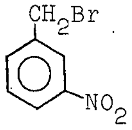
EXAMPLE 17

2-bromo-4′-phenylacetophenone



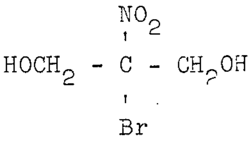
EXAMPLE 18

α-bromo-m-nitrotoluene



EXAMPLE 19

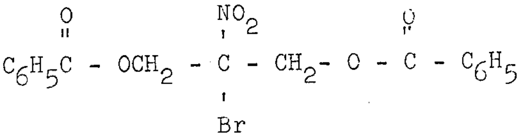
2-bromo-2-nitro-1,3-propanediol



$$\mathrm{HOCH_2-\overset{\displaystyle NO_2}{\underset{\displaystyle Br}{C}}-CH_2OH}$$

EXAMPLE 19-A

1,3-dibenzoyloxy-2-bromo-2-nitropropane



$$\mathrm{C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}-OCH_2-\overset{\displaystyle NO_2}{\underset{\displaystyle Br}{C}}-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5}$$

Another advantage which the described halogen containing stabilizer precursors provide in silver halide photothermographic materials is that they provide enhanced shelf-life or incubation stability at elevated temperatures or long-term keeping at ambient room conditions as described.

EXAMPLES 20–23

Similar results are obtained when the following blocked thione stabilizer precursors are employed in the photothermographic element according to Example 4 in place of Compound A:

EXAMPLE 20

1-methylcarbamoyl-4-phenyl-2-tetrazoline-5-thione

EXAMPLE 21

4-hexylcarbamoyl-1-phenyl-2-tetrazoline-5-thione

EXAMPLE 22

N,N′-hexamethylenebis(1-carbamoyl-4-phenyl-2-tetrazoline-5-thione

EXAMPLE 23

4-phenyl-1-phenylcarbamoyl-2-tetrazoline-5-thione

EXAMPLE 24

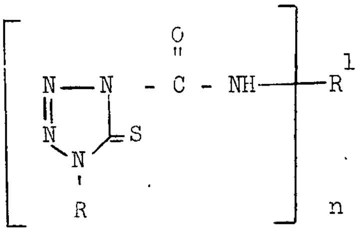
The following example illustrates a photothermographic material according to the invention comprising a base-release agent as described: a composition is prepared by mixing hydroquinone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, guanidinium trichloroacetate, poly(vinyl alcohol) binder in alcohol and water as described in Example 1 of U.S. Pat. No. 3,531,285 of Haist, et al., issued Sept. 29, 1970. 1-Cyclohexylcarbamoyl-4-phenyl-tetrazoline-5-thione and tetrabromobutane also are added to the composition. The composition is coated on a photographic paper containing a gelatino, silver bromide photographic layer. Upon imagewise exposure to light followed by overall heating the element to about 190°C. for a few seconds, a developed and stabilized image results.

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.

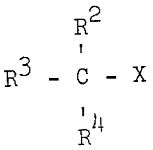
What is claimed is:

1. A photothermographic element comprising a support having thereon at least one layer comprising photosensitive silver halide and a stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor.

2. A photothermographic element as in claim **1** comprising a support having thereon at least one layer comprising photosensitive silver halide and a combination of (a) a blocked thione stabilizer precursor which is a compound represented by the formula:

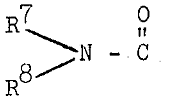


wherein R is aryl containing 6 to 12 carbon atoms and R^1 is alkyl containing 1 to 6 carbon atoms, aryl containing 6 to 12 carbon atoms, cycloalkyl containing 3 to 8 carbon atoms when *n* is 1; or R^1 is alkylene containing 1 to 6 carbon atoms when *n* is 2; *n* is 1 or 2; with (b) a halogen containing stabilizer precursor which is a compound represented by the formula:



