

[54] **PHOTOTHERMIC SILVER HALIDE ELEMENT CONTAINING A BIS-BETA-NAPHTHOL REDUCING AGENT AND A 1, 3-DIHYDROXY-BENZENE REDUCING AGENT**

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[58] Field of Search 96/114.1, 67

[57] **ABSTRACT**

In photosensitive materials for processing with heat, a combination of a bis-beta-naphthol reducing agent with a 1,3-dihydroxybenzene reducing agent, such as 2,4-dihydroxybenzaldehyde or 2,4-dihydroxybenzophenone, provides surprisingly increased relative speed, maximum density and exposure latitude. This combination of reducing agents can be used in photosensitive and thermosensitive materials for processing with heat. These materials can contain addenda commonly employed in photosensitive materials such as activator-toning agents, stabilizers or stabilizer precursors, sensitizing dyes and the like.

[56] **References Cited**

UNITED STATES PATENTS

3,667,958 6/1972 Evans 96/114.1

FOREIGN PATENTS OR APPLICATIONS

1,178,800 1/1970 Great Britain 96/114.1

24 Claims, No Drawings

**PHOTOTHERMIC SILVER HALIDE ELEMENT
CONTAINING A BIS-BETA-NAPHTHOL
REDUCING AGENT AND A
3-DIHYDROXY-BENZENE REDUCING AGENT**

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photosensitive elements, compositions and processes for developing a latent image with heat. In one of its aspects it relates to photosensitive elements for processing with heat containing certain combinations of reducing agents which provide increased relative speed, increased maximum density and greater exposure latitude. In another of its aspects it relates to a photosensitive composition for processing with heat containing the described combination of reducing agents. A further aspect relates to photosensitive and thermosensitive compositions containing the described combination of reducing agents. Another aspect relates to a thermographic combination comprising an oxidation-reduction image-forming combination containing a heavy metal salt oxidizing agent, such as silver behenate, with a described reducing agent combination. A further aspect relates to a process of developing a latent image in an exposed photosensitive and thermosensitive element employing the described combination of reducing agents.

2. Description of the State of the Art

It is known to provide a developed image in a photosensitive material employing so-called dry processing with heat. The photosensitive material can contain a reducing agent. Such photosensitive materials are described, for example, in U.S. Pat. No. 3,152,903 of Shepard et al. issued Oct. 13, 1964; U.S. Pat. No. 3,152,904 of Sorensen et al. issued Oct. 13, 1964; U.S. Pat. No. 3,392,020 of Yutzy and Yackel issued July 9, 1968; U.S. Pat. No. 3,457,075 of Morgan and Shely issued July 22, 1969; British Pat. No. 1,161,777 and Belgian Pat. No. 705,872. There has been a continuing need to provide combinations of reducing agents in photosensitive materials for processing with heat which provide increased relative speed and maximum density.

In thermographic materials it has been known to employ a reducing agent which is inactivated by image-wise exposure to U.V. radiation. Such an element is described, for example, in U.S. Pat. No. 3,094,619 of Grant issued June 18, 1963. One of the reducing agents employed in this thermographic element can be 1,1'-dihydroxy-2,2'-binaphthol. A similar element employing, for example, an alpha or beta naphthol as a reducing agent and 1-(2H)phthalazinone, as a toning agent, is described, for example, in U.S. Pat. No. 3,080,254 of Grant issued Mar. 5, 1963.

Other bis-naphthol reducing agents which can be employed in photosensitive materials for processing with heat are described in copending U.S. Patent application Ser. No. 33,964 of DeMauriac filed May 1, 1970 now U.S. Pat. No. 3,672,904 issued June 27, 1972.

1,3-Dihydroxybenzene compounds have been employed in photosensitive materials in the past. For instance, U.S. Pat. No. 2,165,421 of Sheppard et al. issued July 11, 1939 indicates that a combination of an aliphatic aldehyde hardening agent with a 1,3-dihydroxybenzene compound can be employed for hardening gelatin. However, when a 1,3-dihydroxybenzene compound such as 2,4-dihydroxybenzaldehyde, is employed in a photosensitive mate-

rial for processing with heat employing an oxidation-reduction image-forming combination, this reducing agent does not provide the desired increased relative speed or increased maximum density. This is demonstrated in the following comparative Example 2 as well as in comparative Examples 4 and 5.

Accordingly, there has been a continuing need to provide a combination of reducing agents in photosensitive elements, compositions and processes for developing a latent image with heat which provide increased relative speed and increased maximum density as well as increased exposure latitude without increased minimum density.

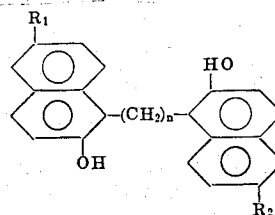
SUMMARY OF THE INVENTION

According to the invention, a combination of a bis-naphthol reducing agent especially a bis-beta-naphthol reducing agent, with a 1,3-dihydroxybenzene compound, as described herein in a photosensitive element, composition or process for developing a latent image with heat provides surprising increased relative speed as well as increased maximum density as well as wider exposure latitude without increased minimum density. This combination of reducing agents provides especially useful results in a photothermographic composition, also described herein as a photosensitive and thermosensitive composition employing photosensitive silver halide with an oxidation-reduction image-forming combination comprising a heavy metal salt oxidizing agent with a described combination of reducing agents.

The described combination of reducing agents provide the described results even in a combination with stabilizer precursors, activator-toning agents, sensitizing dyes and other addenda employed in photosensitive and thermosensitive elements, compositions and processes.

DETAILED DESCRIPTION OF THE INVENTION

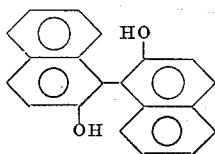
A range of bis-naphthol especially bis-beta-naphthol reducing agents can be employed in the described photosensitive elements, compositions and processes to provide a desired developed image. A bis-naphthol reducing agent which is especially suitable is a bis-beta naphthol of the formula



wherein R_1 and/or R_2 is hydrogen, alkyl with one to three carbon atoms, alkoxy, e.g., alkoxy containing one to two carbon atoms, such as methoxy or ethoxy; halogen, nitro, amino, or a diazonium halide salt and n is 0 or 1.

An especially suitable bis- β -naphthol is 2,2'-dihydroxy-1,1'-binaphthyl of the formula

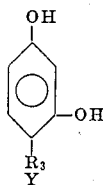
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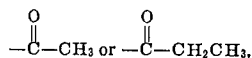
Other examples of suitable bis- β -naphthols which can be employed in the practice of the invention include:

- 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl
- 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl
- bis(2-hydroxy-1-naphthyl)methane.

A range of 1,3-dihydroxybenzene compounds as described herein can also be employed in the described combination of reducing agents. A suitable 1,3-dihydroxybenzene compound is one which provides the desired increase in maximum density, relative speed and exposure latitude without undesired increase in minimum density. A suitable test for determining an acceptable 1,3-dihydroxybenzene compound to be employed in the practice of the invention is set out in Example 1 following. A class of 1,3-dihydroxybenzene compounds which has been found to satisfy this test and provide the desired properties is represented by the formula:



wherein R_3 is alkylene containing one to six carbon atoms, such as methylene, ethylene, propylene, butylene, pentylene and hexylene or arylene containing six to 10 carbon atoms, such as phenylene, methylphenylene, and xylylene, and carbonylalkyl, such as



and carbonylphenyl, Y is hydrogen, oxygen or sulfur. These 1,3-dihydroxybenzene compounds can contain substituent groups which do not adversely affect the described desired properties, such as hydroxyl groups. Examples of suitable 1,3-dihydroxybenzene compounds are

- 2,4-dihydroxy benzaldehyde,
- 2,4-dihydroxy benzophenone, and
- 2',4'-dihydroxy acetophenone.

The described combination of reducing agents is typically employed as a component of a photosensitive element. Accordingly, one of the embodiments of the invention is a photosensitive element comprising a support, a photosensitive component, typically photosensitive silver halide, and a bisnaphthol reducing agent with a 1,3-dihydroxybenzene compound, as described. A photosensitive composition employing the described reducing agent combination typically comprises photo-

sensitive silver halide, a bis-naphthol reducing agent with a 1,3-dihydroxybenzene compound. However, a preferred photosensitive and thermosensitive composition comprises

- 5 a. photosensitive silver halide, with
- b. an oxidation-reduction image-forming combination comprising
 - i. a heavy metal salt oxidizing agent with
 - ii. a bis-naphthol reducing agent and
- 10 c. a 1,3-dihydroxybenzene compound, as described.

The described combination of reducing agents can be employed in a range of concentrations in a photosensitive and thermosensitive element or composition. An especially suitable range of concentration is about 0.4 to about 2.0 moles of reducing agent combination per mole of photosensitive component employed. In a photosensitive and thermosensitive element or composition a preferred concentration range of components comprises 0.01 to 0.50 moles of photosensitive silver halide per mole of heavy metal salt oxidizing agent; 0.42 to 2.0 moles of bis-naphthol reducing agent per mole of heavy metal salt oxidizing agent and a ratio of bis-naphthol reducing agent to 1,3-dihydroxybenzene compound of from 10:1 to 1:5. Employing the photosensitive and thermosensitive composition and element of Example 1 as a typical example, various desired concentrations can be determined by balancing the concentrations of components in the composition and/or element.

The photosensitive and thermosensitive elements and compositions in which the described combination of reducing agents can be employed are described, for example, in U.S. Pat. No. 3,457,075 of Morgen et al. issued July 22, 1969; U.S. Pat. No. 3,152,904 of Sorensen et al. issued Oct. 13, 1964; as well as in copending U.S. patent applications Ser. No. 33,964 of DeMauriac filed May 1, 1970 now U.S. Pat. No. 3,672,904 issued June 27, 1972; Ser. No. 43,171 of Hiller filed June 3, 1970 corresponding to Belgian Patent No. 768,071 issued July 30, 1971; Ser. No. 43,173 of Hiller filed June 3, 1970 corresponding to Belgian Patent No. 768,073 issued July 30, 1971; Ser. No. 33,966 of Bojara and DeMauriac filed May 1, 1970 now U.S. Pat. No. 3,667,959 issued June 6, 1972; and Ser. No. 70,466 of DeMauriac and Gaugh filed Sept. 8, 1970 corresponding to Belgian Patent No. 772,371 issued Oct. 15, 1971.

Other reducing agents can be used in combination with the described bis-naphthol reducing agents and 1,3-dihydroxybenzene reducing agents. These are typically silver halide developing agents and include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones as exemplified by tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone and 2,6-dimethylhydroquinone; catechols and pyrogallol; halo-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy-substituted hydroquinones such as methoxyhydroquinone or ethoxyhydroquinone; methylhydroxynaphthalene; phenylenediamine developing agents; methylgallate; 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 such as those described in U.S. Pat. No. 3,337,342 of Green issued Aug. 22, 1967; hydroxylamine developing agents such

as N,N'-di(2-ethoxy-ethyl)hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone including those described in British Patent 930,572 published July 3, 1963; hydroxytetrone acid, and hydroxytetroneimide developing agents; reductone developing agents such as anhydrodihydropyridino hexose reductone; and the like.

The described photosensitive element and/or composition contains a photosensitive component, preferably a photosensitive silver salt. A typical concentration range of photosensitive silver salt is from about 0.005 to about 0.50 mole of silver salt per mole of heavy metal salt oxidizing agent, such as per mole of silver salt of organic acid, e.g., per mole of silver behenate. A preferred photosensitive component is photosensitive silver halide, e.g., silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, or mixtures thereof. The photosensitive silver halide can be coarse or fine-grain, very fine-grain emulsions being especially useful. An emulsion containing the photosensitive silver halide can be prepared by any of the well-known procedures in the photographic art, such as single-jet emulsion, double-jet emulsions, such as Lippman emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. No. 2,222,264 of Nietz et al. issued Nov. 14, 1940; U.S. Pat. No. 3,320,069 of Illingsworth issued May 15, 1967 and U.S. Pat. No. 3,271,157 of McBride issued Sept. 6, 1966. Surface image silver halide emulsions can be used if desired. Mixtures of surface and internal image silver halide emulsions can be used as described in U.S. Pat. No. 2,996,332 of Luckey et al. issued Apr. 15, 1961. Negative type emulsions can be used. The silver halide emulsion can be a regular grain emulsion such as described in Klein and Moisar, *Journal of Photographic Science*, Volume 12, No. 5, September-October (1964) pages 242-251.

The silver halide employed in the practice of the invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill setting and leaching or the emulsion can be coagulation washed.

The silver halide employed in the practice of the invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium, or tellurium compounds; gold, platinum, or palladium compounds, or combinations of these. Suitable procedures are described, for example, in U.S. Pat. No. 1,623,499 of Shepard issued Apr. 5, 1927; U.S. Pat. No. 2,399,083 of Waller et al. issued Apr. 23, 1946; U.S. Pat. No. 3,297,447 of McVeigh issued Jan. 10, 1967 and U.S. Pat. No. 3,297,446 of Dunn issued Jan. 10, 1967.

Photosensitive silver halide employed in the practice of the invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, e.g., used alone or in combination include, for example, thiazolium salts; azaindenes; mercury salts as described, for example, in U.S. Pat. No. 2,728,663 of Allen et al. issued Dec. 27, 1955; urazoles; sulfocatechols; oximes described, for example, in British Pat. No. 623,448; nitron; nitroindazoles; polyvalent metal salts described, for example, in U.S. Pat. No. 2,839,405 of Jones issued June 17, 1958; platinum, palladium and gold salts described, for example, in U.S. Pat. No.

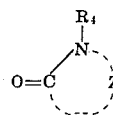
2,566,263 of Trivelli et al. issued Aug. 28, 1951 and U.S. Pat. No. 2,597,915 of Yutzy et al. issued May 27, 1952.

The described photosensitive and thermosensitive elements or compositions comprise an oxidizing agent, especially a heavy metal salt oxidizing agent, such as a heavy metal salt of an organic acid. The heavy metal salts of the organic acids should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable 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 salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate and silver palmitate.

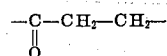
Other suitable carboxylic acid silver salt oxidizing agents, which are not silver salts of long-chain fatty acids, include silver benzoate, silver 4'-n-octadecyloxydiphenyl-4-carboxylate, silver o-aminobenzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver p-phenylbenzoate, silver phenylacetate, silver salicylate, silver butyrate, silver terephthalate, silver phthalate, silver acetate and silver acid phthalate.

Oxidizing agents which are not silver salts of a carboxylic acid can be employed, if desired, such as silver phthalazinone, silver benzotriazole and silver saccharin. Oxidizing agents which are not silver salts can be employed, if desired, such as zinc oxide, gold stearate, mercuric behenate, auric behenate and the like, but silver salts are preferred.

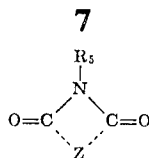
It is desirable to employ a so-called activator-toning agent in the elements, compositions and processes of the invention to obtain a more neutral (black) image, particularly when phenolic reducing agents are used. A suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom and of the formula:



where R_4 is hydrogen, hydroxyl, or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z, represents atoms completing a heterocyclic nucleus, especially a 5 or 6 member heterocyclic nucleus. The atoms completing the heterocyclic nucleus can be, for example,



or an alkylene group containing three or four carbon atoms. The atoms completing the heterocyclic nucleus can contain various substituent groups, such as amino, alkyl amino, e.g. methylamino or ethylamino, hydroxyl, carbamyl and the like. An especially suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom which is preferably a cyclicimide of the formula:



wherein R_5 is hydrogen, hydroxyl, or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z represents carbon atoms of a series completing a cyclic imide nucleus, typically consisting of from five to six carbon atoms, e.g. a phthalimide or succinimide nucleus. The atoms of the cyclic imide nucleus can contain various substituent groups, especially amino, alkyl, such as alkyl containing one to five carbon atoms, such as methyl, ethyl, propyl, butyl or pentyl or aryl, such as aryl containing six to 20 carbon atoms, such as phenyl, tolyl and xylyl. Suitable activator-toning agents which can be employed in the practice of the invention include:

Phthalimide,
N-Hydroxyphthalimide,
N-Potassium phthalimide,
N-Silver phthalimide,
N-Mercury phthalimide,
Succinimide, and/or
N-Hydroxysuccinimide.

Other so-called activator-toning agents can be employed in combination with or in place of the described cyclic imide activator-toning agents. Typically a heterocyclic organic toning agent containing at least two hetero atoms in the heterocyclic ring of which at least one is a nitrogen atom is employed. These are described, for example, in U.S. Pat. No. 3,080,254 of Grant issued Mar. 5, 1963. Suitable toners include, for example, phthalazinone, phthalic anhydride, 2-acetylphthalazinone and 2-phthalylphthalazinone. Other suitable toners are described, for example, in U.S. Pat. No. 3,446,648 of Workman issued May 27, 1969. The described activator-toning agents are suitable in a range of concentration however, they are especially employed at concentration of about 0.10 mole to about 1.05 moles of activator-toning agent per mole of oxidizing agent, e.g., per mole of silver behenate.

It is desirable to employ an image stabilizer or stabilizer precursor in the described elements or compositions of the invention. These can be employed in the practice of the invention to reduce the amount of post-processing print-out due to room light exposure and to reduce the background stain. Suitable stabilizer precursors include azole thioethers and blocked azole thione stabilizer precursors, e.g., 5-acetyl-4-methyl-2-(3-oxobutylthio)thiazole, 4-furoyl-3-methylthio-1,2,4-thiadiazole-5-thione, 5-acetyl-4-methyl-3-(3-oxobutyl)-thiazoline-2-thione and 2,6-di-tert-butyl-4-(1-phenyl-5-tetrazolyl)thiophenol. The described stabilizer precursors are suitable in a range of concentration; however, they are especially suitable at a concentration from about 0.002 mole to about 0.10 mole of stabilizer precursor per mole of oxidizing agent, e.g., per mole of silver behenate in an element or composition as described.

A photosensitive element and composition described and used in the practice of the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable materials are typically hydrophobic but hydrophilic materials can

also be employed. 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(vinyl pyrrolidone), 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. Suitable synthetic polymers include those described in U.S. Pat. No. 3,142,586 of Nottorf issued July 28, 1964; U.S. Pat. No. 3,193,386 of White issued July 6, 1955; U.S. Pat. No. 3,062,674 of Houck et al. issued Nov. 6, 1962; U.S. Pat. No. 3,220,844 of Houck et al. issued Nov. 30, 1965; U.S. Pat. No. 3,287,289 of Ream et al. issued Nov. 22, 1966; and U.S. Pat. No. 3,411,911 of Dykstra issued Nov. 19, 1968. Effective polymers include 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 as described in Canadian Pat. No. 774,054. Preferred high molecular weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid and polyvinyl alcohol.

The photosensitive and thermosensitive layers and other layers of an element employed in the practice of the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinylalcohol) 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 two to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photosensitive and thermosensitive and other hardenable layers of an element used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed-function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguar gum and the like.

The photosensitive and thermosensitive elements used in the practice of the invention can contain anti-static or conducting layers. Such layers can comprise soluble salts such as chlorides, nitrates and the like, evaporated metal layers, ionic polymers such as those described in U.S. Pat. No. 2,861,056 of Minsk issued Nov. 18, 1958 and U.S. Pat. No. 3,206,312 of Sterman et al. issued Sept. 14, 1965 or insoluble inorganic salts such as those described in U.S. Pat. No. 3,428,451 of

Trevo issued Feb. 18, 1969. The photosensitive and thermosensitive elements can also contain antihalation materials and antihalation dyes.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain plasticizers and lubricants. Suitable plasticizers and lubricants include, for example, polyalcohols such as glycerin and diols described, for example, in U.S. Pat. No. 2,960,404 of Milton et al. issued Nov. 1, 1966; fatty acids or esters such as those described in U.S. Pat. No. 2,588,765 of Robijns issued Mar. 11, 1952; U.S. Pat. No. 3,121,060 of Duane issued Feb. 11, 1964; and silicone resins such as those described in British Pat. No. 955,061.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain surfactants such as saponin; anionic compounds such as alkyl aryl sulfonates described, for example, in U.S. Pat. No. 2,600,831 of Baldsiefen issued June 17, 1962; amphoteric compounds such as those described in U.S. Pat. No. 3,133,816 of Ben-Ezra issued May 19, 1964; and adducts of glycidol and an alkyl phenol such as those described in British Pat. No. 1,022,878.

If desired, the photosensitive and thermosensitive elements employed in the practice of the invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads described, for example, in U.S. Pat. No. 2,922,101 of Jelley et al. issued July 11, 1961 and U.S. Pat. No. 2,761,245 of Lynn issued Feb. 1, 1955.

The photosensitive and thermosensitive elements and compositions employed in the practice of the invention can contain brightening agents including stilbenes, triazines, oxazoles, and coumarin brightening agents. Water-soluble brightening agents can be used such as those described in German Pat. No. 972,067 and U.S. Pat. No. 2,933,390 of McFall et al. issued Apr. 19, 1960 or dispersions of brighteners can be used such as those described in German Pat. No. 1,150,274; U.S. Pat. No. 3,406,070 of Oetiker et al. issued Oct. 15, 1968 and French Pat. No. 1,530,244.

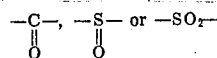
The various layers including the photosensitive and thermosensitive layers of an element employed in the practice of the invention can contain light-absorbing materials, filter dyes, antihalation dyes and absorbing dyes such as those described in U.S. Pat. No. 3,253,921 of Sawdey issued May 31, 1966; U.S. Pat. No. 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Pat. No. 2,527,583 of Silberstein et al. issued Oct. 31, 1950; and U.S. Pat. No. 2,956,879 of VanCampen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. No. 3,282,699 of Jones et al. issued Nov. 1, 1966.

The photosensitive and thermosensitive layers used in the practice of the invention can be coated by various coating procedures including dip coating, airknife 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 by the procedures described in U.S. Pat. No. 2,761,791 of Russell issued Sept. 4, 1956 and British Pat. No. 837,095.

A range of colorless onium halides can be employed in the described elements or compositions to provide an additional increase in photosensitivity, i.e., speed, and in some cases to obtain a reduction in background

density. A suitable speed-increasing onium halide compound is a quaternary ammonium halide, quaternary phosphonium halide and/or a tertiary sulfonium halide, e.g., 1-phenethyl-2-picolinium bromide, tetraethylphosphonium bromide or trimethylsulfonium iodide. An optimum concentration can be determined for each onium halide. An especially suitable onium halide is trimethylphenylammonium bromide which is typically employed at a concentration of about 0.010 mole to about 0.05 mole per mole of catalyst, e.g., per mole of photosensitive silver halide.

A non-aqueous, polar, organic solvent such as a compound containing a



moiety, in a described photosensitive and thermosensitive element or composition suitable for processing with heat can in many cases also provide improved maximum image densities. Suitable non-aqueous solvents include, for example, tetrahydrothiophene-1,1-dioxide, 4-hydroxybutanoic acid lactone and methylsulfanyl methane.

A divalent metal salt which has the property of amplifying the developed image can be employed in the practice of the invention to further cause an increase in maximum image density. A suitable divalent metal salt image amplifier is zinc acetate, cadmium acetate or cupric acetate. The described image-amplifying compounds are suitable in a range of concentration of about 0.005 to about 0.20 mole of divalent metal salt image amplifier per mole of silver salt oxidizing agent; however, they are especially suitable at a concentration from about 0.010 mole to about 0.10 mole of divalent metal salt image amplifier per mole of silver salt oxidizing agent according to the invention in an element as described.

If desired, the photosensitive silver halide can be prepared in situ, in the photosensitive and thermosensitive coatings of an element employed in the practice of the invention. Such a method is described, for example, in U.S. Pat. No. 3,457,075 of Morgan et al. issued July 22, 1969. For example, a dilute solution of a halogen acid such as hydrochloric acid, can be applied to the surface of a thin coating containing an organic silver salt, such as silver behenate, on a suitable substrate followed by removal of the solvent if desired. Silver halide is thus formed in situ throughout the surface of the coating of the organic silver salt.

The photosensitive silver halide can be prepared on the oxidizing agent, such as silver behenate or silver stearate, or other organic silver salt, prior to application of the silver halide on the support employed. This is also described in U.S. Pat. No. 3,457,075 of Morgan et al. issued July 22, 1969, for example, a halogen acid such as hydrochloric acid or hydrobromic acid can be mixed with an organic silver salt in a suitable reaction medium. A halide salt more soluble than the organic silver salt can be added to a suspension of the organic silver salt to form the silver halide. A suitable reaction medium includes water or other solutions which do not interfere with the reaction.

Stability to print out from light exposure is increased by employing highly purified materials; for example, freedom from halides and sulfides increase stability to light exposure. The use of highly purified silver behen-

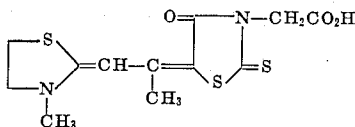
ate can, for example, reduce propensity to print out in background areas of an element prepared according to the invention.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the elements and compositions of 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 as described in British Pat. No. 1,154,781. For optimum results the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing silver halide emulsions are described, for example, in U.S. Pat. No. 2,526,632 of Brooker et al. issued Oct. 24, 1950; U.S. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950; U.S. Pat. No. 2,493,748 of Brooker et al. issued Jan. 10, 1950 and U.S. Pat. No. 3,384,486 of Taber et al. issued May 21, 1968. Spectral sensitizers, which can be used, include the cyanines, merocyanines, complex (trinuclear or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines such as enamine, hemicyanines, oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles, and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl, and enamine groups that can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes can contain the basic nuclei described as well as acid nuclei such as thiohydantoin, rhodanines, oxazolinediones, thiazolinediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamine groups or heterocyclic nuclei. Combinations of these dyes can be used if desired. In addition, supersensitizing addenda which do not absorb visible light may be included such as, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acid as described in U.S. Pat. No. 2,933,390 of McFall et al. issued Apr. 19, 1960 and U.S. Pat. No. 2,937,089 of Jones et al. issued May 17, 1960.

An especially suitable merocyanine dye is 3-carboxymethyl-5-[3-methyl-2(3H)-thiazolinyldene]isopropylidene] rhodanine of the formula:



Other examples of suitable merocyanine dyes which can be employed in the practice of the invention include:

1. 3-p-Carboxyphenyl-5-[β -ethyl-2(3)-benzoxazolylidene] ethylidene]rhodanine,
2. 5-[(3- β -carboxyethyl-2(3)-thiazolinyldene)ethylidene]-3-ethylrhodanine,
3. 3-Carboxymethyl-5-[(3-methylthiazolinyldene)- α -ethyl-ethylidene]-rhodanine,
4. 1-Carboxymethyl-5-[(3-ethyl-2-(3H)-benzoxazolylidene) ethylidene]-3-phenyl-2-thiohydantoin,
5. 5-[(3-ethyl-2-benzoxazolinyldene)-1-methyl-ethylidene]-3-[3-pyrrolin-1yl]-propyl]rhodanine, and/or
6. 3-ethyl-5-[(3-ethyl-2(3H)-benzothiazolylidene) isopropylidene]-2-thio-2,4-oxazolinedione.

A range of concentration of spectral sensitizing dye can be employed in the practice of the invention to provide spectral sensitivity. The desired concentration will be influenced by the desired spectral sensitivity, other components in the system, the desired image, processing conditions and the like. Typically a concentration of the described spectral sensitizing dye is typically about 50 mg. to about 2 grams of spectral sensitizing dye per mole catalyst, e.g., per mole of photosensitive silver halide.

The sensitizing dyes and other addenda used in the practice of the invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including, for example, those described in U.S. Pat. No. 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Pat. No. 3,342,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Pat. No. 2,996,287 of Audran issued Aug. 15, 1961; and U.S. Pat. No. 3,425,835 of Johnson et al. issued Feb. 4, 1969.

A preferred photosensitive and thermosensitive element and composition according to the invention comprises

- a. photosensitive silver halide,
- b. silver behenate,
- c. 2,2'-dihydroxy-1,1'-binaphthyl,
- d. 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone,
- e. phthalimide,
- f. 5-acetyl-2-benzyloxycarbonyl thio-4-methylthiazole, and
- g. 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene) isopropylidene]rhodanine.

After exposure of the described photosensitive element, the resulting latent image can be developed merely by heating the element. Accordingly, another embodiment of the invention is a process of developing a latent image in an exposed photosensitive and thermosensitive element comprising a support,

- a. photosensitive silver halide,
- b. an oxidation-reduction image-forming combination comprising
 - i. a heavy metal salt oxidizing agent as described with
 - ii. a bis-naphthol reducing agent, and
- c. a 1,3-dihydroxybenzene compound, as described, comprising heating said element to about 80°C. to about 250°C.

While a temperature range of about 80°C. to about 250°C. is suitable, usually a temperature range of about 120°C. to about 180°C. is employed for developing a desired image. By increasing or decreasing the length of time of heating, a higher or lower temperature within the described range can be employed. A developed image is typically produced within a few seconds, such as about 0.5 seconds to about 60 seconds but preferably within about 0.5 seconds to about 5 seconds.

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

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.

In some cases, if desired, an element can be prepared wherein the described silver halide can be in one layer and other components in other layers. For example, an element according to the invention can comprise a support, a layer containing photographic silver halide and a layer comprising a so-called thermographic combination or composition comprising

- a. a heavy metal salt oxidizing agent, as described, and
- b. a reducing agent combination, as described, preferably with
- c. an activator-toning agent, as described.

This composition and/or silver halide layer can contain other addenda, as described, also.

A typical thermographic combination is a composition comprising

- a. silver behenate, with
- b. 2,2'-dihydroxy-1,1'-binaphthyl and a 1,3-dihydroxybenzene compound which is 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone and/or 2',4'-dihydroxyacetophenone.

Typically, a polyvinylbutyral binder is employed with this composition.

Other addenda known to be useful in photosensitive and thermosensitive elements of this type, such as described in British Pat. No. 1,161,777 published Aug. 20, 1969; U.S. Pat. No. 3,152,904 of Sorensen and Shepard issued Oct. 13, 1964 and U.S. Pat. No. 3,457,075 of Morgan and Shely patented July 22, 1969 can be employed in the practice of the invention.

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

EXAMPLE 1

This illustrates the invention.

A photosensitive silver halide-silver behenate dispersion is prepared by ball-milling the following components together for about 72 hours:

Silver behenate	84.0 g
Behenic acid	64.0 g
Polyvinyl butyral	30.0 g
Phthalimide	17.0 g
Acetone-toluene (1:1 parts by volume)	1000.0 ml

When the ball-milling procedure is completed, 150 milliliters of an acetone solution of lithium bromide (1.0 percent by weight lithium bromide in acetone) is added to the resulting composition and the composition stirred for about 16 hours. The resulting silver pho-

tosensitive silver halide-silver behenate dispersion is designated as Dispersion I.

2.0 Milliliters of Dispersion I is mixed with the following components

5	Sensitizing dye (0.01% by weight in acetone)*	1.0 ml
	2,2'-dihydroxy-1,1'-binaphthyl (5.0% by weight in acetone)	2.0 ml
	5-acetyl-2-benzoyloxycarbonyl thio-4-methylthiazole (1% by weight in acetone)	0.5 ml
10	2,4-dihydroxybenzaldehyde (5.0% by weight in methanol)	0.3 ml
	acetone-toluene (1:1 parts by volume) to a total volume about	8.0 ml

*Dye I is 3-Carboxymethyl-5-[3-methyl-2(3H)-thiazolinyldene] isopropylidene]rhodanine

The resulting photosensitive composition is coated on a suitable photographic paper support at a wet thickness of 0.004 inches. Samples of the resulting photosensitive element are exposed for 1 second to tungsten light at a contact printer. The exposed photosensitive element is heated by contacting the side opposite the photosensitive coating with a curved hot metal block for 4 seconds while the metal block is at a temperature of 145°C.

The resulting developed image has a maximum reflection density of 1.40, a minimum reflection density of 0.02, a relative speed, compared to a control which contains no bis-naphthol reducing agent, of 468, and on an exposure scale provides 11 visible steps.

EXAMPLE 2

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the described benzaldehyde compound is omitted from the photosensitive element.

The resulting developed image has a maximum reflection density of 0.21 and a minimum reflection density of 0.02 with a relative speed of 100. On an exposure scale the developed image provides 8 visible steps.

This illustrates the surprising increase in maximum density, relative speed and exposure latitude, demonstrated by the increased number of visible steps, provided by the combinations of reducing agents of the invention.

EXAMPLE 3

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the described bis-naphthol reducing agent is omitted from the photosensitive element.

The resulting developed image provides a maximum reflection density of 0.14 and a minimum reflection density of 0.02 with a relative speed of 16 compared to the photosensitive element of Examples 1 and 2. On an exposure scale the developed image provides 7 visible steps.

EXAMPLE 4

This is a comparative example.

The procedure set out in Example 2 is repeated with the exception that the photosensitive element is heated for 7 seconds at 135°C.

The resulting developed image provides a maximum reflection density of 0.59, a minimum reflection density

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of 0.02 with a relative speed of 69 with 9 visible steps developed.

EXAMPLE 5

This is a comparative example.

The procedure set out in Example 2 is repeated with the exception that the photosensitive element is heated for 15 seconds at 135°C.

The resulting developed image provides a maximum reflection density of 1.24 with a minimum reflection density of 0.02 and a relative speed of 100. The developed image provides 11 visible steps.

EXAMPLE 6

This is a comparative example.

The procedure set out in Example 3 is repeated with the exception that the photosensitive element is heated for 7 seconds at 135°C.

The resulting developed image provides a maximum reflection density of 0.04 with a minimum reflection density of 0.02. Four visible steps are developed.

EXAMPLE 7

This is a comparative example.

The procedure set out in Example 3 is repeated with the exception that the photosensitive element is heated for 15 seconds at 135°C.

The resulting developed image provides a maximum reflection density of 0.14 with a minimum reflection density of 0.02. Six visible steps are developed.

EXAMPLE 8

This illustrates the invention.

The procedure set out in Example 1 is repeated with the exception that the photosensitive element is heated for 7 seconds at 135°C.

The resulting developed image provides a maximum reflection density of 1.36 with a minimum reflection density of 0.02. The relative speed is 110 and the developed image provides 11 visible developed steps.

Examples 4-8 illustrate that the reducing agent combination of the invention provides increased maximum density with reduced processing time with increased relative speed and exposure latitude without increased minimum density.

EXAMPLE 9

This illustrates the invention.

A photosensitive and thermosensitive element is prepared by mixing the following components

Dispersion 1 (from Example 1)	2.0 ml
Dye I (0.01% by weight acetone)	1.0 ml
1,1'-Bi-2-naphthol (5.0% by weight acetone)	1.0 ml
2',4'-Dihydroxyacetophenone (5.0% by weight acetone)	0.3 ml
5-Acetyl-2-benzoyloxycarbonylthio-4-methylthiazole (1.0% by weight acetone)	0.5 ml
Acetone-toluene (1:1 parts by volume) to a total volume of about	8.0 ml

The resulting composition is coated on a photographic paper support at a wet thickness of 0.004 inches. A sample of the resulting photosensitive and thermosensitive element is exposed for one second to tungsten light in a contact printer. The exposed photosensitive element is heated by contacting the side opposite the photosensitive coating with a curved hot metal block for 4 seconds while the metal block is at a tem-

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perature of 145°C. A dark black line image having 11 visible steps on a white background is produced.

EXAMPLE 10

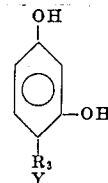
5 The procedure set out in Example 9 is repeated with the exception that 0.5 ml of an acetone solution of 2,4-dihydroxy-benzophenone (5.0 percent by weight in acetone) is employed in place of the described 2',4'-dihydroxyacetophenone.

10 A visible line, black image on a beige background is produced upon heating the photosensitive element for 4 seconds on a hot metal block at a temperature of 145°C. The developed image provides 9 visible developed steps.

15 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. photosensitive silver halide,
 - b. an oxidation-reduction image forming combination comprising
 - i. a heavy metal salt oxidizing agent with
 - ii. a bis-beta-naphthol reducing agent, and
 - c. a 1,3-dihydroxybenzene compound of the formula:

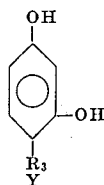


wherein R_3 is alkylene containing one to six carbon atoms, arylene containing six to 10 carbon atoms, carbonylalkyl containing two to three carbon atoms or carbonylphenyl, and Y is hydrogen, oxygen or sulfur.

2. A photothermographic element as in claim 1 comprising a support having thereon
 - a. photosensitive silver halide,
 - b. an oxidation-reduction image forming combination comprising
 - i. silver behenate with
 - ii. 2,2'-dihydroxy-1,1'-binaphthyl, and
 - c. 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone, or 2',4'-dihydroxyacetophenone.
3. A photothermographic element as in claim 1 also comprising an activator-toning agent.
4. A photothermographic element as in claim 1 also comprising phthalimide or phthalazinone.
5. A photothermographic element as in claim 1 also comprising a stabilizer precursor.
6. A photothermographic element as in claim 1 also comprising 5-acetyl-2-benzoyloxycarbonylthio-4-methylthiazole.
7. A photothermographic element as in claim 1 also comprising a sensitizing dye.
8. A photothermographic element as in claim 1 also comprising 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)isopropylidene] rhodanine.
9. A photothermographic element as in claim 1 comprising 0.01 to 0.50 moles of said photosensitive silver halide per mole of said heavy metal salt oxidizing agent; 0.4 to 2.0 moles of said bis-beta-naphthol reducing

agent per mole of said heavy metal salt oxidizing agent; and wherein the ratio of said bis-beta-naphthol reducing agent to said 1,3-dihydroxybenzene compound is from 10:1 to 1:5.

10. A photothermographic element comprising a support having thereon
- photosensitive silver halide,
 - silver behenate,
 - 2,2'-dihydroxy-1,1'-binaphthyl,
 - 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone,
 - phthalimide,
 - 5-acetyl-2-benzyloxycarbonylthio-4-methylthiazole, and
 - 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)isopropylidene]rhodanine.
11. A photothermographic composition comprising
- photosensitive silver halide, with
 - an oxidation-reduction image forming combination comprising
 - a heavy metal salt oxidizing agent with
 - a bis-beta-naphthol reducing agent, and
 - a 1,3-dihydroxybenzene compound of the formula:

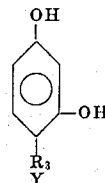


wherein R_3 is alkylene containing one to six carbon atoms, arylene containing six to 10 carbon atoms, carbonylalkyl containing two to three carbon atoms or carbonylphenyl, and Y is hydrogen, oxygen or sulfur.

12. A photothermographic composition as in claim 11 comprising
- photosensitive silver halide
 - an oxidation-reduction image forming combination comprising
 - silver behenate with
 - 2,2'-dihydroxy-1,1'-binaphthyl, and
 - 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone, or 2',4'-dihydroxyacetophenone.
13. A photothermographic composition as in claim 11 also comprising an activator-toning agent.
14. A photothermographic element as in claim 11 also comprising phthalimide or phthalazinone.
15. A photothermographic composition as in claim 11 also comprising a stabilizer precursor.
16. A photothermographic composition as in claim 11 also comprising 5-acetyl-2-benzyloxycarbonylthio-4-methylthiazole.
17. A photothermographic composition as in claim 11 also comprising a sensitizing dye.
18. A photothermographic composition as in claim 11 also comprising 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)isopropylidene]rhodanine.
19. A photothermographic composition as in claim 11 comprising 0.01 to 0.50 moles of said photosensitive silver halide per mole of said heavy salt oxidizing agent; 0.4 to 2.0 moles of said bis-beta-naphthol reducing

agent per mole of said heavy metal salt oxidizing agent; and wherein the ratio of said bis-beta-naphthol reducing agent to said 1,3-dihydroxybenzene compound is from 10:1 to 1:5.

20. A photothermographic composition comprising
- photosensitive silver halide,
 - silver behenate,
 - 2,2'-dihydroxy-1,1'-binaphthyl,
 - 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone, or 2,4-dihydroxyacetophenone,
 - phthalimide,
 - 5-acetyl-2-benzyloxycarbonylthio-4-methylthiazole, and
 - 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)isopropylidene]rhodanine.
21. A process of developing a latent image in an exposed photothermographic element comprising a support having thereon
- photosensitive silver halide,
 - an oxidation-reduction image forming combination comprising
 - a heavy metal salt oxidizing agent with
 - a bis-beta-naphthol reducing agent, and
 - a 1,3-dihydroxybenzene compound represented by the formula:



wherein R_3 is alkylene containing one to six carbon atoms, arylene containing six to 10 carbon atoms, carbonylalkyl containing two to three carbon atoms or carbonylphenyl, and Y is hydrogen, oxygen or sulfur, comprising heating said element to about 80°C. to about 250°C.

22. The process of claim 28 wherein said element is heated to about 80°C. to about 250°C. for about 0.5 to about 60 seconds.

23. A process of developing and stabilizing a latent image in an exposed photothermographic element comprising a support having thereon

- photosensitive silver halide,
 - silver behenate,
 - 2,2'-dihydroxy-1,1'-binaphthyl,
 - 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone,
 - phthalimide,
 - 5-acetyl-2-benzyloxycarbonylthio-4-methylthiazole, and
 - 3-carboxymethyl-5-[(3-methyl-2(3H)-thiazolinyldene)isopropylidene]rhodanine,
- comprising heating said element to about 80°C. to about 250°C.

24. The process of claim 30 wherein said element is heated to about 120°C. to about 180°C. for about 0.5 to about 5 seconds.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,249 Dated August 7, 1973

Inventor(s) Gary L. Hiller

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

Column 12, line 14, "3-pyrrolin-1 yl" should read ---3-pyrrolin-1-yl---

In the Claims:

Column 18, line 59, "claim 30" should read ---claim 23---

Signed and sealed this 27th day of November 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGMEYER
Acting Commissioner of Patents