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3,700,457

USE OF DEVELOPMENT INHIBITOR RELEASING COMPOUNDS IN PHOTOTHERMOGRAPHIC ELEMENTS

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15 Claims

ABSTRACT OF THE DISCLOSURE

A silver halide development inhibitor releasing compound, such as a developing agent or coupler containing a development inhibitor moiety which is releasable upon heating, in a photographic and thermosensitive element suitable for dry processing, provides improved black tone, reduced background print-out, improved image stability, and reduction of exposure and processing time in some cases. A combination of a silver halide development inhibitor releasing compound, such as one containing a heat releasable phenylmercaptotetrazole group, in combination with a stable source of silver for physical development are useful in photographic elements for dry processing. The element can contain a sensitizing dye and a stable developed image can be provided by heating the element after exposure. The photographic component can be photographic silver halide, or other suitable photographic metal salts.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic elements, compositions and processes for developing and stabilizing a latent image using so-called dry processing with heat. In one of its aspects, it relates to photographic elements suitable for dry processing with heat containing a silver halide development inhibitor releasing compound, especially one containing a heat releasable phenylmercaptotetrazole moiety. In another of its aspects, it relates to a photographic emulsion suitable for dry processing with heat containing a silver halide development inhibitor releasing compound. A further aspect relates to a dry process of developing and stabilizing an image in a photographic element containing a silver halide development inhibitor releasing compound as described.

Description of the prior art

It is known to develop a latent image in a photographic silver halide element using a silver halide developing agent in so-called dry processing with heat, the photographic element can contain a silver halide developing agent as well as a stabilizer component. After exposure, the resulting latent image is developed and stabilized by heating the photographic element. Such a process is described, for example, in U.S. Pat. 3,301,678 of Humphlett et al. issued Jan. 31, 1967.

Other methods of so-called dry processing with heat are described, for example, in U.S. Pat. 3,152,904 of Sorensen et al. issued Oct. 13, 1964. For example, (1) an organic silver salt which is an oxidizing agent, (2) an organic reducing agent and a low concentration of photographic silver halide are provided in a light-sensitive element. After image-wise exposure, the resulting latent image is developed by heating the element. Methods of this type are also described, for example, in French Pat. 1,441,619 and Belgian Pat. 705,872.

Phenylmercaptotetrazole compounds, such as 1-phenyl-5-mercaptotetrazole, have been proposed in certain photographic and thermosensitive materials. These compounds

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can improve the image tone as described in U.S. Pat. 3,257,205 of Cassiers et al. issued June 21, 1966. They have been employed in heat developable photographic materials as described in British Pat. 1,055,144 to improve stability. And, mercaptoazole compounds can be antifoggants, such as described in British Pat. 711,025. Unfortunately, phenylmercaptotetrazole presents a problem because it desensitizes photographic silver compounds at concentrations which produce stabilization and toning. For example, in a photographic element suitable for so-called dry processing with heat phenylmercaptotetrazole causes only a faint image to be developed due to desensitization. This is demonstrated in the following Example 4. Accordingly there has been a continuing need for a photographic element suitable for so-called dry processing with heat which has improved stability, including reduced background print-out upon exposure to light after processing, improved black tone, increased sensitivity including reduced exposure and processing time and improved preprocessing spectral sensitivity when a spectral sensitizing dye is not employed.

SUMMARY OF THE INVENTION

According to the invention, improved stability, including reduced background print-out upon exposure to light after processing, improved black tone and increased sensitivity is provided in a photographic and thermosensitive element, composition and/or process employing a silver halide development inhibitor releasing compound, especially a compound which releases a phenylmercaptotetrazole moiety upon heating.

DESCRIPTION OF PREFERRED EMBODIMENTS

A range of compounds can be employed which are silver halide development inhibitor releasing compounds, especially compounds which release a phenylmercaptotetrazole moiety upon heating. Any silver halide development inhibitor releasing compound is suitable which releases a silver halide development inhibitor, especially a phenylmercaptotetrazole moiety, upon heating, which provides improved stability, including reduced background print-out upon exposure to light after processing, does not adversely affect the latent image before processing and does not cause desensitization. Typical silver halide development inhibitor releasing compounds are (1) development inhibitor releasing couplers, also known as DIR couplers, as described, for example, in U.S. Pat. 3,227,554 of Barr et al. issued Jan. 4, 1966 and (2) development inhibitor releasing silver halide developing agents as described, for example, in U.S. Pat. 3,379,529 of Porter et al. issued Apr. 23, 1968 and Belgian Patent 713,448.

The development inhibitor moiety which is released upon heating is usually a mercaptan. The mercaptan is believed to form a stable silver mercaptide with unexposed silver halide in the photographic element upon heating. But, the mechanism of stabilization and the reasons, in so-called dry processing, for the improved black tone, increased sensitivity, and in some cases improved preprocessing spectral sensitivity, when a spectral sensitizing dye is not employed, is not fully understood.

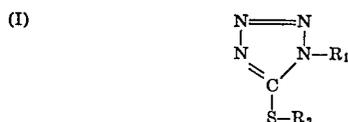
Suitable mercapto groups which can be released upon heating include, for example:

(a) Mercaptoalkylamidobenzothiazoles, such as described in U.S. Patent 2,503,861 of Weissberger issued Apr. 11, 1950; (b) mercaptoalkylamidothiazoles, such as described in U.S. Patent 2,657,136 of Knott et al. issued Oct. 27, 1953 or U.S. Patent 2,697,099 of Knott issued Dec. 14, 1954; (c) mercaptoazines such as described in U.S. Patent 2,753,027 of Troendly et al. issued Oct. 30, 1951; (d) mercaptoazoles, such as described in U.S.

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Patent 2,590,775 of Kendall et al. issued Mar. 25, 1952; U.S. Patent 2,668,113 of Schwalenstocker issued Feb. 2, 1954; and U.S. Patent 2,566,659 of Fry issued Sept. 4, 1951; (e) mercaptocysteines, such as described in U.S. Patent 2,363,777 of Downing et al. issued Nov. 28, 1944; (f) mercaptogluthathiones, such as described in U.S. Patent 2,110,178 of Ruskin issued Mar. 8, 1938; (g) mercaptooxadiazoles, such as described in U.S. 2,843,491 of Hallen et al. issued July 15, 1958; (h) mercaptopyrimidines, such as described in U.S. Patent 2,304,962 of Shepard et al. issued Dec. 15, 1942; U.S. Patent 2,232,707 of Kendall issued Feb. 25, 1941; U.S. Patent 2,231,127 of Kendall issued Feb. 11, 1948; and U.S. Patent 2,173,628 of Kendall issued Sept. 19, 1939; (i) mercaptotetrazoles, such as described in U.S. Patent 2,697,040 of Parnell issued Dec. 14, 1954; U.S. Patent 2,465,149 of Dersch et al. issued Mar. 22, 1949; U.S. Patent 2,453,087 of Dersch et al. issued Nov. 2, 1948; and U.S. Patent 2,403,927 of Kendall et al. issued July 16, 1946; (j) mercaptothiadiazoles, such as described in U.S. Patent 2,743,184 of Kendall issued Apr. 24, 1956; (k) mercaptothiazoles, such as described in U.S. Patent 2,824,001 of Hallen et al. issued Feb. 18, 1958; (l) mercaptothiophenes, such as described in U.S. Patent 2,214,446 of Falbers et al. issued Sept. 10, 1940; and U.S. Patent 1,758,576 of Mattheis et al. issued May 13, 1930; (m) mercaptotriazines, such as described in U.S. Patent 2,476,536 of Dersch issued July 19, 1949.

The mercaptan moiety which is preferred is a 5-tetrazolylthio moiety of the formula:



wherein R_1 is alkyl, such as alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl, propyl, butyl or pentyl or aryl, such as aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl and xylyl. Alkyl or aryl, as described, can contain a range of substituents which do not adversely affect the stabilization desired upon heating, such as alkoxy, e.g. alkoxy containing 1 to 5 carbon atoms, such as methoxy, ethoxy, propoxy, butoxy, and pentoxy; halogen, cyano, nitro, amino, sulfo, sulfamyl, sulfonylphenyl, sulfonylalkyl, sulfonamidophenyl, sulfonamidoalkyl, carboxy, carboxylate, carbamyl, carbamylphenyl and carbamylalkyl. R_2 is a coupler moiety or silver halide developing agent moiety.

A range of couplers can be employed which have developer inhibitor releasing moieties as described. The color coupler portion of the compound is typically a 5-pyrazolone coupler moiety, a phenolic coupler including alpha-naphthols, or an open chained ketomethylene coupler moiety. In color processes such couplers reacting with oxidized color developing agents form magenta, cyan and yellow dyes, respectively. While the present invention can be employed in elements for producing a color image, such as described in Belgian Patent 705,872 issued Apr. 30, 1968, it is preferably employed in a black-and-white process. In the described couplers, the developer inhibitor releasing moiety is typically in the coupling position of such couplers. The 5-pyrazolone coupler radicals couple typically at the carbon atom in the 4 position, the phenolic coupler compounds couple typically at the carbon atom in the 4 position and the open chained ketomethylene coupler compounds couple at the carbon atom forming the methylene moiety. The couplers can contain so-called balasting and solubilizing groups in the practice of the invention. Balasting groups are groups which contain a so-called "bulky" organic moiety such as an alkyl group or aryl group containing about 8 to about 22 or more carbon atoms attached to the coupler moiety. Typical solubilizing groups include,

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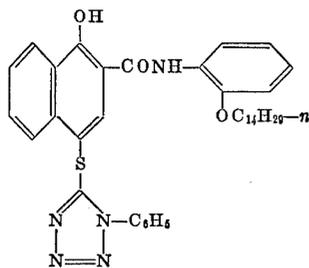
for example, carboxyl, sulfonyl, sulfonamido and hydroxy groups.

Examples of suitable couplers which can be employed in the practice of the invention and contain a phenyl-mercaptotetrazole moiety include:

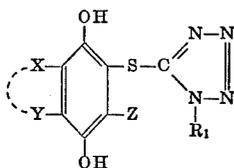
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2'-tetradecyloxy-2-naphthanilide
- 4-(1-phenyl-5-tetrazolylthio)phenol
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-3',5'-dicarbomethoxy-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-3',5'-dicarboxy-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-N-[β-(3,5-dichlorosulfonylbenzamido)ethyl]-2-naphthamide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-N-[β-(3,5-disulfobenzamido)ethyl]-2-naphthamide dipotassium salt
- phenyl 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-naphthoate
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-5'-carbomethoxy-2'-methoxy-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-4'-(2,4-di-tert-amylphenoxy)-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2'-(2,4-di-tert-amylphenoxy)-5'-(3,5-dicarbomethoxyphenylcarbamyl)-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2'-(2,4-di-tert-amylphenoxy)-5'-(3,5-dicarbomethoxyphenylcarbamyl)-2-naphthanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-3',5'-dicarbomethoxy-N-octadecyl-2-naphthanilide
- 1-phenyl-3-octadecylamino-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-[4-(4-tert-butylphenoxy)phenyl]-3-phenyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-phenyl-3-pentadecyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-(4-stearamidophenyl)-3-ethoxy-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-4-tert-butylphenoxy]propionamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-(4-tert-butylphenoxy)propionamido]-4-[1-(4-carbomethoxyphenyl)-5-tetrazolylthio]-5-pyrazolone
- 1-(2,4-dichloro-6-methoxyphenyl)-3-[α-(3-pentadecylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-dodecyl-3-[α-(2,4-di-tert-amylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-hexyl-3-[α-(2,4-di-n-amylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-phenyl-3-benzamido-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-phenyl-3-[α-(2,4-di-tert-amylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-phenyl-3-[γ-(2,4-di-tert-amylphenoxy)butyramido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-phenyl-3-octadecylcarbamyl-4-methyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-(2,4,6-trichlorophenyl)-3-{3-[α-(2,4-di-tert-amylphenoxy)acetamido]benzamido}-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- α-{3-[α-(2,4-di-tert-amylphenoxy)acetamido]benzoyl}-α-(1-phenyl-5-tetrazolylthio)-2-fluoroacetanilide
- α-Benzoyl-α-[1-(3-pelargonamidophenyl)-5-tetrazolylthio]acetanilide
- 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-naphthoic acid

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An especially suitable developer inhibitor releasing coupler is 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-(2'-n-tetradecyloxy)-naphthanilide of the formula:



While developer inhibitor releasing couplers are especially suitable in the practice of the invention, other developer inhibitor releasing compounds can be employed, such as developer inhibitor releasing developing agents such as (1-phenyl-5-tetrazolylthio) hydroquinone silver halide developing agents. Such compounds and preparation of the compounds is described, for example, in U.S. Patent 3,379,529 of Porter et al. issued Apr. 23, 1968. Useful compounds which are silver halide developing agents containing a development inhibitor releasing moiety are compounds of the formula:



wherein X, Y and Z are each hydrogen, alkyl, especially alkyl containing 1 to 20 carbon atoms, such as methyl, ethyl, propyl, butyl, octyl, decyl, and eicosyl, hydroxyl, amino, aryl, especially aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl and xylyl, halogen, such as chlorine, bromine and iodine, heterocyclic, especially mercaptotetrazolyl; R₁ is as described; and X and Y can be members of a carbocyclic ring, especially a 6-member carbocyclic ring.

Examples of suitable silver halide developing agents containing a developer inhibitor release moiety are:

- 2-methyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone
- (1-phenyl-5-tetrazolylthio)-trimethyl hydroquinone
- 2-n-octadecyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone
- (1-phenyl-5-tetrazolylthio) hydroquinone
- 2,5-bis(1-phenyl-5-tetrazolylthio) hydroquinone
- 2-tert-butyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone
- 2-(4-methylphenyl)-5-(1-phenyl-5-tetrazolylthio)hydroquinone
- 5,8-ethano-2-(1-phenyl-5-tetrazolylthio)-5,8-dihydro-1,4-naphthohydroquinone
- 2,5-bis-(2-chloroacetoxy)-3-(1-phenyl-5-tetrazolylthio) hydroquinone
- 2,5-dimethyl-3-(1-phenyl-5-tetrazolylthio) hydroquinone
- 2,6-dimethyl-3-(1-phenyl-5-tetrazolylthio) hydroquinone
- 2,3-dimethyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone
- 2-n-pentadecyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone

The described developer inhibitor releasing compounds are especially suitable according to the invention in an element which is photosensitive and thermosensitive, especially a photographic element which is suitable for processing with heat. Photographic and thermosensitive elements which are suitable for dry processing with heat can provide a developed image by physical development, such as described in U.S. Patent 3,457,075 of Morgan et al. issued July 22, 1969. Other elements of this type are described, for example, in U.S. Patent 3,429,706 of Shepard et al. issued Feb. 25, 1969 and U.S. Patent 3,152,904 of Sorensen et al. issued Oct. 13, 1964. In elements, as described, typically a support is provided with

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a light-stable organic silver salt oxidizing agent, an organic reducing agent, and photographic silver salt, especially silver halide, which provides a photographic and heat-sensitive element. A visible image on the photographic and thermosensitive element can be produced within a few seconds after exposure by heating the element to moderately elevated temperatures.

Accordingly, one embodiment of the invention is a photographic and thermosensitive element, comprising a support,

- (a) a silver halide development inhibitor releasing compound, and
- (b) a stable source of silver for physical development of a latent image in a photographic element.

The silver halide development inhibitor releasing compound is typically a developer inhibitor releasing coupler or developer inhibitor releasing silver halide developing agent, as described.

The described silver halide development inhibitor releasing compounds can be employed in a photographic and thermosensitive element containing a silver-dye complex, a silver halide developing agent, a source of silver for physical development, as described, especially silver behenate or silver stearate and a binder, especially polyvinylbutyral. Suitable silver-dye complexes are set out in U.S. Patent 3,446,619 of Gilman et al. issued May 27, 1969. The silver-dye complex is a reaction product of silver ions, e.g. silver nitrate in aqueous solution, with a spectral sensitizing dye which upon exposure to radiation forms active sites for physical development. Typical sensitizing dyes include cyanines, merocyanines, oxonols, hemicyanines, hemioxonols, styryls and benzylidenes. A typical photographic and thermosensitive element containing such a silver-dye complex comprises a support having a layer containing a silver-merocyanine dye complex, silver behenate, hydroquinone, a binder, such as cellulose acetate, polyvinyl acetate or polyvinylbutyral and a developer inhibitor releasing compound, as described. The photographic and thermosensitive element can contain a stabilizing agent such as an organic acid stabilizing agent, e.g. phthalic acid, salicylic acid or benzoic acid.

The described elements can comprise a silver salt of an organic acid, as an oxidizing agent. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver 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 oxidizing agents are silver 5-nitrosalicylaldoxime, silver 5-chlorosalicylaldoxime, silver-benzoate, silver-phthalazinone, silver-benzotriazole, silver-saccharin, silver-4'-n-octadecyloxydiphenyl-4-carboxylic acid, silver-ortho-aminobenzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver p-phenylbenzoate, silver phenyl acetate, silver salicylate, silver meta-nitrobenzoate, silver butyrate, silver terephthalate, silver phthalate, silver acetate, and silver acid phthalate. 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.

An organic reducing agent is employed in the practice of the invention to provide a desired developed image. Such reducing agents are typically silver halide developing agents. Suitable silver halide developing agents or organic reducing agents include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g. hydroquinone, alkyl-substituted hydroquinones as exemplified by tertiary butyl hydroquinone, methyl hydroquinone, 2,5-dimethyl hydroquinone and 2,6-dimeth-

yl hydroquinone; catechols and pyrogallol; halo-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy-substituted hydroquinones such as methoxy hydroquinone or ethoxy hydroquinone; methylhydroxy naphthalene; phenylenediamine developing agents; methylgalate; 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. 3,337,342 of Green issued Aug. 22, 1967; hydroxylamine developing agent such as N,N-di(2-ethoxyethyl) 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 Pat. 930,572 published July 3, 1963; hydroxytetric acid, and hydroxytetric imide developing agents; reductone developing agents such as anhydro dihydro piperidino hexose reductone or anhydro dihydro pyrrolidino hexose reductone; and the like.

The described element contains a photographic salt, especially a photographic silver salt. Suitable photographic silver salts include silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The photographic silver halide can be coarse or fine-grain, very fine grain emulsions being especially useful. The emulsion containing the photographic silver halide can be prepared by any of the well-known procedures in the photographic art, such as single-jet emulsions, double-jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. 2,222,264 of Nietz et al. issued Nov. 14, 1940; U.S. Pat. 3,320,069 of Illingsworth issued May 15, 1967 and U.S. Pat. 3,271,157 of McBride issued Sept. 6, 1966. Surface image silver halide emulsions can be used or internal image silver halide emulsions such as those described in U.S. Pat. 2,592,250 of Davey et al. issued Apr. 8, 1952; U.S. 3,206,313 of Porter et al. issued Sept. 14, 1965; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; and U.S. Pat. 3,447,927 of Bacon et al. issued June 3, 1969. If desired, mixtures of surface and internal image silver halide emulsions can be used as described in U.S. Pat. 2,996,382 of Luckey et al. issued Apr. 15, 1961. Negative type emulsions can be used or direct positive silver halide emulsions such as those described in U.S. Pat. 2,184,013 of Leermakers issued Dec. 19, 1939; U.S. Pat. 2,541,472 of Kendall et al. issued Feb. 13, 1951; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; British Pat. 723,019; French Pat. 1,520,821; U.S. Pat. 2,563,785 of Ives issued Aug. 7, 1951; U.S. Pat. 2,456,953 of Knott et al. issued Dec. 21, 1968; and U.S. Pat. 2,861,885 of Land issued Nov. 25, 1958. The silver halide emulsion can be a regular grain emulsion such as described in Klein and Moisar, *Journal of Photographic Science*, vol. 12, No. 5, September-October (1964) pp. 242-251.

The silver halide emulsions 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 bleaching 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; silver, selenium, or tellurium compounds; gold, platinum, or palladium compounds; or combinations of these. Suitable procedures are described, for example, in U.S. Pat. 1,623,499 of Shepard issued Apr. 5, 1927; U.S. Pat. 2,399,083 of Waller et al. issued Apr. 23, 1946; U.S. Pat. 3,297,447 of McVeigh issued Jan. 10, 1967; and U.S. Pat. 3,297,446 of Dunn issued Jan. 10, 1967.

Photographic silver halide emulsions employed in the practice of the invention can be protected against the production of fog and can be stabilized against loss of sensitiv-

ity 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. Patent 2,728,663 of Allen et al. issued Dec. 27, 1955; urazoles; sulfocatechols; oximes described, for example in British Patent 623,448; nitron; nitroindazoles; polyvalent metal salts described, for example, in U.S. Patent 2,839,405 of Jones issued June 17, 1958; platinum, palladium and gold salts described, for example, in U.S. Patent 2,566,263 of Trivelli et al. issued Aug. 28, 1951 and U.S. Patent 2,597,915 of Yutzy et al. issued May 27, 1952.

A photographic and thermosensitive element and emulsions described and used in the practice of the invention can contain various colloids alone or in combination as vehicles, biding 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 polvinyl 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. Patent 3,142,586 of Nottorf issued July 28, 1964; U.S. Patent 3,193,386 of White issued July 6, 1955; U.S. Patent 3,062,674 of Houck et al. issued Nov. 6, 1962; U.S. Patent 3,220,844 of Houck et al. issued Nov. 30, 1965; U.S. Patent 3,287,289 of Ream et al. issued Nov. 22, 1966; and U.S. Patent 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 Patent 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, polyvinyl alcohol, and high molecular weight ethylene oxide polymers.

The photographic 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(vinylacetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically a flexible support is employed, especially a paper support which can be partially acetylated or coated with baryta and/or an alpha olefin polymer, particularly a polymer of an alpha olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

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 photographic and thermosensitive elements used in the practice of the invention can contain antistatic 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. Patent 2,861,056 of Minsk issued Nov. 18, 1958 and U.S. Patent 3,206,312 of Sterman et al. issued Sept. 14, 1965 or insoluble inorganic salts such as those described in U.S. Patent 3,428,451 of Trevoy issued Feb. 18, 1960. The photographic and thermosensitive elements can also contain antihalation materials and antihalation dyes.

The photographic 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. Patent 2,960,404 of Milton et al. issued Nov. 1, 1966; fatty acids or esters such as those described in U.S. Patent 2,588,765 of Robijns issued Mar. 11, 1952; U.S. Patent 3,121,060 of Duane issued Feb. 11, 1964; and silicone resins such as those described in British 955,061.

The photographic 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. Patent 2,600,831 of Baldsiefen issued June 17, 1962; amphoteric compounds such as those described in U.S. Patent 3,133,816 of Ben-Ezra issued May 19, 1964; and adducts of glycidol and an alkyl phenol such as those described in British Patent 1,022,878.

If desired, the photographic 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. Patent 2,922,101 of Jelley et al. issued July 11, 1961 and U.S. Patent 2,701,245 of Lynn issued Feb. 1, 1955.

The photographic and thermosensitive elements 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. 072,067 and U.S. Patent 2,933,390 of McFall et al. issued Apr. 19, 1960 or dispersions of brighteners can be used such as those described in German Patent 1,150,274; U.S. Patent 3,406,070 of Oetiker et al. issued Oct. 15, 1968 and French Patent 1,530,244.

The various layers including the photographic and thermosensitive layers of an element employed in the practice of the invention can contain light-absorbing materials and filter dyes such as those described in U.S. Patent 3,253,921 of Sawdey issued May 31, 1966; U.S. Patent 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Patent 2,527,583 of Silberstein et al. issued Oct. 31, 1950; and U.S. Patent 2,956,879 of VanCampen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Patent 3,282,699 of Jones et al. issued Nov. 1, 1966.

The photographic 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. Patent 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. Patent 2,761,791 of Russell issued Sept. 4, 1956 and British 837,095.

If desired, the photographic silver halide can be prepared in situ in the photographic and thermosensitive coatings of an element employed in the practice of the invention. Such a method is described, for example, in U.S. Patent 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 photographic 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. Patent 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 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 behenate can, for example, reduced light sensitivity of an element according to the invention.

Accordingly one embodiment of the invention is in a photographic and thermosensitive element comprising a support, a photographic silver salt, a source of silver for physical development of the silver salt, an organic reducing agent, and a binder; the improvement comprising a silver halide development inhibitor releasing compound which has the properties of releasing a silver halide development inhibitor at above about 70° C. As described, the stable source of silver for physical development is typically a silver salt of an organic acid. The organic reducing agent can be a silver halide developing agent, as described.

When a so-called developer inhibitor releasing coupler is employed as the silver halide development inhibitor releasing compound as described, it is surprisingly found that the sensitivity of the photographic element to radiation outside the inherent blue region of the spectrum, such as sensitivity to tungsten light, is improved even without the use of a sensitizing dye. However spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light-sensitive silver halide employed in the practice 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 Patent 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. Patent 2,526,632 of Brooker et al. issued Oct. 24, 1950; U.S. Patent 2,503,776 of Sprague issued Apr. 11, 1950; U.S. Patent 2,493,748 of Brooker et al. issued Jan. 10, 1950 and U.S. Patent 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) merocyanines, complex (trinuclear or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines such as enamines, 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, alkyl-amino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition super-sensitizing addenda which do not absorb visible light may be included such as, for instance, ascorbic acid deriva-
 5 tives, azaindenes, cadmium salts, and organic sulfonic acid as described in U.S. Patent 2,933,390 of McFall et al. issued Apr. 19, 1960 and U.S. Patent 2,937,089 of Jones et al. issued May 17, 1960.

The sensitizing dyes and other addenda used in the practice of the invention can be added from water solu-
 10 tions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including, for example, those described in U.S. Patent 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Patent 3,342,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Patent 2,996,287 of Audran issued Aug. 15, 1961; and U.S. Patent 3,425,835 of Johnson et al. issued Feb. 4, 1969.

A range of concentration of dye can be employed in the practice of the invention. 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 sensitizing dye is about 0.05 to about 1 milligram per square foot of the described photographic and thermosensitive element, usually about 0.1 milligram per square foot of dye being employed.

It is often advantageous to employ a so-called toner in the described photographic and thermosensitive elements. Various toners can be employed for this purpose. 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. Patent 3,080,254 of Grant issued Mar. 5, 1963. Suitable toners include, for example, phthalazinone, phthalic anhydride, 2-acetyl phthalazinone, 2-phthalyl phthalazinone. Other suitable toners are described, for example, in U.S. Patent 3,446,648 of Work-
 40 man issued May 27, 1969.

Accordingly another embodiment of the invention is a photographic and thermosensitive element, as described,

- (a) wherein the development inhibitor releasing compound is a coupler having a tetrazolylthio moiety,
- (b) the source of silver for physical development is silver behenate or silver stearate,
- (c) the photographic silver salt is photographic silver halide,
- (d) the binder is polyvinyl butyral,
- (e) the reducing agent is a phenolic reducing agent, and also
- (f) comprising a toner.

For example, the photographic and thermosensitive element as described can comprise,

- (a) polyvinyl butyral binder,
- (b) silver behenate,
- (c) a phenolic reducing agent,
- (d) photographic silver halide,
- (e) a phthalazinone toner,
- (f) 1-hydroxy-4-(1 - phenyl - 5 - tetrazolylthio)-2-(2'-n-tetradecyloxy)-naphthanilide, and
- (g) a sensitizing dye.

Another embodiment of the invention is a photographic and thermosensitive emulsion comprising (a) a silver halide development inhibitor releasing compound as described, (b) a stable source of silver for physical develop-
 65 ment, and (c) a photographic silver salt, especially photographic silver halide. The photographic and thermosensitive emulsion can comprise, for instance,

- (a) a silver halide development inhibitor releasing compound which has the property of releasing a silver halide development inhibitor at above about 70° C.,

especially a developer inhibitor releasing coupler as described,

- (b) silver behenate,
- (c) photographic silver halide,
- (d) a phenolic reducing agent,
- (e) polyvinyl butyral, and
- (f) a sensitizing dye.

After exposure of the described photographic and thermosensitive element the resulting latent image is developed and the developed image stabilized merely by heating the element. Accordingly another embodiment of the invention is: in a process of developing a latent image in a photographic and thermosensitive element and stabilizing the resulting development image with heat, the improvement comprising heating an exposed photographic and thermosensitive element comprising

- (a) a photographic component,
- (b) a source of metal for physical development of the photographic component,
- (c) a development inhibitor releasing compound which has the property of releasing a silver halide development inhibitor at above about 70° C., and
- (d) a reducing agent,

to 70° C. to 250° C. A temperature range of about 75° C. to about 100° C. is suitable for developing and stabilizing 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 and stable image is typically produced within a few seconds such as about 1 second to about 60 seconds.

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

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 processing composition comprising

- (a) a silver salt of an organic acid,
- (b) a silver halide developing agent, and
- (c) a silver halide development inhibitor releasing compound, as described, which has the property of releasing a silver halide development inhibitor at above about 70° C.

A processing composition of this type is a photographic processing composition comprising

- (a) silver behenate,
- (b) a silver halide developing agent, and
- (c) 1-hydroxy-4-(1 - phenyl - 5 - tetrazolylthio)-2-(2'-n-tetradecyloxy)-naphthanilide.

Typically a polyvinyl butyral binder is employed with this processing composition.

Various means can be employed in providing the necessary heating of the described photographic and thermosensitive elements. The heating means can be a simple hot plate, iron or the like.

Other addenda known to be useful in photographic and thermosensitive elements of this type such as described in British Patent 1,161,777 published Aug. 20, 1969 and U.S. Patent 3,152,904 of Sorensen et al. issued Oct. 13, 1964 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 photographic element is prepared as follows:

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A coating composition is prepared by mixing the following components:

polyvinyl butyral—10.0 g.
silver behenate (about 60% pure, other components not identified)—28.0 g.
methanol—133.0 ml.
acetone—133.0 ml.
toluene—133.0 ml.

After mixing, the following solutions are added to the resulting dispersion:

	MI.
Methanol containing 2% by weight salicylic acid	40.0
Acetone containing 2.5% by weight 1-hydroxy-4-(1-phenyl - 5 - tetrazolythio)-2-(2'-n-tetradecyloxy)-naphthanilide	400.0
Methanol containing 10% by weight 4-phenyl-catechol	40.0

The composition is mixed and then coated on a water-resistant paper support at 5 milliliters per square foot of support and dried providing a photographic and thermosensitive element containing 30 milligrams per square foot of silver.

The photographic element is exposed sensitometrically with ultraviolet light for 5 seconds. The resulting latent image is developed by holding the photographic element in contact with a metal block at 85° C. for 5 seconds.

A developed image is produced. The developed image is held in room fluorescent light for 14 days at about 20° C. and during that period shows no visible change. The visible image is accordingly considered stable. The maximum density of the image is 1.80 and the minimum density is 0.20 with very low background stain.

EXAMPLE 2

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the 1 - hydroxy - 4 - (1-phenyl-5-tetrazolythio) - 2 - (2' - n-tetradecyloxy)-naphthanilide is omitted from the described photographic and thermosensitive element.

The resulting developed image is held in room fluorescent light for 14 days. During the first 24 hours the background rapidly darkens until the maximum density about equals the minimum density of the image.

This demonstrates the undesired instability in the absence of a development inhibitor releasing compound according to the invention.

EXAMPLE 3

The procedure set out in Example 1 is repeated with the exception that 0.1 milligram per square foot of support of a sensitizing dye which is 1-carboxymethyl-5-[(3-ethyl - 2(3H) - benzoxazolylidene) - ethylidene] - 3-phenyl - 2 - thiohydantoin is employed in the described photographic and thermosensitive element.

The photographic element is exposed sensitometrically with tungsten light (120 watt light bulb in a contact printer) for 5 seconds. The resulting latent image is developed by holding the photographic element in contact with a metal block at 85° C. for 30 seconds.

A developed image is produced. The developed image is held in room fluorescent light for 14 days at about 20° C. and during that period shows no visible change. This developed image is considered stable. The maximum density of the image is 1.80 and the minimum density is 0.20 with very low background stain.

EXAMPLE 4

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that an equimolar concentration of 1-phenyl - 5 - mercaptotetrazole is employed in place of 1 - hydroxy - 4 - (1 - phenyl - 5 - tetrazolythio)-2-(2'-n-tetradecyloxy)-naphthanilide.

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This provides an image which is barely visible and having a gray background.

This demonstrates that 1 - phenyl-5-mercaptotetrazole causes undesired desensitization in a photographic element as described.

EXAMPLE 5

This illustrates the invention employing a developer inhibitor releasing developing agent.

A photographic and thermosensitive element is prepared as follows:

polyvinyl butyral—10.0 g.
silver behenate—28.0 g.
acetone-toluene (1:1 by volume)—400.0 ml.

The following is added to 10 milliliters of the resulting dispersion:

	MI.
Ammonium iodide (0.6% by weight acetone solution)	2.0
2 - mercapto - 5 - phenyl - 1,3,4 - oxadiazole (1.0% by weight acetone solution)	5.0
1 - hydroxy - 4 - (1 - phenyl - 5 - tetrazolythio)-2 - (2'-n-tetradecyloxy)-naphthanilide (2% by weight acetone solution)	20.0
Trimethyl (1 - phenyl - 5 - tetrazolythio) - hydroquinone (2% by weight acetone solution)	15.0

The ammonium iodide reacts with the silver behenate to form photographic silver iodide. The resulting composition is coated on a paper support at 30 to 75 milligrams of silver per square foot of support to produce a photographic and thermosensitive element. This element is exposed to ultraviolet light for 5 to 10 seconds. The resulting latent image is developed by holding the photographic element in contact with a metal block at 85° C. for 5 seconds.

A developed image is produced. The developed image is held in room fluorescent light, at about 20° C., and after 15 months the image has a black tone with a light yellow background. This demonstrates the stability of an image according to the invention.

EXAMPLE 6

The procedure set out in Example 5 is repeated with the exception that a polyethylene terephthalate film support is employed in place of a paper support.

The resulting developed image is black. The image is held in room fluorescent light at about 20° C., and after 15 months the image has a brown-black tone and a yellow-brown background.

EXAMPLE 7

This illustrates the invention.

A photographic and thermosensitive element is prepared as follows:

A coating composition is prepared by mixing the following components:

polyvinyl butyral—10.0 g.
silver behenate (about 60% pure, other components not identified)—28.0 g.
acetone-toluene (1:1 by volume)—400.0 ml.

The following is added to 20 milliliters of the resulting dispersion:

	MI.
Phthalic acid (2.0% by weight acetone solution)	2.0
Benztotriazole (1.0% by weight acetone solution)	1.0
Dimethyl (1 - phenyl-5-tetrazolythio)-hydroquinone (2.0% by weight acetone solution)	2.0
3 - (dihexylaminomethyl) - 5 - phenyl catechol (10.0% by weight acetone solution)	0.2

It is believed that the phthalic acid and benztotriazole function as toning agents. The resulting composition is coated on a polyethylene coated paper support at 30 to 75 milligrams of silver per square foot of support to pro-

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duce a photographic and thermosensitive element. This element is exposed to ultraviolet light for 5 to 10 seconds. The resulting latent image is developed by holding the photographic element in contact with a metal block at 85° C. for 5 seconds.

The resulting photographic image is dark brown and has a light brown background.

EXAMPLE 8

Similar results are obtained as in Example 1 also employing phthalazinone, as a toner, in the described element.

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.

I claim:

1. A photothermographic element comprising a support having thereon
 - (a) photographic silver salt,
 - (b) a source of silver for physical development which is a silver salt of an organic acid,
 - (c) an organic reducing agent,
 - (d) a binder, and
 - (e) a silver halide development inhibitor releasing compound which is a compound having a tetrazolythio moiety which is released from said inhibitor releasing compound at above about 70° C.
2. A photothermographic element as in claim 1 wherein said organic reducing agent is a silver halide developing agent.
3. A photothermographic element as in claim 1 comprising a sensitizing dye.
4. A photothermographic element as in claim 1 wherein said development inhibitor releasing compound is a coupler having a tetrazolythio moiety.
5. A photothermographic element as in claim 1 wherein said development inhibitor releasing compound is 1-hydroxy - 4 - (1-phenyl-5-tetrazolythio)-2-(2'-n-tetradecyloxy)-naphthanilide.
6. A photothermographic element as in claim 1 comprising a toner.
7. A photothermographic element comprising a support having thereon:
 - (a) polyvinyl butyral binder,
 - (b) silver behenate,
 - (c) a phenolic reducing agent,
 - (d) photographic silver halide,
 - (e) a phthalazinone toner,
 - (f) 1 - hydroxy - 4-(1-phenyl-5-tetrazolythio)-2-(2'-n-tetradecyloxy)-naphthanilide, and
 - (g) a sensitizing dye.
8. A photothermographic composition comprising
 - (a) a silver halide development inhibitor releasing compound which is a compound having a tetrazolythio moiety which is released from said compound at above about 70° C.,
 - (b) silver behenate,
 - (c) photographic silver halide,
 - (d) a phenolic reducing agent,
 - (e) polyvinyl butyral, and
 - (f) a sensitizing dye.
9. A photographic processing composition comprising
 - (a) silver behenate, (b) a silver halide developing agent, and (c) 1-hydroxy-4-(1-phenyl-5-tetrazolythio)-2-(2'-n-tetradecyloxy)-naphthanilide.
10. A photographic processing composition as in claim 9 comprising a polyvinyl butyral binder.
11. A photothermographic element comprising a support having thereon
 - (a) photographic silver halide,

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(b) a source of silver for physical development which is a compound selected from the group consisting of silver behenate and silver stearate,

(c) a phenolic reducing agent,

(d) a polymeric binder, and

(e) a silver halide development inhibitor releasing compound which is a coupler having a tetrazolythio moiety which is released from said coupler at above about 70° C.,

(f) a toner, and

(g) a sensitizing dye.

12. A photothermographic composition comprising

(a) photographic silver salt,

(b) a source of silver for physical development which is a silver salt of an organic acid, and

(c) a silver halide development inhibitor releasing compound which is a compound having a tetrazolythio moiety which is released from said inhibitor releasing compound at above about 70° C.

13. A process of developing a latent image in a photothermographic element comprising a support having thereon

(a) a photographic silver salt,

(b) a source of silver for physical development which is a silver salt of an organic acid,

(c) a binder,

(d) an organic reducing agent and a silver halide development inhibitor releasing compound which is a compound having a tetrazolythio moiety which is released from said inhibitor releasing compound at above about 70° C., and stabilizing the resulting developed image comprising heating said element from about 70° C. to about 250° C.

14. A process of developing a latent image in a photothermographic element comprising a support having thereon

(a) photographic silver halide,

(b) silver behenate,

(c) polyvinyl butyral binder,

(d) a phenolic reducing agent,

(e) 1 - hydroxy-4-(1-phenyl-5-tetrazolythio)-2-(2'-tetradecyloxy)-naphthanilide,

(f) a phthalazinone toner, and

(g) a sensitizing dye,

and stabilizing the resulting developed image comprising heating said element from about 70° C. to about 250° C.

15. A photographic processing composition comprising

(a) a silver salt of an organic acid,

(b) a silver halide developing agent and

(c) a silver halide development inhibitor releasing compound which is a compound having a tetrazolythio moiety which is released from said inhibitor releasing compound at above about 70° C.

References Cited

UNITED STATES PATENTS

Re. 26,719	11/1969	Sorensen	96—50
3,180,731	4/1965	Roman	96—114.1
3,227,554	1/1966	Barr	96—3
3,379,529	4/1968	Porter	96—36
3,457,075	7/1969	Morgan	96—114.1
3,429,706	2/1969	Shepard	117—34

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96—66; 117—36.7

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,700,457

Dated October 24, 1972

Inventor(s) Mary J. Youngquist

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

Column 1, line 24, "developmnet" should read
---development---

Column 6, line 33, "styrlys" should read
---styryls---

Column 7, line 11, "agent" should read ---agents---.
Line 50, "723,,019" should read ---723,019---

Column 8, line 16, "biding" should read ---binding---.
Line 73, "photoghaphic" should read ---photographic---

Column 9, line 6, "1960" should read ---1969---.
Line 8, "nad" should read ---and---. Line 40, "072,067"
should read ---972,067---

Column 10, line 72, "mercocyanine" should read
---merocyanine---

Column 12, line 14, "development" should read
---developed---

Column 14, line 13, "benhenate" should read
---behenate---

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents