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(54) Thiosulfonate esters as antifoggants, shelf-life stabilizers, and post-processing stabilizers for photothermographic elements.

(57) Thiosulfonate esters have been found to improve resistance to fog, shelf-life stability, and post-processing stability of photothermographic imaging elements. These elements comprise :
(a) a photosensitive silver halide ;
(b) a non-photosensitive, reducible silver source ;
(c) a reducing agent for the non-photosensitive, reducible silver source ;
(d) a binder ; and
(e) a thiosulfonate ester of the formula :

$$R^1\text{-}SO_2\text{-}SR^2$$

wherein :

R^1 and R^2 independently represent an alkyl group, an aryl group, an aralkyl group, an alkaryl group, or an alkenyl group.

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FIELD OF THE INVENTION

The invention relates to a photothermographic silver halide material and a method for producing in such a material improved resistance to fog, shelf-life stability, and post-processing stability by incorporating thiosulfonate esters.

BACKGROUND OF THE ART

Silver halide-containing, photothermographic imaging materials (i.e., heat-developable photographic materials) processed with heat, and without liquid development, have been known in the art for many years. These materials, also known as "dry silver" compositions or emulsions, generally comprise a support having coated thereon: (1) a photosensitive material that generates atomic silver when irradiated, (2) a non-photosensitive, reducible silver source, and (3) a reducing agent for the non-photosensitive, reducible silver source, and (4) a binder. The photosensitive material is generally photographic silver halide which must be in catalytic proximity to the non-photosensitive, reducible silver source. Catalytic proximity requires an intimate physical association of these two materials so that when silver specks or nuclei are generated by the irradiation or light exposure of the photographic silver halide, those nuclei are able to catalyze the reduction of the reducible silver source. It has long been understood that elemental silver (Ag°) is a catalyst for the reduction of silver ions, and a progenitor of the photosensitive photographic silver halide may be placed into catalytic proximity with the non-photosensitive, reducible silver source in a number of different fashions, such as by partial metathesis of the reducible silver source with a halogen-containing source (see, for example, U.S. Patent No. 3,457,075), coprecipitation of silver halide and reducible silver source material (see, for example, U.S. Patent No. 3,839,049), and other methods that intimately associate the photosensitive photographic silver halide and the non-photosensitive, reducible silver source.

The non-photosensitive, reducible silver source is a material that contains silver ions. The preferred non-photosensitive reducible silver source comprises silver salts of long chain aliphatic carboxylic acids, typically having from 10 to 30 carbon atoms. The silver salt of behenic acid or mixtures of acids of similar molecular weight are generally used. Salts of other organic acids or other organic materials, such as silver imidazolates, have been proposed, and U.S. Patent No. 4,260,677 discloses the use of complexes of inorganic or organic silver salts as non-photosensitive, reducible silver sources.

In both photographic and photothermographic emulsions, exposure of the photographic silver halide to light produces small clusters of silver atoms (Ag°). The imagewise distribution of these clusters is known in the art as a latent image. This latent image generally is not visible by ordinary means and the photosensitive emulsion must be further processed in order to produce a visible image. The visible image is produced by the reduction of silver ions, which are in catalytic proximity to silver halide grains bearing the clusters of silver atoms, i.e. the latent image. This produces a black and white image.

A variety of ingredients may be added to these basic components to enhance performance. For example, toning agents may be incorporated to improve the color of the silver image of the photothermographic emulsions, as described in U.S. Patent Nos. 3,846,136; 3,994,732; and 4,021,249.

As the visible image is produced entirely by elemental silver (Ag°), one cannot readily decrease the amount of silver in the emulsion without reducing the maximum image density. However, reduction of the amount of silver is often desirable in order to reduce the cost of raw materials used in the emulsion.

One conventional way of attempting to increase the maximum image density of photographic and photothermographic emulsions without increasing the amount of silver in the emulsion layer is by incorporating dye-forming materials in the emulsion. Color images can be formed by incorporation of leuco dyes into the emulsion. Leuco dyes are the reduced form of a color-bearing dye. Upon imaging, the leuco dye is oxidized, and the color-bearing dye and a reduced silver image are simultaneously formed in the exposed region. In this way, a dye enhanced silver image can be produced, as shown, for example, in U.S. Patent Nos. 3,531,286; 4,187,108; 4,426,441; 4,374,921; and 4,460,681.

Multicolor photothermographic imaging elements typically comprise two or more monocolor-forming emulsion layers (often each emulsion layer comprises a set of bilayers containing the color-forming reactants) maintained distinct from each other by barrier layers. The barrier layer overlaying one photosensitive, photothermographic emulsion layer typically is insoluble in the solvent of the next photosensitive, photothermographic emulsion layer. Photothermographic elements having at least 2 or 3 distinct color-forming emulsion layers are disclosed in U.S. Patent Nos. 4,021,240 and 4,460,681. Various methods to produce dye images and multicolor images with photographic color couplers and leuco dyes are well known in the art as represented by U.S. Patent Nos. 4,022,617; 3,531,286; 3,180,731; 3,761,270; 4,460,681; 4,883,747; and *Research Disclosure*, March 1989, item 29963.

Photothermographic emulsions, in a manner similar to photographic emulsions and other light-sensitive systems, tend to suffer from fog. Fog is spurious image density which appears in unexposed areas of the element and is often reported in sensitometric results as D_{min}. Traditionally, photothermographic materials have suffered from fog upon coating. The fog level of freshly prepared photothermographic materials will be referred to as initial fog or Initial D_{min}.

A great deal of effort has been directed towards minimizing the initial fog of photothermographic silver halide materials and toward stabilizing the fog level on shelf-aging. Mercuric salts are described as antifoggants in U.S. Patent No. 3,589,903. Fog reduction has been described for organic carboxylic acids such as benzoic and phthalic acids in U.S. Patent No. 4,152,160, for benzoyl benzoic acid compounds in U.S. Patent No. 4,784,939, for indane or tetralin carboxylic acids in U.S. Patent No. 4,569,906, for dicarboxylic acids in U.S. Patent No. 4,820,617 and for heteroaromatic carboxylic acids in U.S. Patent No. 4,626,500. Halogenated compounds have also been shown to be strong antifoggants and are described in U.S. Patent Nos. 4,546,075, 4,756,999, 4,452,885, 3,874,946 and 3,955,982. Halogen molecules or halogen molecules associated with a heteroatom ring are also useful antifoggants and are described in U.S. Patent No. 5,028,523. Other materials finding applications as photothermographic antifoggants include palladium compounds found in U.S. Patent No. 4,102,312 and G.B. Patent No. 1,502,670; iron group metals found in U.S. Patent No. 4,128,428; substituted-triazoles as in U.S. Patent Nos. 4,123,274, 4,128,557 and 4,125,430; sulfur compounds as in U.S. Patent Nos. 4,213,784 and 4,245,033; thiouracils as in U.S. Patent No. 4,002,479. However, these compounds individually or in combination were not found to produce sufficient fog stability of the photothermographic element, without other undesirable effects such as speed loss, toxicity, or skin sensitivity.

Metal salts of thiosulfonic acids have also been used as antifoggants in combination with other materials in U.S. Pat. Nos. 4,125,403, 4,152,160 and 4,307,187 and Japanese Pat. Nos. 53-020,923 and 53-019825. These materials caused a loss in reactivity in our photothermographic system, leading to poor speed and low maximum image densities. Therefore, it was necessary to find materials which prevent fog while allowing maximum image speed and density.

In addition, the fog level often rises steadily as the materials age. This type of fog will be referred to herein as shelf-aging fog. Adding to the difficulty of fog control on shelf-aging is the fact that the developer is incorporated in the photothermographic element. This is not the case in conventional silver halide photographic systems. Thus, the need for shelf life stabilizers in photothermographic elements is therefore considered to be very important.

Earlier efforts at improving the shelf-aging characteristics of photothermographic materials include the addition of vinyl sulfones and β-halo sulfones as described in copending U.S. Patent Application Serial No. 07/983,304, filed on November 30, 1992 and the combination of isocyanates and halogenated compounds as described in copending U.S. Patent Application Serial No. 07/983,125, filed on November 30, 1992.

A third problem that exists with photothermographic systems is the instability of the image following processing. The photoactive silver halide still present in the developed image may continue to catalyze formation of metallic silver (known as "silver print-out") during room light exposure. Thus, there exists a need for stabilization of the unreacted silver halide. The addition of separate post-processing image stabilizers or stabilizer precursors is often used to provide the desired post-processing stability. Most often these are sulfur-containing compounds such as mercaptans, thiones, thioethers, and 5-mercapto-1,2,4-triazoles.

U.S. Patent No. 5,061,614 describes silver halide emulsions reduction-sensitized during precipitation of silver halide grains in the presence of thiosulfonic acid compounds. These emulsions are used in conventional silver halide photographic elements. Thiosulfonate esters are described as one class of possible compounds. No mention is made of the use of thiosulfonate esters in photothermographic elements.

Some of the problems with these stabilizers include thermal fogging during processing or losses in photographic sensitivity, maximum density, or contrast at effective stabilizer concentrations.

Thus, there has been a continued need for improved post-processing stabilizers that do not fog or desensitize the photographic materials. Due to the magnitude of these problems, it was found necessary to search for additional materials to further improve the fog resistance, shelf-aging stability, and post-processing stability of photothermographic materials.

SUMMARY OF THE INVENTION

The present invention provides a heat-developable, photothermographic elements comprising a support bearing at least one photosensitive, image-forming photothermographic emulsion layer comprising:

(a) a photosensitive silver halide;

(b) a non-photosensitive, reducible silver source;

(c) a reducing agent for the non-photosensitive, reducible silver source;

(d) a binder; and

(e) a thiosulfonate ester of the formula:

$$R^1\text{-}SO_2\text{-}SR^2$$

wherein:

R^1 and R^2 independently represent an alkyl group, an aryl group, an aralkyl group, an alkaryl group, or an alkenyl group; preferably, R^1 and R^2 independently represent a C_1 to C_{12} alkyl, aryl, aralkyl, alkaryl, or alkenyl group;

and more preferably, R^1 and R^2 independently represent a C_1 to C_6 alkyl, aryl, aralkyl, alkaryl, or alkenyl group.

The reducing agent for the non-photosensitive silver source may optionally comprise a compound capable of being oxidized to form or release a dye. Preferably, the dye-forming material is a leuco dye.

The photothermographic elements of this invention may be used to prepare black-and-white, monochrome, or full color images. The photothermographic material of this invention can be used, for example, in conventional black-and-white or color photothermography, in electronically generated black and white or color hardcopy recording, in the graphic arts area, and in digital color proofing. The material of this invention provides high photographic speed, provides strongly absorbing black-and-white or color images, and provides a dry and rapid process.

As used herein, the term "emulsion layer" means a layer of a photothermographic element that contains photosensitive silver salt and silver source material.

As is well understood in this technical area, a large degree of substitution is not only tolerated, but is also often advisable and substitution is anticipated on the compounds of the present invention. As a means of simplifying the description of substituent groups, the terms "group" (or "nucleus") and "moiety" are used to differentiate between those chemical species that may be substituted and those which may not be so substituted. Thus, when the term "group," "aryl group," or "central nucleus" is used to describe a substituent, that substituent includes the use of additional substituents beyond the literal definition of the basic group. Where the term "moiety" is used to describe a substituent, only the unsubstituted group is intended to be included. For example, the phrase, "alkyl group" is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, propyl, *t*-butyl, cyclohexyl, iso-octyl, octadecyl and the like, but also alkyl chains bearing substituents known in the art, such as hydroxyl, alkoxy, phenyl, halogen atoms (F, Cl, Br, and I), cyano, nitro, amino, carboxy, etc. For example, alkyl group includes ether groups (e.g., $CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}$), haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. On the other hand, the phrase "alkyl moiety" is limited to the inclusion of only pure hydrocarbon alkyl chains, such as methyl, ethyl, propyl, t-butyl, cyclohexyl, iso-octyl, octadecyl, and the like. Substituents which react with active ingredients, such as very strongly electrophilic or oxidizing substituents, would of course be excluded by the ordinarily skilled artisan as not being inert or harmless.

Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides heat-developable, photothermographic elements capable of providing stable, high density images of high resolution. These heat-developable, photothermographic elements comprising a support bearing at least one photosensitive, image-forming photothermographic-emulsion layer comprising:

(a) a photosensitive silver halide;

(b) a non-photosensitive, reducible silver source;

(c) a reducing agent for the non-photosensitive, reducible silver source;

(d) a binder; and

(e) a thiosulfonate ester of the formula:

$$R^1\text{-}SO_2\text{-}SR^2$$

wherein:

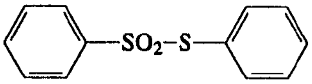
R^1 and R^2 independently represent an alkyl group, an aryl group, an aralkyl group, an alkaryl group, or an alkenyl group; preferably, R^1 and R^2 independently represent a C_1 to C_{12} alkyl, aryl, aralkyl, alkaryl, or alkenyl group; and more preferably, R^1 and R^2 independently represent a C_1 to C_6 alkyl, aryl, aralkyl, alkaryl, or alkenyl group.

The reducing agent for the non-photosensitive silver source may optionally comprise a compound capable of being oxidized to form or release a dye. Preferably, the dye-forming material is a leuco dye.

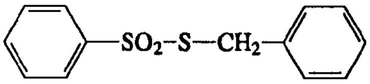
According to the present invention, the thiosulfonate ester is added either to one or more emulsion layers or to a layer or layers adjacent to one or more emulsion layers. Layers that are adjacent to emulsion layers may be, for example, topcoat layers, primer layers, image-receiving layers, interlayers, opacifying layers, antihalation layers, barrier layers, auxiliary layers, etc.

Non-limiting representative examples of thiosulfonate esters useful as antifoggants, shelf-life stabilizers, and post-processing stabilizers according to the present invention are shown in Table I.

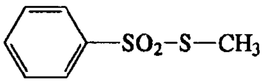
Table I - Representative Thiosulfonate Ester Compounds



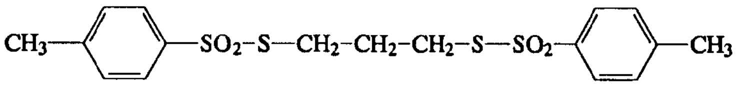
Thiosulfonate Ester A



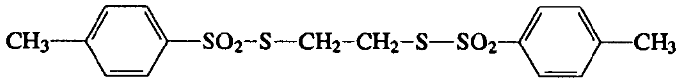
Thiosulfonate Ester B



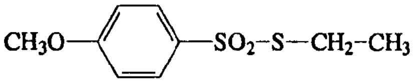
Thiosulfonate Ester C



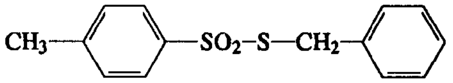
Thiosulfonate Ester D



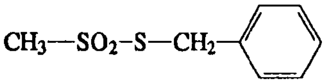
Thiosulfonate Ester E



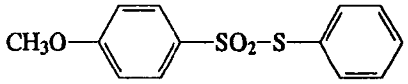
Thiosulfonate Ester F



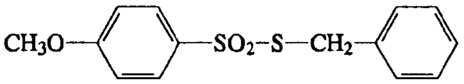
Thiosulfonate Ester I



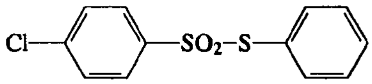
Thiosulfonate Ester G



Thiosulfonate Ester J



Thiosulfonate Ester H



Thiosulfonate Ester K

When used as antifoggants, shelf-life stabilizers, or post-processing stabilizers in photothermographic elements, the thiosulfonate esters of the invention may contain other antifoggants, shelf-life stabilizers, or post-processing stabilizers or stabilizer precursors in combination with the compounds of this invention, as well as other additives in combination with the compounds of the invention such as toners, development accelerators, and other image-modifying agents.

The amounts of the above-described thiosulfonate esters that are added to the emulsion layer according to the present invention may be varied depending upon the particular compound used an upon the type of emulsion layer (i.e., black-and-white or color).

The thiosulfonate esters are used in a general amount of at least 0.001 moles per mole of silver. Usually the range is between 0.005 and 5 moles of the compounds per mole of silver and preferably, between 0.01

and 0.50 moles of compounds per mole of silver.

The compounds of the present invention typically comprise from about 0.01 wt% to 10 wt% of the dry photothermographic composition. They may be incorporated directly into the silver-containing layer or into an adjacent layer.

The Photosensitive Silver Halide

The photosensitive silver halide can be any photosensitive silver halide, such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide, etc. The photosensitive silver halide can be added to the emulsion layer in any fashion so long as it is placed in catalytic proximity to the non-photosensitive reducible silver source materail. The light-sensitive silver halide used in the present invention can be employed in a range of 0.005 mole to 0.5 mole and, preferably, from 0.01 mole to 0.15 mole per mole of silver salt.

The silver halide used in the present invention may be employed without modification. However, it may be chemically and spectrally sensitized in a manner similar to that used to sensitize conventional wet process silver halide or heat-developable photographic materials. For example, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulfur, selenium or tellurium etc., or a compound containing gold, platinum, palladium, ruthenium, rhodium or iridium, etc., a reducing agent such as a tin halide, etc., or a combination thereof. The details of these procedures are described in T.H. James, *The Theory of the Photographic Process*, Fourth Edition, Chapter 5, pages 149 to 169. Suitable chemical sensitization procedures are also described in Shepard, U.S. Patent No. 1,623,499; Waller, U.S. Patent No. 2,399,083; McVeigh, U.S. Patent No. 3,297,447; and Dunn, U.S. Patent No. 3,297,446.

The photosensitive silver halides may be spectrally sensitized with various known dyes that spectrally sensitize silver halide. Non-limiting examples of sensitizing dyes that can be employed include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxanol dyes. Of these dyes, cyanine dyes, merocyanine dyes, and complex merocyanine dyes are particularly useful. The dyes may sensitize the silver halide in any region of the electromagnetic spectrum such as the visible or infra-red.

An appropriate amount of sensitizing dye added is generally in the range of from about 10^{-10} to 10^{-1} mole, and preferably, from about 10^{-8} to 10^{-3} moles per mole, of silver halide.

The Non-Photosensitive Reducible Silver Source Material

The non-photosensitive reducible silver source which can be used in the present invention is a silver salt which is comparatively stable to light, but forms a silver image when heated to 80°C or higher in the presence of an exposed photo-catalyst (such as silver halide) and a reducing agent and can be any material that contains a source of reducible silver ions. Complexes of organic or inorganic silver salts, wherein the ligand has a gross stability constant for silver ion of between 4.0 and 10.0, are also useful in this invention.

Silver salts of organic acids, particularly silver salts of long chain fatty carboxylic acids, are preferred. The chains typically contain 10 to 30, preferably 15 to 28 carbon atoms. Suitable organic silver salts include silver salts of organic compounds having a carboxyl group. Examples thereof include a silver salt of an aliphatic carboxylic acid and a silver salt of an aromatic carboxylic acid. Preferred examples of the silver salts of aliphatic carboxylic acids include silver behenate, silver stearate, silver oleate, silver laureate, silver caprate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartarate, silver furoate, silver linoleate, silver butyrate and silver camphorate, mixtures thereof, etc. Silver salts which are substitutable with a halogen atom or a hydroxyl group can also be effectively used. Preferred examples of the silver salts of aromatic carboxylic acid and other carboxyl group-containing compounds include silver benzoate, a silver-substituted benzoate such as silver 3,5-dihydroxybenzoate, silver o-methylbenzoate, silver *m*-methylbenzoate, silver *p*-methylbenzoate, silver 2,4-dichlorobenzoate, silver acetamidobenzoate, silver *p*-phenylbenzoate, etc., silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellilate, a silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione or the like as described in U.S. Patent No. 3,785,830, and a silver salt of an aliphatic carboxylic acid containing a thioether group as described in U.S. Patent No. 3,330,663.

Silver salts of compounds containing mercapto or thione groups and derivatives thereof can also be used. Preferred examples of these compounds include a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, a silver salt of 2-mercaptobenzimidazole, a silver salt of 2-mercapto-5-aminothiadiazole, a silver salt of 2-(2-ethylglycolamido)benzothiazole, a silver salt of thioglycolic acid such as a silver salt of a S-alkylthioglycolic acid (wherein the alkyl group has from 12 to 22 carbon atoms) as described in Japanese Patent Application No. 28221/73, a silver salt of a dithiocarboxylic acid such as a silver salt of dithioacetic acid, a silver salt of thioamide, a silver salt of 5-carboxylic-1-methyl-phenyl-4-thiopyridine, a silver salt of mercaptotriazine, a silver salt of 2-mercaptobenzoxazole, a silver salt as described in U.S. Patent No. 4,123,274, for example, a silver salt of 1,2,4-mercaptothiazole derivative such as a silver salt of 3-amino-5-benzylthio-1,2,4-thiazole, a silver salt of a thione compound such as a silver salt of 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione as disclosed in U.S. Patent No. 3,201,678.

Furthermore, a silver salt of a compound containing an imino group may be used. Preferred examples of these compounds include silver salts of benzotriazole and derivatives thereof, for example, silver salts of benzotriazoles such as silver methylbenzotriazolate, etc., silver salt of halogen-substituted benzotriazoles, such as silver 5-chlorobenzotriazolate, etc., silver salts of carboimidobenzotriazole, etc., silver salt of 1,2,4-triazoles or 1-*H*-tetrazoles as described in U.S. Patent No. 4,220,709, silver salts of imidazoles and imidazole derivatives, and the like. Various silver acetylide compounds can also be used, for instance, as described in U.S. Patent Nos. 4,761,361 and 4,775,613.

It is also found convenient to use silver half soaps, of which an equimolar blend of silver behenate and behenic acid, prepared by precipitation from aqueous solution of the sodium salt of commercial behenic acid and analyzing about 14.5 percent silver, represents a preferred example. Transparent sheet materials made on transparent film backing require a transparent coating and for this purpose the silver behenate full soap, containing not more than about 4 or 5 percent of free behenic acid and analyzing about 25.2 percent silver, may be used.

The method used for making silver soap dispersions is well known in the art and is disclosed in *Research Disclosure* April 1983 (22812), *Research Disclosure* October 1983 (23419) and U.S. Patent No. 3,985,565.

The silver halide and the non-photosensitive reducible silver source material that form a starting point of development should be in reactive association. By "reactive association" is meant that they should be in the same layer, in adjacent layers, or in layers separated from each other by an intermediate layer having a thickness of less than 1 micrometer (1 μm). It is preferred that the silver halide and the non-photosensitive reducible silver source material be present in the same layer.

The silver halide may be "pre-formed" and mixed with the organic silver salt in a binder prior to use to prepare a coating solution. It is also effective to blend the silver halide and organic silver salt in a ball mill for a long period of time. Materials of this type are often referred to as pre-formed emulsions. It is also effective to use an *in situ* process which comprises adding a halogen-containing compound to the organic silver salt to partially convert the silver of the organic silver salt to silver halide.

Methods of preparing these silver halide and organic silver salts and manners of blending them are described in *Research Disclosure*, No. 17029, U.S. Patent No. 3,700,458, and Japanese Patent Application Nos. 32928/75, 42529/76, 13224/74 and 17216/75.

Pre-formed silver halide emulsions when used in the material of this 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, e.g., by the procedures described in U.S. Patent Nos. 2,618,556; 2,614,928; 2,565,418; 3,241,969; and 2,489,341. The silver halide grains may have any crystalline habit including, but not limited to, cubic, tetrahedral, orthorhombic, tabular, laminar, platelet, etc.

Photothermographic emulsions containing pre-formed silver halide in accordance with this invention can be sensitized with chemical sensitizers, or with spectral sensitizers as described above.

The source of reducible silver material generally constitutes from 15 to 70 percent by weight of the emulsion layer. It is preferably present at a level of 30 to 55 percent by weight of the emulsion layer.

The Reducing Agent for the Non-Photosensitive Reducible Silver Source

The reducing agent for the organic silver salt may be any material, preferably organic material, that can reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful, but hindered phenol reducing agents are preferred.

A wide range of reducing agents has been disclosed in dry silver systems including amidoximes such as phenylamidoxime, 2-thienylamidoxime and *p*-phenoxyphenylamidoxime, azines (e.g., 4-hydroxy-3,5-dimethoxybenzaldehydeazine); a combination of aliphatic carboxylic acid aryl hydrazides and ascorbic acid, such as 2,2'-bis(hydroxymethyl)propionylbetaphenyl hydrazide in combination with ascorbic acid; a combination of polyhydroxybenzene and hydroxylamine, a reductone and/or a hydrazine, e.g., a combination of hydroquinone and bis(ethoxyethyl)hydroxylamine, piperidinohexose reductone or formyl-4-methylphenylhydrazine, hydroxamic acids such as phenylhydroxamic acid, *p*-hydroxyphenylhydroxamic acid, and *o*-alaninehydroxamic acid; a combination of azines and sulfonamidophenols, e.g., phenothiazine and 2,6-dichloro-4-benzenesulfonamidophenol; α-cyanophenylacetic acid derivatives such as ethyl α-cyano-2-methylphenylacetate, ethyl α-cyano-phenylacetate; bis-*o*-naphthols as illustrated by 2,2'-dihydroxy-1-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, and bis(2-hydroxy-1-naphthyl)methane; a combination of bis-*o*-naphthol and a 1,3-dihydroxybenzene derivative, (e.g., 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone); 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones as illustrated by dimethylaminohexose reductone, anhydrodihydroaminohexose reductone, and anhydrodihydropiperidonehexose reductone; sulfamidophenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol, and *p*-benzenesulfonamidophenol; 2-phenylindane-1,3-dione and the like; chromans such as 2,2-dimethyl-7-t-butyl-6--hydroxychroman; 1,4-dihydropyridines such as 2,6-dimethoxy-3,5-dicarbethoxy-1,4-dihydropyridine; bisphenols, e.g., bis(2-hydroxy-3-*t*-butyl-5-methyl phenyl) methane; 2,2-bis(4-hydroxy-3-methylphenyl)propane; 4,4-ethylidene-bis(2-*t*-butyl 6-methylphenol); and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane; ascorbic acid derivatives, e.g., 1-ascorbylpalmitate, ascorbylstearate and unsaturated aldehydes and ketones, such as benzyl and diacetyl; 3-pyrazolidones; and certain indane-1,3-diones.

The reducing agent should be present as 1 to 12 percent by weight of the imaging layer. In multilayer constructions, if the reducing agent is added to a layer other than an emulsion layer, slightly higher proportions, of from about 2 to 15 percent, tend to be more desirable.

The Optional Dye-Releasing Material

As noted above, the reducing agent for the reducible source of silver may be a compound that can be oxidized to form or release a dye.

The optional dye-forming or dye-releasing material may be any colorless or lightly colored compound that can be oxidized to a colored form, when heated, preferably to a temperature of from about 80°C to about 250°C (176°F to 482°F) for a duration of from about 0.5 to about 300 seconds. When used with a dye-receiving layer, the dye can diffuse through emulsion layers and interlayers into the image-receiving layer of the element of the invention.

Leuco dyes are one class of dye-releasing material that forms a dye upon oxidation. Any leuco dye capable of being oxidized by silver ion to form a visible image can be used in the present invention. Leuco dyes that are both pH sensitive and oxidizable can be used, but are not preferred. Leuco dyes that are sensitive only to changes in pH are not included within scope of dyes useful in this invention because they are not oxidizable to a colored form.

As used herein, the term "change in color" includes: (1) a change from an uncolored or lightly colored state (optical density less than 0.2) to a colored state (an increase in optical density of at least 0.2 units), and (2) substantial change in hue.

Representative classes of leuco dyes that are suitable for use in the present invention include, but are not limited to, bisphenol and bisnaphthol leuco dyes, phenolic leuco dyes, indoaniline leuco dyes, imidazole leuco dyes, azine leuco dyes, oxazine leuco dyes, diazine leuco dyes, and thiazine leuco dyes. Preferred classes of dyes are described in U.S. Patent Nos. 4,460,681 and 4,594,307.

One class of leuco dyes useful in this invention are those derived from imidazole dyes. Imidazole leuco dyes are described in U.S. Patent No. 3,985,565.

Another class of leuco dyes useful in this invention are those derived from so-called "chromogenic dyes." These dyes are prepared by oxidative coupling of a *p*-phenylenediamine with a phenolic or anilinic compound. Leuco dyes of this class are described in U.S. Patent No. 4,594,307. Leuco chromogenic dyes having short chain carbamoyl protecting groups are described in copending application U.S. Serial No. 07/939,093, incorporated herein by reference.

A third class of dyes useful in this invention are "aldazine" and "ketazine" dyes. Dyes of this type are described in U.S. Patent Nos. 4,587,211 and 4,795,697.

Another preferred class of leuco dyes are reduced forms of dyes having a diazine, oxazine, or thiazine nucleus. Leuco dyes of this type can be prepared by reduction and acylation of the color-bearing dye form. Methods of preparing leuco dyes of this type are described in Japanese Patent No. 52-89131 and U.S. Patent Nos. 2,784,186; 4,439,280; 4,563,415; 4,570,171; 4,622,395; and 4,647,525.

Another class of dye-releasing materials that form a dye upon oxidation are known as pre-formed-dye-release (PDR) or redox-dye-release (RDR) materials. In these materials the reducing agent for the organic silver compound releases a preformed dye upon oxidation. Examples of these materials are disclosed in U.S. Patent No. 4,981,775.

Also useful are neutral, phenolic leuco dyes such as 2-(3,5-di-*t*-butyl-4-hydroxyphenyl)-4,5,-diphenylimidazole, or bis(3,5-di-*t*-butyl-4-hydroxyphenyl) phenylmethane. Other phenolic leuco dyes useful in practice of the present invention are disclosed in U.S. Patent Nos. 4,374,921; 4,460,681; 4,594,307; and 4,782,010.

Other leuco dyes may be used in imaging layers as well, for example, benzylidene leuco compounds cited in U.S. Patent No. 4,923,792, incorporated herein by reference. The reduced form of the dyes should absorb less strongly in the visible region of the electromagnetic spectrum and be oxidized by silver ions back to the original colored form of the dye. Benzylidene dyes have extremely sharp spectral characteristics giving high color purity of low gray level. The dyes have large extinction coefficients, typically on the order of 10^4 to 10^5 liter/mole-cm, and possess good compatibility and heat stability. The dyes are readily synthesized and the reduced leuco forms of the compounds are very stable. Leuco dyes such as those disclosed in U.S. Patent Nos. 3,442,224; 4,021,250; 4,022,617; and 4,368,247 are also useful in the present invention.

The dyes formed from the leuco dye in the various color-forming layers should, of course, be different. A difference of at least 60 nm in reflective maximum absorbance is preferred. More preferably, the absorbance maximum of dyes formed will differ by at least 80 - 100 nm. When three dyes are to be formed, two should preferably differ by at least these minimums, and the third should preferably differ from at least one of the other dyes by at least 150 nm, and more preferably, by at least 200 nm. Any leuco dye capable of being oxidized by silver ion to form a visible dye is useful in the present invention as previously noted.

The dyes generated by the leuco compounds employed in the elements of the present invention are known and are disclosed, for example, in *The Colour Index*; The Society of Dyes and Colourists: Yorkshire, England, 1971; Vol. 4, p. 4437; and Venkataraman, K. *The Chemistry of Synthetic Dyes*; Academic Press: New York, 1952; Vol. 2, p. 1206; U.S. Patent No. 4,478,927, and Hamer, F.M. *The Cyanine Dyes and Related Compounds*; Interscience Publishers: New York, 1964; p. 492.

Leuco dye compounds may readily be synthesized by techniques known in the art. Suitable methods are disclosed, for example, in: F.X. Smith et al. *Tetrahedron Lett.* **1983**, *24*(45), 4951-4954; X. Huang., L. Xe, *Synth. Commun.* **1986**, 16(13) 1701-1707; H. Zimmer et al. *J. Org. Chem.* **1960**, 25, 1234-5; M. Sekiya et al. *Chem. Pharm. Bull.* **1972**, 20(2),343; and T. Sohda et al. *Chem. Pharm. Bull.* **1983**, 31(2) 560-5; H. A. Lubs *The Chemistry of Synthetic Dyes and Pigments*; Hafner; New York, NY; **1955** Chapter 5; in H. Zollinger *Color Chemistry*: *Synthesis, Properties and Applications of Organic Dyes and Pigments*; VCH; New York, NY; pp. 67-73, **1987**, and in U.S. Patent No. 5,149,807; and EPO Laid Open Application No. 0,244,399.

Further, as other image-forming materials, materials where the mobility of the compound having a dye part changes as a result of an oxidation-reduction reaction with silver halide, or an organic silver salt at high temperature can be used, as described in Japanese Patent Application No. 165054 (1984). Many of the above-described materials are materials wherein an imagewise distribution of mobile dyes corresponding to exposure is formed in the photosensitive material by heat development. Processes of obtaining visible images by transferring the dyes of the image to a dye fixing material (diffusion transfer) have been described in the above described cited patents and Japanese Patent Application Nos. 168,439 (1984) and 182,447 (1984).

Still further the reducing agent may be a compound that releases a conventional photographic dye coupler or developer on oxidation as is known in the art. When the heat developable, photosensitive material used in this invention is heat developed in a substantially water-free condition after or simultaneously with imagewise exposure, a mobile dye image is obtained simultaneously with the formation of a silver image either in exposed areas or in unexposed areas with exposed photosensitive silver halide.

The total amount of optional leuco dye used as a reducing agent utilized in the present invention should preferably be in the range of 0.5-25 weight percent, and more preferably, in the range of 1-10 weight percent, based upon the total weight of each individual layer in which the reducing agent is employed.

The Binder

It is preferred that the binder be sufficiently polar to hold the other ingredients of the emulsion in solution. It is preferred that the binder be selected from polymeric materials, such as, for example, natural and synthetic resins, such as gelatin, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, methacrylate copolymers, maleic anhydride ester copolymers, butadiene-styrene copolymers, and the like. Copolymers, e.g. terpolymers, are also included in the definition of polymers. The poly(vinyl acetals), such as poly(vinyl butyral) and poly(vinyl formal), and vinyl copolymers, such as poly(vinyl acetate) and poly(vinyl chloride), are particularly preferred. The binders can be used individually or in combination with one another. Although the binder may be hydrophilic or hydrophobic, it is preferably hydrophobic.

The binders are generally used at a level of from about 20 to about 80 percent by weight of the emulsion layer, and preferably from about 30 to about 55 percent by weight. Where the proportions and activities of the components require a particular developing time and temperature, the binder should be able to withstand those conditions. Generally, it is preferred that the binder not decompose or lose its structural integrity at 200°F (90°C) for 30 seconds, and more preferred that it not decompose or lose its structural integrity at 300°F (149°C) for 30 seconds.

Optionally, these polymers may be used in combination of two or more thereof. Such a polymer is used in an amount sufficient to carry the components dispersed therein, that is, within the effective range of the action as the binder. The effective range can be appropriately determined by one skilled in the art.

Dry Silver Formulations

The formulation for the photothermographic emulsion layer can be prepared by dissolving and dispersing the binder, the photosensitive silver halide, the non-photosensitive source of reducible silver, the reducing agent for the non-photosensitive reducible silver source (as, for example, the optional leuco dye), the thiosulfonate ester and optional additives, in an inert organic solvent, such as, for example, toluene, 2-butanone, or tetrahydrofuran.

The use of "toners" or derivatives thereof which improve the image is highly desirable, but is not essential to the element. Toners may be present in amounts of from 0.01 to 10 percent by weight of the emulsion layer, preferably from 0.1 to 10 percent by weight. Toners are well known materials in the photothermographic art as shown in U.S. Patent Nos. 3,080,254; 3,847,612; and 4,123,282.

Examples of toners include phthalimide and N-hydroxyphthalimide; cyclic imides such as succinimide, pyrazoline-5-ones, and quinazolinone, 1-phenylurazole, 3-phenyl-2-pyrazoline-5-one, quinazoline and 2,4-thiazolidinedione; naphthalimides such as N-hydroxy-1,8-naphthalimide; cobalt complexes such as cobaltic hexamine trifluoroacetate; mercaptans as illustrated by 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole and 2,5-dimercapto-1,3,4-thiadiazole; N-(aminomethyl)aryldicarboximides, e.g. (N,N-dimethylaminomethyl)-phthalimide, and N-(dimethylaminomethyl)-naphthalene-2,3-dicarboximide; and a combination of blocked pyrazoles, isothiuronium derivatives and certain photobleach agents, e.g., a combination of N,N'-hexamethylene-bis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis(isothiuronium)trifluoroacetate and 2-(tribromomethylsulfonyl benzothiazole); and merocyanine dyes such as 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)-1-methyl-ethylidene]-2-thio-2,4-*o*-azolidinedione; phthalazinone, phthalazinone derivatives or metal salts or these derivatives such as 4-(1-naphthyl)-phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione; a combination of phthalazine plus one or more phthalic acid derivatives, e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride; quinazolinediones, benzoxazine or naphthoxazine derivatives; rhodium complexes functioning not only as tone modifiers but also as sources of halide ion for silver halide formation in situ, such as ammonium hexachlororhodate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodate (III); inorganic peroxides and persulfates, e.g., ammonium peroxydisulfate and hydrogen peroxide; benzoxazine-2,4-diones such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidines and asym-triazines, e.g., 2,4-dihydroxypyrimidine, 2-hydroxy-4-aminopyrimidine, and azauracil, and tetrazapentalene derivatives, e.g., 3,6-dimercapto-1,4-diphenyl-*1H,4H*-2,3a,5,6a-tetrazapentalene, and 1,4-di(*o*-chlorophenyl)-3,6-dimercapto-*1H,4H*-2,3a,5,6a-tetrazapentalene.

Photothermographic emulsions used in this invention may be further protected against the additional production of fog and can be stabilized against loss of sensitivity during keeping. While not necessary for the practice of the invention, it may be advantageous to add mercury (II) salts to the emulsion layer(s) as an antifoggant. Preferred mercury (II) salts for this purpose are mercuric acetate and mercuric bromide.

Additional antifoggants and stabilizers may be used in combination with the thiosulfonate esters of this invention. Suitable antifoggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in U.S. Patent Nos. 2,131,038 and U.S. Patent No. 2,694,716; the azaindenes described in U.S. Patent Nos. 2,886,437 and 2,444,605; the mercury salts described in U.S. Patent No. 2,728,663; the urazoles described in U.S. Patent No. 3,287,135; the sulfocatechols described in U.S. Patent No. 3,235,652; the oximes described in British Patent No. 623,448; the polyvalent metal salts described in U.S. Patent No. 2,839,405; the thiuronium salts described in U.S. Patent No. 3,220,839; and palladium, platinum and gold salts described in U.S. Patent Nos. 2,566,263 and 2,597,915.

Emulsions used in the invention may contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in U.S. Patent No. 2,960,404; fatty acids or esters such as those described in U.S. Patent Nos. 2,588,765 and 3,121,060; and silicone resins such as those described in British Patent No. 955,061.

The photothermographic elements of the present invention may include image dye stabilizers. Such image dye stabilizers are illustrated by U.K. Patent No. 1,326,889; and U.S. Patent Nos. 3,432,300; 3,698,909; 3,574,627; 3,573,050; 3,764,337; and 4,042,394.

Photothermographic elements containing stabilized emulsion layers according to the present invention can be used in photographic elements which contain light-absorbing materials and filter dyes such as those described in U.S. Patent Nos. 3,253,921; 2,274,782; 2,527,583 and 2,956,879. If desired, the dyes can be mordanted, for example, as described in U.S. Patent No. 3,282,699.

Photothermographic elements containing emulsion layers described herein may contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in U.S. Patent Nos. 2,992,101 and 2,701,245.

Emulsions in accordance with this invention may be used in photothermographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk, U.S. Patent Nos. 2,861,056, and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Patent No. 3,428,451.

Photothermographic Constructions

The photothermographic dry silver emulsions of this invention may be constructed of one or more layers on a substrate. Single layer constructions should contain the silver source material, the silver halide, the developer, and binder as well as optional materials such as toners, coating aids, and other adjuvants. Two-layer constructions should contain the silver source and silver halide in one emulsion layer (usually the layer adjacent to the substrate) and some of the other ingredients in the second layer or both layers, although two layer constructions comprising a single emulsion layer coating containing all the ingredients and a protective topcoat are envisioned. Multicolor photothermographic dry silver constructions may contain sets of these bilayers for each color or they may contain all ingredients within a single layer as described in U.S. Patent No. 4,708,928. In the case of multilayer, multicolor photothermographic elements, the various emulsion layers are generally maintained distinct from each other by the use of functional or non-functional barrier layers between the various photosensitive layers as described in U.S. Patent No. 4,460,681.

Photothermographic emulsions used in this invention can be coated by various coating procedures including, wire wound rod coating, dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in U.S. Patent No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in U.S. Patent No. 2,761,791 and British Patent No. 837,095. Typical wet thickness of the emulsion layer can range from about 10 to about 100 micrometers (μm), and the layer can be dried in forced air at temperatures ranging from 20°C to 100°C. It is preferred that the thickness of the layer be selected to provide maximum image densities greater than 0.2, and more preferably in the range 0.5 to 2.5, as measured by a MacBeth Color Densitometer Model TD 504 using the color filter complementary to the dye color.

Additionally, it may be desirable in some instances to coat different emulsion layers on both sides of a transparent substrate, especially when it is desirable to isolate the imaging chemistries of the different emulsion layers.

Barrier layers, preferably comprising a polymeric material, may also be present in the photothermographic element of the present invention. Polymers for the material of the barrier layer can be selected from natural and synthetic polymers such as gelatin, polyvinyl alcohols, polyacrylic acids, sulfonated polystyrene, and the like. The polymers can optionally be blended with barrier aids such as silica.

Alternatively, the formulation may be spray-dried or encapsulated to produce solid particles, which can then be redispersed in a second, possibly different, binder and then coated onto the support.

The formulation for the emulsion layer can also include coating aids such as fluoroaliphatic polyesters.

The substrate with backside resistive heating layer may also be used in color photothermographic imaging systems such as disclosed in U.S. Patent Nos. 4,460,681 and 4,374,921.

Development conditions will vary, depending on the construction used, but will typically involve heating the imagewise exposed material at a suitably elevated temperature, e.g. from about 80°C to about 250°C., preferably from about 120°C to about 200°C., for a sufficient period of time, generally from 1 second to 2 minutes.

In some methods, the development is carried out in two steps. Thermal development takes place at a higher temperature, e.g. about 150°C for about 10 seconds, followed by thermal diffusion at a lower temperature, e.g. 80°C, in the presence of a transfer solvent. The second heating step at the lower temperature prevents further development and allows the dyes that are already formed to diffuse out of the emulsion layer to the receptor layer.

The support

Photothermographic emulsions used in the invention can be coated on a wide variety of supports. The support or substrate can be selected from a wide range of materials depending on the imaging requirement. Substrates may be transparent or opaque. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related 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 α-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. Preferred polymeric materials for the support include polymers having good heat stability, such as polyesters. A particularly preferred polyester is poly(ethylene terephthalate).

The image-Receiving Layer

The photothermographic element may further comprise an image-receiving layer. Images derived from the photothermographic elements employing compounds capable of being oxidized to form or release a dye, as for example, leuco dyes are typically transferred to an image-receiving layer.

When the reactants and reaction products of photothermographic systems that contain compounds capable of being oxidized to form or release a dye remain in contact after imaging, several problems can result. For example, thermal development often forms turbid and hazy color images because of dye contamination of the reduced metallic silver image on the exposed area of the emulsion. In addition, the resulting prints tend to develop color in unimaged background areas. This "background stain" is caused by slow reaction between the dye-forming or dye-releasing compound and reducing agent during storage. It is therefore desirable to transfer the dye formed upon imaging to a receptor, or image-receiving layer.

When used, the image-receiving layer can be any flexible or rigid, transparent layer made of thermoplastic polymer. The image-receiving layer preferably has a thickness of at least 0.1 micrometer (0.1 μm), more preferably from about 1 to about 10 micrometers, and a glass transition temperature of from about 20°C to about 200°C. In the present invention, any thermoplastic polymer or combination of polymers can be used, provided the polymer is capable of absorbing and fixing the dye. Because the polymer acts as a dye mordant, no additional fixing agents are required. Thermoplastic polymers that can be used to prepare the image-receiving layer include polyesters, such as poly(ethylene terephthalates); polyolefins, such as polyethylene; cellulosics, such as cellulose acetate, cellulose butyrate, cellulose propionate; polystyrene; poly(vinyl chloride); poly(vinylidine chloride); poly(vinyl acetate); copolymer of vinylchloride-vinylacetate; copolymer of vinylidene chloride-acrylonitrile; copolymer of styreneacrylonitrile; and the like.

The optical density of the dye image and even the actual color of the dye image in the image-receiving layer is very much dependent on the characteristics of the polymer of the image-receiving layer, which acts as a dye mordant, and, as such, is capable of absorbing and fixing the dyes. A dye image having a reflection optical density in the range of from 0.3 to 3.5 (preferably from 1.5 to 3.5) or a transmission optical density in the range of from 0.2 to 2.5 (preferably from 1.0 to 2.5) can be obtained with the present invention.

The image-receiving layer can be formed by dissolving at least one thermoplastic polymer in an organic solvent (e.g., 2-butanone, acetone, tetrahydrofuran) and applying the resulting solution to a support base or substrate by various coating methods known in the art, such as curtain coating, extrusion coating, dip coating, air-knife coating, hopper coating, and any other coating method used for coating solutions. After the solution is coated, the image-receiving layer is dried (e.g., in an oven) to drive off the solvent. The image-receiving layer may be strippably adhered to the photothermographic element. Strippable image-receiving layers are described in U.S. Patent No. 4,594,307, incorporated herein by reference.

Selection of the binder and solvent to be used in preparing the emulsion layer significantly affects the strippability of the image-receiving layer from the photosensitive element. Preferably, the binder for the image-receiving layer is impermeable to the solvent used for coating the emulsion layer and is incompatible with the binder used for the emulsion layer. The selection of the preferred binders and solvents results in weak adhesion between the emulsion layer and the image-receiving layer and promotes good strippability of the emulsion layer.

The photothermographic element can also include coating additives to improve the strippability of the emulsion layer. For example, fluoroaliphatic polyesters dissolved in ethyl acetate can be added in an amount of from about 0.02 to about 0.5 weight percent of the emulsion layer, preferably from about 0.1 to about 0.3 weight percent. A representative example of such a fluoroaliphatic polyester is "Fluorad™ FC 431", (a fluorinated surfactant, available from 3M Company, St. Paul, MN). Alternatively, a coating additive can be added to the image-receiving layer in the same weight range to enhance strippability. No solvents need to be used in the stripping process. The strippable layer preferably has a delaminating resistance of 1 to 50 g/cm and a tensile strength at break greater than, preferably at least two times greater than, its delaminating resistance.

Preferably, the image-receiving layer is adjacent to the emulsion layer to facilitate transfer of the dye that forms after the imagewise exposed emulsion layer is subjected to thermal development, for example, in a heated shoe-and-roller type heat processor.

Multi-layer constructions containing blue-sensitive emulsions containing a yellow leuco dye of this invention may be overcoated with green-sensitive emulsions containing a magenta leuco dye of this invention. These layers may in turn be overcoated with a red-sensitive emulsion layer containing a cyan leuco dye. Imaging and heating form the yellow, magenta, and cyan images in an imagewise fashion. The dyes so formed may migrate to an image-receiving layer. The image-receiving layer may be a permanent part of the construction or may be removable "i.e., strippably adhered" and subsequently peeled from the construction. Color-forming layers may be maintained distinct from each other by the use of functional or non-functional barrier layers between the various photosensitive layers as described in U.S. Patent No. 4,460,681. False color address, such as that shown in U.S. Patent No. 4,619,892, may also be used rather than blue-yellow, green-magenta, or red-cyan relationships between sensitivity and dye formation.

In another embodiment, the colored dye released in the emulsion layer can be transferred onto a separately coated image-receiving sheet by placing the exposed emulsion layer in intimate face-to-face contact with the image-receiving sheet and heating the resulting composite construction. Good results can be achieved in this second embodiment when the layers are in uniform contact for a period of time of from 0.5 to 300 seconds at a temperature of from about 80°C to about 220°C.

Multi-color images can be prepared by superimposing in register, imaged image-receiving layers as prepared above. The polymers of the individual imaged image-receiving layers must be sufficiently adherent to provide useful multi-color reproduction on a single substrate.

Objects and advantages of this invention will now be illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All percentages are by weight unless otherwise indicated.

EXAMPLES

Starting materials used in the following examples were readily available from commercial sources such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. All compounds were characterized by their ^1H and ^{13}C NMR and IR spectra. The following additional terms and materials were used.

Acryloid™ B-21 is a poly(methyl methacrylate) available from Rohm and Haas, Philadelphia, PA.

Butvar™ B-76 and Butvar™ B-79 are poly(vinyl butyral) resins available from Monsanto Company, St. Louis, MO.

CAO-5™ is an antioxidant available from Rohm and Haas Co., Philadelphia, PA.

CA 394-60S and CA 398-6 are cellulose acetate resins, available from Eastman Kodak Co.

CAB 171-15S is a cellulose acetate butyrate available from Eastman Kodak Co.

CBBA is 2-(4-chlorobenzoyl)benzoic acid.

FC-431 is a fluorinated polymeric surfactant available from 3M Company.

Gelva V 15 is a poly(vinyl acetate) available from Monsanto.

MEK is methyl ethyl ketone (2-butanone).

MMBI is 4-methyl-2-mercaptobenzimidazole.

Permanax WSO is 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane [CAS RN=7292-14-0] and is available from Vulnax International, Ltd. It is also known as Nonox.

PHP is pyridinium hydrobromide perbromide.

PHZ is phthalazine.

PET is poly(ethylene terephthalate).

THDI is Desmodur™ N-100, a biuretized hexamethylene diisocyanate available from Mobay Chemical Co.

Evaluation of Thiosulfonate Esters

Densitometry measurements were made on a custom-built computer-scanned densitometer and are believed to be comparable to measurements obtainable from commercially available densitometers.

Preparation of Thiosulfonate Esters

Preparation of S-benzyl-4-methoxybenzenethiosulfonate (Thiosulfonate Ester H): 4-Methoxybenzenesulfonylhydrazide (6.0 g, 29.7 mmol, available from Lancaster Chemical Co.) was stirred with 7.0 g pyridine in 90 mL methylene chloride under nitrogen. In a separate flask, sulfuryl chloride (6.0 g) was added in a slow stream to an ice cooled solution of dibenzyl disulfide (11.0 g) in 30 mL methylene chloride with two drops of triethylamine. The resulting sulfenyl chloride solution was stirred for 15 minutes, then the hydrazide solution was added dropwise over two hours. The solution was washed twice with water, once with 0.1N HCl, and once with sodium bicarbonate solution, and the solvent was removed under vacuum. The resulting oil was subjected to flash chromatography on silica gel with 15% ethyl acetate in hexane, and the desired material further purified by recrystallization from ether/hexane. 4.07 g (47%) of S-benzyl-4-methoxybenzenethiosulfonate were obtained.

Thiosulfonate esters B, C, F, G, I, J, and K (Table 1) were synthesized in a manner analogous to that described above using the appropriate hydrazide and the appropriate sulfuryl chloride. Appropriate hydrazides are available from Lancaster Chemical Co.

Thiosulfonate esters A and E (Table 1) were obtained from Aldrich Chemical Company. Thiosulfonate ester D (Table 1) was obtained from Fluka Chemical Company.

Example 1

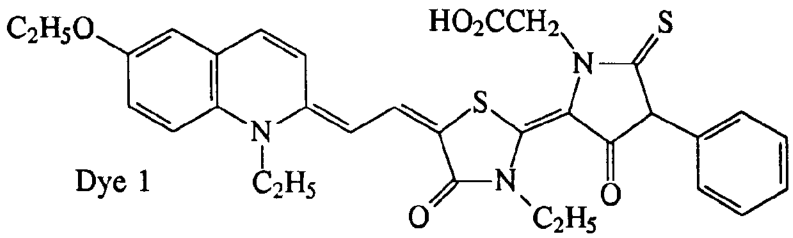
This example demonstrates the use of thiosulfonate esters as antifoggants and to improve shelf-life stability.

A 13.6 wt% dispersion of silver behenate/behenic acid half soap was made in acetone by homogenization. To 201.5 g of this dispersion was added ButvarT™ B-76 (1.12 g) and the mixture was stirred for an additional 30 minutes. Three 1.00 ml aliquots of a solution of 10.0 g zinc bromide in 100.0 ml methanol were added sequentially with stirring for 10 minutes after each addition. Toluene (66.66 g) was added and the mixture was stirred for an additional 15 minutes. A solution (2.40 ml) containing 4.00 g of pyridine in 100 ml 2-butanone was added with continued stirring for 15 minutes. The mixture was allowed to stand for 4 hours.

To the mixture was added Butvar™ B-76 (31.75 g) followed by stirring for 30 minutes. A solution of 2.73 ml of 1.33 g N-bromo-succinimide in 100 ml methanol was then added. CAO-5™ (4.20 g) was added with stirring for 5 minutes. Acryloid B-21™ (27.22 g) was added with stirring for 5 minutes.

The following steps were carried under green safelights.

A 6.00 ml aliquot of a solution of 0.03 g Dye 1, 25.00 ml methanol, and 75 ml toluene was added to the above mixture and the mixture was stirred for 5 minutes. The viscosity of the resultant solution should be between 180 and 220 centipoise. If it was greater than 220 centipoise, acetone was added to bring the viscosity into the appropriate range. Dye 1 is described in U.S. Patent No. 3,719,495 and has the following structure:



The silver containing formulation was coated at 4.4 mils (112 μm) wet thickness (to give a dry coating weight of 1.25 g/ft^2) onto paper and dried at 180°F for one minute.

A topcoat solution was coated onto the coated samples prepared above. A master batch of topcoat solution was prepared by mixing: 164.728 g acetone, 82.350 g 2-butanone, 33.300 g methanol, 13.500 g of Eastman CA 398-6, 1.542 g phthalazine, 1.068 g 4-methylphthalic acid, 0.636 g tetrachlorophthalic acid, and 0.800 g tetrachlorophthalic anhydride. Each thiosulfonate ester was added to 7.00 g of the master bach topcoat solution before coating. The compounds were tested in the dry silver paper topcoat formulation at concentration levels of 4.0, 0.8, and 0.2 mmol/100.00 g of topcoat master batch.

The topcoat formulation was coated at 2.8 mils (7 μm), wet thickness, on top of the silver emulsion and dried for 3 minutes at 70°C to provide a dry coating weight of 0.24 g/ft^2.

The coated paper was imaged by exposing with an Eastman Kodak #101 sensitometer using a tungsten light source. After exposure, the strips (1 inch x 7 inches) were processed at 250°F (121°C) by heating for 6 seconds in a hot roll processor. The images obtained were evaluated by a computer densitometer. Sensitometeric results include D_{min}, D_{max}, and speed. In these samples, the lower the speed number, the "faster" the paper. The sensitometric results, shown below, demonstrate that the thiosulfonate esters of this invention are as good or better in providing low D_{min} than a control sample containing no thiosulfonate ester (labeled 0.00 mmol).

Sensitometric Results

Sample & Amount (per 100g of Top Coat)	D_{min}	D_{max}	Speed*
Thiosulfonate Ester A			
control (0.0 mmol)	0.522	1.851	n/m[1]
(4.0 mmol)	0.144	1.724	0.95
(0.8 mmol)	0.234	1.722	1.01
(0.2 mmol)	0.235	1.726	0.97
Thiosulfonate Ester E			
control (0.0 mmol)	0.482	1.843	n/m[1]
(4.0 mmol)	0.144	1.72	0.95
(0.8 mmol)	0.234	1.722	1.01
Thiosulfonate Ester D			
control (0.0 mmol)	0.522	1.851	n/m[1]
(4.0 mmol)	0.151	1.732	1.11
(0.8 mmol)	0.361	1.732	1.04
Thiosulfonate Ester H			
control (0.0 mmol)	0.351	1.70	0.84
(4.0 mmol)	0.163	1.689	0.87
(0.8 mmol)	0.26	1.71	0.85
(0.2 mmol)	0.353	1.69	0.82
Thiosulfonate Ester J			
control (0.0 mmol)	0.351	1.70	0.84
(4.0 mmol)	0.338	1.70	0.74
(0.8 mmol)	0.221	1.70	0.73
(0.2 mmol)	0.202	1.70	0.76

*Log exposure corresponding to density of 0.6 above D_{min}

[1] n/m = not measured

Improvement in D_{min} for aged coatings was shown by reprocessing samples after 2 months of natural aging. In most cases, the compounds of this invention not only provided lower initial fog levels than a control with no additives, but on aging showed continued low fog and in some cases a substantial decrease in fog. The samples were processed at 120°C for 10 seconds with a hot roll processor.

Shelf-Aged Response

Sample & Amount[1]		D_{min} initial	D_{min} 2 months	D_{max} initial	D_{max} 2 months
Control	0.00	0.55	0.57	1.85	1.82
Thiosulfonate Ester A					
	4.0	0.25	0.29	1.87	1.83
	0.8	0.61	0.20	1.84	1.82
	0.2	0.42	0.19	1.85	1.81
Thiosulfonate Ester E					
	4.0	0.19	0.15	1.84	1.80
	0.8	0.42	0.15	1.87	1.82
	0.2	0.14	0.15	1.81	1.77
Thiosulfonate Ester F					
	4.0	0.15	0.16	1.85	1.85
	0.8	0.27	0.21	1.84	1.85
	0.2	0.45	0.45	1.83	1.83

[1] Amounts are mmol/100 g of top-coat

Example 2

This example demonstrates the use of thiosulfonate esters as antifoggants.

A silver halide-silver behenate dry soap was prepared by the procedures described in U.S. Patent No. 3,839,049. The total silver content of the dry soap comprised 9% silver halide and 91% silver behenate. The silver halide was a 0.055 micron silver bromoiodide emulsion with 2% iodide.

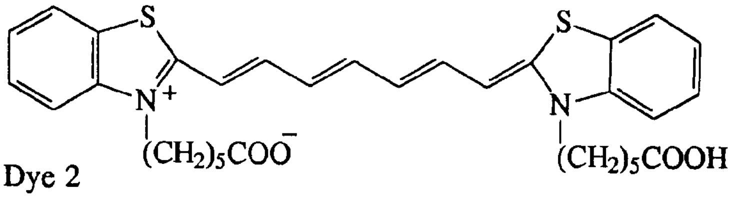
The following steps were carried out under green safelights.

A photothermographic emulsion was prepared by homogenizing 300 g of the silver halide-silver behenate dry soap described above with 525 g toluene, 1675 g 2-butanone, and 50 g of Butvar™ B-76.

The homogenized photothermographic emulsion (510 g) was cooled to 55°F with stirring. A solution of PHP (0.63 g) and methanol (3.16 g) was added and stirred for 2 hours. The addition of 3.25 ml of a calcium bromide solution (1 g $CaBr_2$ in 10 ml of methanol) was followed by 30 minutes of stirring. An additional 108.5 g of Butvar™ B-76 was added and stirred for 20 minutes. The mixture was allowed to stand for 16 hours.

The following steps were carried out under IR safelights.

To the stirring mixture was added a mixture of 0.37 g of methylmercaptobenzimidazole (MMBI), 4.19 g of 2-(4-chlorobenzoyl)benzoic acid (CBBA), and 0.07 g of Dye 2 in 25.10 g of methanol. Dye 2 has the following structure:



Dye 2

This mixture was allowed to stir for 20 minutes at which time 15.9 g of Permanax WSO was added followed by 1.00 g of THDI in 7.0 g 2-butanone.

The silver trip formulation was coated at 4.3 mils wet thickness onto 3 mil polyester base by means of a knife coater and dried for four minutes at 175°F to give a dry coating weight of 1.97 g/ft^2.

A master batch of topcoat solution was coated onto the coated samples prepared above. A master batch of topcoat solution was prepared by mixing: 510 g 2-butanone, 60.00 g methanol, 48.00 g CAB 171-15S cellulose acetate butyrate, 1.08 g tetrachlorophthalic acid, 1.62 g 4-methylphthalic acid, and 3.30 g phthalazine.

Each thiosulfonate ester was added to 7.00 g of master batch topcoat solution before coating. The compounds were tested in the topcoat formulation at three concentration levels. The topcoat formulation was coated at 2.8 mils, wet thickness, on top of the silver emulsion and dried for 3 minutes at 70°C to provide a dry coating weight of 0.24 g/ft^2.

The coated film was imaged by exposing with a laser sensitometer with an IR light source emitting at 811 nm. After exposure, the strips (1 inch x 7 inches; 2.5 cm x 17.8 cm) were processed at 250°F (121°C) by heating for 15 seconds in a hot roll processor. The images obtained were evaluated by a computer densitometer. Sensitometeric results include D_{min}, D_{max}, and speed. In these samples, the higher the speed number, the "faster" the film. The sensitometric results, shown below, demonstrate a reduction in fog (lower D_{min}) without detrimental effect on D_{max} or speed. The control sample contains no thiosulfonate esters and is labeled 0.00 mmol.

Sensitometric Results

Amount (per 100g of Topcoat)	D_{min}	D_{max}	**Speed**
Thiosulfonate Ester I			
control (0.0 mmol)	0.32	4.16	1.44
(4.0 mmol)	0.27	4.14	1.59
(0.8 mmol)	0.27	4.28	1.56
(0.2 mmol)	0.27	4.22	1.55
Thiosulfonate Ester H			
control (0.0 mmol)	0.32	4.16	1.44
(4.0 mmol)	0.24	4.07	1.57
(0.8 mmol)	0.25	4.21	1.56
(0.2 mmol)	0.27	4.13	1.57

Example 3

This example demonstrates the use of thiosulfonate esters as post-processing stabilizers.

A clear polyester base was coated by the procedure described in Example 2 with an emulsion of the following composition:

Homogenized photothermographic emulsion (prepared as described in Example 2)	73.441%
PHP	0.083%
in Methanol	0.440%
$CaBr_2$	0.063%
in Methanol	0.440%
Butvar™ B-79	13.738%
4-methyl-2-mercaptobenzimidazole	0.039%
CBBA	0.460%
Dye-2	0.008%
in Methanol	3.060%
Permanax WSO	3.030%
2-(tribromomethanesulfonyl)thiadiazole	0.300%
in 2-butanone	4.709%
THDI	0.130%
in 2-butanone	0.060%
Total	100%

The silver-containing layer was coated at a dry weight of 2.15 g/ft^2.

A master batch of topcoat solution was prepared by mixing: 149.5 g acetone, 35 g ethanol, 8.78 g CA 394-60S cellulose acetate, 1.98 g Acryloid™ B-21, 1.38 g Gelva V 15, 1.42 g phthalazine, 0.74 g 4-methylphthalic acid, 0.46 g tetrachlorophthalic acid, 0.64 g tetrachlorophthalic anhydride, and 0.08 g FC-431. Thiosulfonate Ester I was evaluated by adding it to 20 g of master batch of topcoat solution at 0.5 mmol. The topcoat was coated at 4 mil (101.6 μm) wet thickness over the pre-coated silver layer and dried at 140°F for 3 minutes.

Once coated, samples in quadruplicate were exposed using a 780 nm laser and processed for 10 seconds at 260°F. Testing for post-processing stability testing was done under two sets of conditions:

A) in an environment chamber at 1200 foot-candles (daylight fluorescent bulbs), 113°F, 20% relative humidity for 2 hours, and

B) at 100 foot-candles, 70°F, 80% relative humidity for 24 hours.

ΔD_{min} is a measure of the post-processing stability of the sample. As shown below, Thiosulfonate Ester I gave a substantial improvement in post-processing stability (ΔD_{min}) under both test conditions with no detriment to inital sensitometric performance.

Sample and Amount	Initial D_{min}	Initial D_{max}	ΔD_{min}A	ΔD_{min}B
Control	0.221	3.248	0.598	0.017
Thiosulfonate Ester I (0.5 mmol)	0.220	3.308	0.400	0.009

The invention has been described with reference to various specific and preferred embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the spirit and scope of the invention as claimed.

Claims

1. A heat-developable, photothermographic element comprising a support bearing at least one photosensitive, image-forming photothermographic emulsion layer comprising:
   (a) a photosensitive silver halide;

(b) a non-photosensitive, reducible silver source;
(c) a reducing agent for the non-photosensitive, reducible silver source;
(d) a binder; and
(e) a thiosulfonate ester of the formula:

$$\mathbf{R^1\text{-}SO_2\text{-}SR^2}$$

wherein:

R¹ and **R²** independently represent an alkyl group, an aryl group, an aralkyl group, an alkaryl group, or an alkenyl group.

2. The element of Claim 1 wherein R^1 and R^2 independently represent a C_1 to C_{12} aryl, alkyl, aralkyl, alkaryl, or alkenyl group.

3. The element of Claim 2 wherein R^1 and R^2 independently represent a C_1 to C_6 aryl, alkyl, aralkyl, alkaryl, or alkenyl group.

4. The element of Claim 1 wherein said non-photosensitive, reducible silver source is a silver salt of a C_{10}-C_{30} carboxylic acid.

5. The element of Claim 1 wherein said non-photosensitive, reducible silver source comprises silver behenate.

6. The element of Claim 1 wherein said reducing agent for silver ion comprises a leuco dye.

7. The element of Claim 1 wherein said reducing agent for silver ion is a hindered phenol.

8. The element of Claim 1 wherein said photosensitive silver halide comprises silver bromide, silver chloride, silver iodide, or mixtures thereof.

9. The element of Claim 1 wherein said binder is hydrophobic.

10. The element of Claim 1 wherein said binder is hydrophilic.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94402613.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
D,A	US - A - 5 061 614 (TAKADA et al.) * Claims 1,10,11 * --	1-3	G 03 C 1/498 G 03 C 1/34 G 03 C 1/37
D,A	US - A - 4 307 187 (IKENOUE et al.) * Abstract * --	1	
A	EP - A - 0 497 053 (MINNESOTA MINING AND MANUFACTURING COMPANY) * Claims 1-6 * --	1,4,8	
A	EP - A - 0 535 400 (MINNESOTA MINING AND MANUFACTURING COMPANY) * Claims * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.6)
			G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	30-12-1994	WOLF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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