$$\mathrm{R^3-\overset{\displaystyle R^2}{\underset{\displaystyle R^4}{C}}-X}$$

wherein X is chloro, bromo or iodo; R^2, R^3 and R^4 are individually selected from the group consisting of hydrogen; alkyl containing 1 to 10 carbon atoms; hydroxyalkyl containing 1 to 10 carbon atoms; acyloxyalkyl containing 2 to 10 carbon atoms; nitro; nitroalkyl containing 1 to 10 carbon atoms; aryl containing 6 to 12 carbon atoms; acyl of the formula $R'' - CO -$ wherein R'' is alkyl containing 1 to 5 carbon atoms, or aryl containing 6 to 12 carbon atoms; amido represented by the formula



wherein R^7 and R^8 are individually selected from the group consisting of hydrogen, alkyl containing 1 to 5 carbon atoms, phenyl and naphthyl; sulfonyl represented by the formula

$$R^9 - SO_2 -$$

wherein R^9 is alkyl containing 1 to 5 carbon atoms, or aryl containing 6 to 12 carbon atoms; bromo; chloro; and iodo; and wherein at least one of R^2, R^3 and R^4 is hydroxyalkyl, acyloxyalkyl, acyl, amido or sulfonyl as defined.

3. A photothermographic element as in claim **1** wherein said blocked thione stabilizer precursor is 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione.

4. A photothermographic element as in claim **1** wherein said halogen containing stabilizer precursor is a compound selected from the group consisting of

a. tetrabromobutane,
b. α-bromo-gamma-nitro-β-phenylbutyrophenone,
c. 2-bromo-2-p-tolylsulfonylacetamide,
d. 2-tribromomethylsulfonylbenzothiazole,
e. 2,2-dibromo-2-phenylsulfonylacetamide,
f. 1,3-dibenzoyloxy-2-bromo-2-nitropropane,
g. 2-bromo-2-nitro-1,3-di-(4-nitrobenzoyloxy)propane,
h. 2-bromo-1,3-di-(4-methoxybenzoyloxy)-2-nitropropane, and combinations thereof.

5. A photothermographic element as in claim **1** wherein said stabilizer precursor combination comprises (a) about 0.005 to about 0.035 mole of said blocked thione stabilizer per mole of total silver with (b) about 0.001 to about 1.0 mole of said halogen containing stabilizer precursor per mole of total silver.

6. In a photothermographic element comprising a support having thereon a layer comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction imageforming combination comprising (i) a heavy metal salt oxidizing agent with (ii) an organic reducing agent, (C) a polymeric binder for said layer, and (D) a stabilizer precursor, the improvement wherein said stabilizer precursor comprises a stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor.

7. A photothermographic element as in claim **6** wherein said stabilizer precursor comprises a stabilizer precursor combination of (a) about 0.005 to about 0.035 mole of a blocked thione stabilizer precursor per mole of total silver with (b) about 0.001 to about 1.0 mole of a halogen containing stabilizer precursor per mole of total silver in said element.

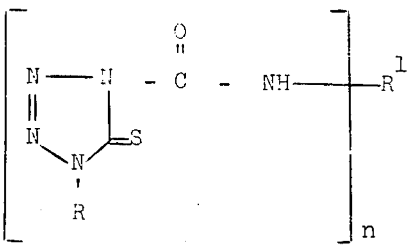
8. A photothermographic element as in claim **6** comprising a support having thereon a layer comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a sulfonamidophenol reducing agent, (C) a poly(vinyl butyral) binder for said layer, (D) a stabilizer precursor combination comprising (I) 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione with (II) 2-bromo-2-p-tolylsulfonylacetamide, (E) a spectral sensitizing dye, and (F) a toner comprising succinimide, N-hydroxy-1,8-naphthalimide or phthalazinone.

9. In a photothermographic element comprising a support having thereon a layer comprising (A) photosensitive silver halide, (B) a silver halide developing agent, (C) a development activator precursor, (D) a polymeric binder for said layer and (E) a stabilizer precursor, the improvement wherein said stabilizer precursor comprises a combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor.

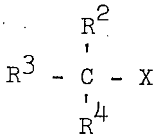
10. A photographic composition comprising photosensitive silver halide, a polymeric binder for said composition and a stabilizer precursor combination comprising (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor.

11. A photographic composition as in claim **10** also comprising a silver halide developing agent.

12. A photographic composition as in claim **10** wherein said stabilizer precursor combination comprises (a) a blocked thione stabilizer precursor represented by the formula:

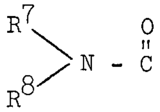


wherein R is aryl containing 6 to 12 carbon atoms and R^1 is alkyl containing 1 to 6 carbon atoms, aryl containing 6 to 12 carbon atoms, cycloalkyl containing 3 to 8 carbon atoms when *n* is 1; or R^1 is alkylene containing 1 to 6 carbon atoms when *n* is 2; *n* is 1 or 2; with (b) a halogen containing stabilizer precursor which is a compound represented by the formula:



$$R^3 - \overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle R^4}{|}}{C}} - X$$

wherein X is chloro, bromo or iodo; R^2, R^3 and R^4 are individually selected from the group consisting of hydrogen; alkyl containing 1 to 10 carbon atoms; hydroxyalkyl containing 1 to 10 carbon atoms; acyloxyalkyl containing 2 to 10 carbon atoms; nitro; nitroalkyl containing 1 to 10 carbon atoms; aryl containing 6 to 12 carbon atoms; acyl of the formula $R'' - CO -$ wherein R'' is alkyl containing 1 to 5 carbon atoms, or aryl containing 6 to 12 carbon atoms; amido represented by the formula



wherein R^7 and R^8 are individually selected from the group consisting of hydrogen, alkyl containing 1 to 5 carbon atoms, phenyl and naphthyl; sulfonyl represented by the formula

$$R^9 - SO_2 -$$

wherein R^9 is alkyl containing 1 to 5 carbon atoms, or aryl containing 6 to 12 carbon atoms; bromo; chloro; and iodo; and wherein at least one of R^2, R^3 and R^4 is hydroxyalkyl, acyloxyalkyl, acyl, amido or sulfonyl as defined.

13. A photographic composition as in claim **10** wherein said blocked thione stabilizer precursor is 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione.

14. A photographic composition as in claim **10** wherein said halogen containing stabilizer precursor is a compound selected from the group consisting of

a. tetrabromobutane,
b. α-bromo-gamma-nitro-β-phenylbutyrophenone,
c. 2-bromo-2-p-tolylsulfonylacetamide,
d. 2-tribromomethylsulfonylbenzothiazole,
e. 2,2-dibromo-2-phenylsulfonylacetamide,
f. 1,3-dibenzoyloxy-2-bromo-2-nitropropane,
g. 2-bromo-2-nitro-1,3-di-(4-nitrobenzoyloxy)propane,
h. 2-bromo-1,3-di-(4-methoxybenzoyloxy)-2-nitropropane, and combinations thereof.

15. In a photothermographic composition comprising (A) photosensitive comprising halide in association with (B) an oxidation-reduction image-forming combination omprising (i) a heavy metal salt oxidizing agent with (ii) an organic reducing agent, (C) a polymeric binder for said layer, and (D) a stabilizer precursor, the improvement wherein said stabilizer precursor comprises a stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor.

16. A photographic composition as in claim **15** wherein said stabilizer precursor combination comprises (a) about 0.005 to about 0.035 mole of said blocked thione stabilizer precursor per mole of total silver with (b) about 0.001 to about 1.0 mole of said halogen containing stabilizer precursor per mole of total silver in said composition.

17. A photothermographic composition comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) a silver salt of a long-chain fatty acid with (ii) an organic reducing agent, (C) a polymeric binder for said composition, and (D) a stabilizer precursor, the improvement wherein said stabilizer precursor comprises a stabilizer precursor combination of (a) about 0.005 to about 0.035 mole of blocked thione stabilizer precursor per mole of total silver with (b) about 0.001 to about 1.0 mole of a halogen containing stabilizer precursor per mole of total silver in said composition.

18. A photothermographic composition as in claim **17** comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a sulfonamidophenol reducing agent, (C) a poly(vinyl butyral) binder for said composition, (D) a stabilizer precursor combination comprising (I) 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione with (II) 2-bromo-2-p-tolylsulfonylacetamide, (E) a spectral sensitizing dye, and (F) a toner comprising succinimide, N-hydroxy-1,8-naphthalimide or phthalazinone.

19. A photothermographic composition comprising (a) photosensitive silver halide in association with (b) a silver halide developing agent, (c) a development activator precursor, (d) a polymeric binder for said composition and (e) a stabilizer precursor for said silver halide, the improvement wherein said stabilizer precursor comprises a combination of (i) a blocked thione stabilizer precursor with (ii) a halogen containing stabilizer precursor.

20. A process of stabilizing an image in a photothermographic element comprising a support having thereon at least one layer comprising a photosensitive silver halide and a stabilizer precursor combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor for said silver salt, comprising heating said element to about 80° to about 250°C.

21. A process as in claim **20** wherein said element is heated at about 80° to about 250°C. for about 0.5 to about 60 seconds.

22. A process of developing and stabilizing an image in a photothermographic element comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) a silver salt of a long-chain fatty acid with (ii) an organic reducing agent, (C) a polymeric binder for said layer, and (D) a stabilizer precursor comprising a combination of (a) a blocked thione stabilizer precursor with (b) a halogen containing stabilizer precursor, comprising heating said element to about 80° to about 250°C.

23. A process of developing and stabilizing an image in a photothermographic element comprising a support having thereon a layer comprising (A) photosensitive silver halide in association with (B) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a sulfonamidophenol reducing agent, (C) a poly(vinyl butyral) binder for said layer, (D) a stabilizer precursor combination comprising (I) 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione with (II) 2-bromo-2-p-tolysulfonylacetamide, (E) a spectral sensitizing dye and (F) a toner comprising succinimide, N-hydroxy-1,8-naphthalimide or phthalazinone; comprising heating said element to about 120° to about 160°C. for about 0.5 to about 30 seconds.

24. A photographic silver halide image stabilizer precursor composition comprising (a) a polymeric binder for said composition with (b) a blocked thione, silver halide image stabilizer precursor and (c) a halogen containing stabilizer precursor.

25. A photographic silver halide image stabilizer precursor composition comprising (a) a poly(vinyl butyral) binder for said composition with (b) 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione, and (c) a halogen containing stabilizer precursor which is a compound selected from the group consisting of

i. tetrabromobutane,
ii. α-bromo-gamma-nitro-β-phenylbutyrophenone,
iii. 2-bromo-2-p-tolylsulfonylacetamide,
iv. 2-tribromomethylsulfonylbenzothiazole,
v. 2,2-dibromo-2-phenylsulfonylacetamide,
vi. 2-bromo-2-nitro-1,3-propanediol,
vii. 1,3-dibenzoyloxy-2-bromo-2-nitropropane,
viii. 2-bromo-2-nitro-1,3-di-(4-nitrobenzoyloxy)propane,
ix. 2-bromo-1,3-di-(4-methoxybenzoyloxy)-2-nitropropane, and combinations thereof.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,877,940
DATED : April 15, 1975
INVENTOR(S) : Ronald H. Ericson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 8, "percursor" first occurrence should read -- precursor --.

Column 7, line 26, "2-bromo-2phenylacetophenone" should read --- 2-bromo-2-phenylacetophenone ---. Line 64, "cencentration" should read ---concentration---.

Column 16, Table I, under the column 120 hrs., "0.39" should read --- 0.30 ---.

Column 19, line 34, "imageforming" should read --- image-forming ---.

Column 21, line 20, after "photosensitive" delete "comprising" and insert ---silver---. Line 22, "omprising" should read ---comprising---. Line 44, after "mole of" insert ---a---.

Column 22, line 36, "tolysulfonylacetamide" should read ---tolylsulfonylacetamide---.

Signed and Sealed this

third **Day of** *February 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks