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(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center, P.O. Box 33427
St. Paul, Minnesota 55133-3427(US)

(72) Inventor: **Philip, James B., Jr., c/o Minnesota Mining and**
Manufacturing Co., 2501 Hudson Road, PO Box 33427
St. Paul, Minnesota 55133-3427(US)
Inventor: **Featherstone, Gary L., c/o Minnesota Mining and**
Manufacturing Co., 2501 Hudson Road, PO Box 33427
St. Paul, Minnesota 55133-3427(US)

(74) Representative: **VOSSIUS & PARTNER**
Postfach 86 07 67
D-81634 München (DE)

(54) Photothermographic elements.

(57) Mercapto substituted heteroaromatic compounds have been found to be supersensitizers for infrared sensitized photothermographic imaging elements. These elements comprise a photosensitive silver halide, silver salt oxidizing agent and reducing agent for silver ion in a binder.

Rank Xerox (UK) Business Services
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The present invention relates to materials which produce an increase in infrared sensitivity when added to infrared sensitized photothermographic imaging elements. These elements comprise a photosensitive silver halide, silver salt oxidising agent, infrared sensitizing dye, and reducing agent for silver ion in a binder. The infrared supersensitizers of the present invention comprise mercapto substituted heteroaromatic compounds.

Silver halide photothermographic imaging materials, often referred to as "dry silver" compositions because no liquid development is necessary to produce the final image, have been known in the art for many years. These imaging materials basically comprise a light insensitive, reducible silver source, a light sensitive material which generates silver when irradiated, and a reducing agent for the silver source. The light sensitive material is generally photographic silver halide which must be in catalytic proximity to the light insensitive silver source. Catalytic proximity is 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 silver source by the reducing agent. It has been long understood that silver is a catalyst for the reduction of silver ions and the silver-generating light sensitive silver halide catalyst progenitor may be placed into catalytic proximity with the silver source in a number of different fashions, such as partial metathesis of the silver source with a halogen-containing source (e.g., U.S. Pat. No. 3,457,075), coprecipitation of the silver halide and silver source material (e.g., U.S. Pat. No. 3,839,049), and any other method which intimately associates the silver halide and the silver source.

Silver halide photothermographic imaging materials can undergo spectral sensitization which enables the silver halide grains to benefit from radiation in regions of the electromagnetic spectrum where the silver halide would ordinarily not absorb. Dyes which absorb radiation and can transfer energy to the grains to help in the photoreduction of silver ions to clusters of silver metal are conventionally used to effect spectral sensitization. Infrared absorbing dyes are required to sensitize silver halide into the infrared region (750 nm to 1300 nm) and are described by Mees in The Theory of the Photographic Process, third edition (MacMillan, 1966), pages 198-201. Problems arise since 5 or more commonly 7 carbon atoms in conjugated methine chains are necessary to sensitize to the infrared versus shorter methine chains for visible dyes. The longer methine chain of the IR dyes lead to poor sensitizing efficiency and poor stability on shelf aging. Therefore, IR sensitization is very different and often more difficult than visible sensitization.

Supersensitization has developed as a method to improve the efficiency and often the stability of infrared sensitization. The supersensitizers are used in combination with the infrared sensitizing dye. The addition of the supersensitizer, frequently in quantities ranging from an equivalent molar rate to a 100 fold molar excess of supersensitizer to dye, can increase the spectrally sensitized speed of the emulsion by more than an order of magnitude. Some supersensitizers are dyes themselves, but many others do not absorb radiation in significant amounts in the visible portion of the electromagnetic spectrum. Therefore, the effect of the supersensitizers on spectral sensitization is not clearly dependent on the ability of compounds to absorb radiation in the visible or infrared portion of the spectrum. Certain supersensitizers are sometimes more effective with one sensitizing dye class versus a second dye class. Due to supersensitizer-dye specificity and the large sensitivity increases generated by supersensitizers, an expanded selection of supersensitizers is desired.

Supersensitization has been used effectively in silver halide photographic systems to minimize the inefficiency of infrared sensitizing dyes. The supersensitizers have included diazenyl and triazenyl stilbenes as described in U.S. Pat. No. 2,875,058 and Great Britain Patent No. 2,140,928, benzotriazoles as described in U.S. Pat. No. 4,030,927 and 4,105,454, thioureas as described in U.S. Pat. No. 4,607,006, U.S. Pat. No. 3,458,318 and U.S. Pat. No. 3,954,481, thiatriazoles as described in U.S. Pat No. 4,780,404 and 4,914,015, tetraazaindenes as described in U.S. Pat. No. 3,695,888 and certain heterocyclic salts as described in U.S. Pat. No. 4,596,767.

Mercapto aromatic compounds have also been used in silver halide photographic elements as infrared supersensitizers and include mercapto-substituted oxazine, oxazole, thiazole, thiadiazole, imidazole or tetrazole as described in U.S. Pat. No. 3,457,078 and mercapto substituted triazoles as described in U.S. Pat. No. 4,910,129.

Infrared supersensitization in photothermographic systems has been previously demonstrated with metal chelating agents in U.S. Pat. No. 4,873,184 and with pyridine, pyrimidine and triazine derivatives in J6 3,023,145A. However, due to dye specificity and the dramatic benefits created by supersensitization, more chemical classes of supersensitizers are desirable.

The photothermographic, infrared supersensitizers of the present invention are aromatic, heterocyclic mercapto or disulphide compounds. These compounds have been used extensively in photothermographic elements. Mercapto heterocycles have appeared as antifoggants and development restrainers in U.S. Pat.

Nos. 4,639,408; 4,451,561; 3,961,963; 4,678,735 and 4,837,141 as post print stabilizers in U.S. Pat. Nos. 3,617,289 and 3,997,346 in the preparation of silver soaps as in U.S. Pat. Nos. 4,138,265; 4,728,600 and 4,859,580 as toners in U.S. Pat. No. 4,201,582 and as speed enhancers in U.S. Pat. No. 3,359,105 for an N-vinyl carbazole and an organic halogen dye-forming, thermal imaging system.

U.S. Patent No. 4,968,597 describes the use of mercapto substituted heteroaromatic compounds in a blue sensitive silver halide layer of a color, heat-developable material. No supersensitization was observed in systems similar to those of the present invention which had been spectrally sensitized to the blue, green, or red. Only in infrared sensitive systems was supersensitization noted.

U.S. Patent No. 4,245,033 describes the use of a number of classes of sulfur compounds in heat developable photosensitive compositions. That system varies from the present invention in that thioethers and nonaromatic thiols work as well as aromatic thiols. In addition, there are no infrared sensitized examples.

U.S. Patent No. 4,105,451, describes the use of mercapto-aromatic compounds in combination with a silver salt of a heterocyclic thione in a photothermographic material incorporating very high levels of silver iodide. No infrared sensitizing dyes are shown.

Photothermographic emulsions which have been spectrally sensitized to the infrared and near infrared regions of the electromagnetic spectrum are supersensitized by the addition of mercapto substituted heteroaromatic compounds.

Silver halide crystals have an inherent photosensitivity only in the ultraviolet and blue regions of the electromagnetic spectrum. In order to provide the crystals with sensitivity to other portions of the electromagnetic spectrum, dyes are used. These dyes which extend the range of sensitivity of the silver halide are generally referred to as spectral sensitizing dyes. As noted above, supersensitizers increase the efficiency of these spectral sensitizing dyes.

Traditionally, emulsions which have been spectrally sensitized to the infrared regions of the spectrum have been sensitized inefficiently. The relative sensitivities of infrared sensitized emulsions tend to be lower than the relative sensitivities of emulsions spectrally sensitized to the visible regions of the spectrum. The need for supersensitizers in the infrared is therefore considered to be generally very important.

It has been found in the present invention that heteroaromatic mercapto compounds (I) or heteroaromatic disulfide compounds (II) are effective supersensitizers for photothermographic emulsions spectrally sensitized to wavelengths longer than 750 nm (e.g. 750-1300 nm, preferably 750 to 950 nm).

Ar-SM (I)

Ar-S-S-Ar (II)

wherein M represents a hydrogen atom or an alkali metal atom,

Ar represents an aromatic ring or fused aromatic ring containing one or more of nitrogen, sulfur, oxygen, selenium or tellurium atoms. Preferably the heteroaromatic ring is benzimidazole, naphthimidazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, bensotellurazole, imidazole, oxazole, pyrazole, triazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine, pyrazine, pyridine, purine, quinoline or quinazolinone. However, other heteroaromatic rings are envisioned under the breadth of this invention.

The heteroaromatic ring may also carry substituents with examples of preferred substituents being selected from the class consisting of halogen (e.g. Br and Cl), hydroxy, amino, carboxy, alkyl (e.g. of 1 or more carbon atoms, preferably 1 to 4 carbon atoms) and alkoxy (e.g. of 1 or more carbon atoms, preferably of 1 to 4 carbon atoms).

Specific examples of mercapto substituted heteroaromatic compounds are set forth below.

M-1	2-mercaptobenzimidazole
M-2	2-mercaptobenzoxazole
M-3	2-mercaptobenzothiazole
M-4	2-mercapto-5-methylbenzimidazole
M-5	6-ethoxy-2-mercaptobenzothiazole
M-6	2,2'-Dithiobis-(benzothiazole)
M-7	3-mercapto-1,2,4-triazole
M-8	4,5-diphenyl-2-imidazolethiol
M-9	2-mercaptoimidazole
M-10	1-ethyl-2-mercaptobenzimidazole
M-11	2-mercaptoquinoline

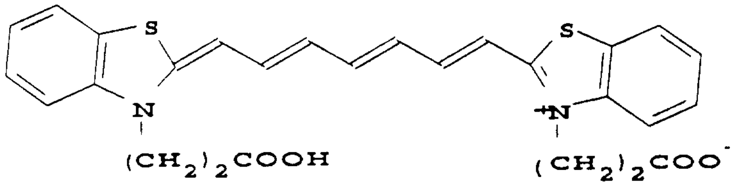
M-12	8-mercaptopurine
M-13	2-mercapto-4(3H)-quinazolinone
M-14	7-trifluoromethyl-4-quinolinethiol
M-15	2,3,5,6-tetrachloro-4-pyridinethiol
M-16	4-amino-6-hydroxy-2-mercaptopyrimidine monohydrate
M-17	2-amino-5-mercapto-1,3,4-thiadiazole
M-18	3-amino-5-mercapto-1,2,4-triazole
M-19	4-hydroxy-2-mercaptopyrimidine
M-20	2-mercaptopyrimidine
M-21	4,6-diamino-2-mercaptopyrimidine
M-22	2-mercapto-4-methylpyrimidine hydrochloride
M-23	3-mercapto-5-phenyl-1,2,4-triazole
M-24	2-mercapto-4-phenyloxazole

The supersensitizers are used in general amount of at least 0.001 moles/mole of silver in the emulsion layer. Usually the range is between 0.001 and 1.0 moles of the compound per mole of silver and preferably between 0.01 and 0.3 moles of compound per mole of silver.

Supersensitization of infrared sensitized photothermographic elements by mercapto substituted heteroaromatic compounds has been shown to be effective with a broad range of infrared sensitizing dyes. The preferred infrared dyes are tricarbocyanine dyes described in U.S. Pat. No. 4,536,473 and rigidized tricarbocyanine dyes described in U.S. Pat. No. 4,515,888 and 4,959,294. Other effective classes of infrared dyes are 4-quinoline pentamethine dyes described in U.S. Pat. No. 4,536,473, merocyanine infrared dyes and trinuclear dyes.

The infrared sensitizing dye used in the present invention is incorporated in the silver photothermographic layer in a content of 1 x 10^{-5} mole to 1 x 10^{-2} mole preferably 5 x 10^{-5} to 5 x 10^{-3} mole, per mole of total silver.

Specific examples of the infrared sensitizing dyes used in the present invention are listed below.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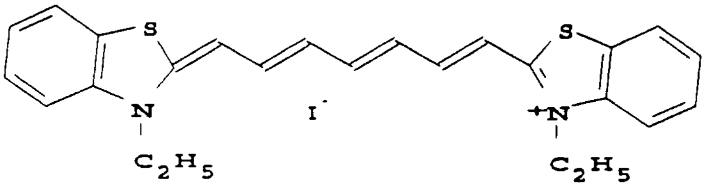
(CH2)2COOH
S
+N
(CH2)2COO-

D·1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N
C2H5
I-
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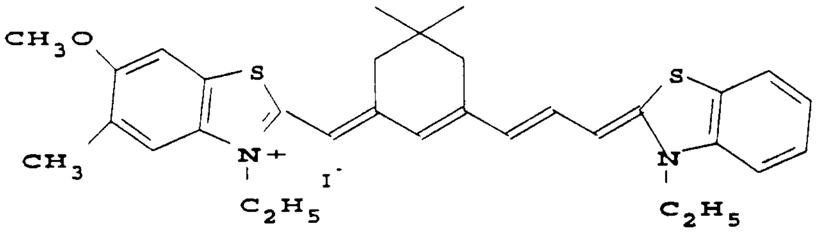
+N
C2H5

D·2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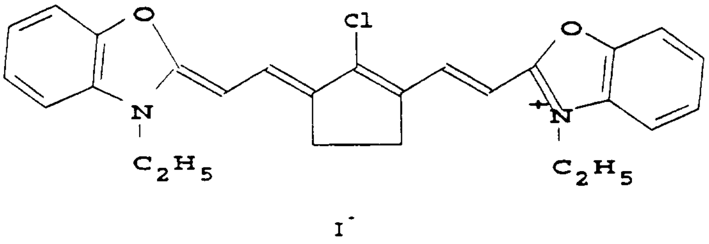
CH3
S
N+
C2H5
I-
S
N
C2H5

D·3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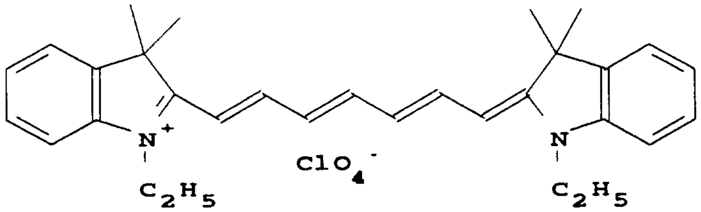
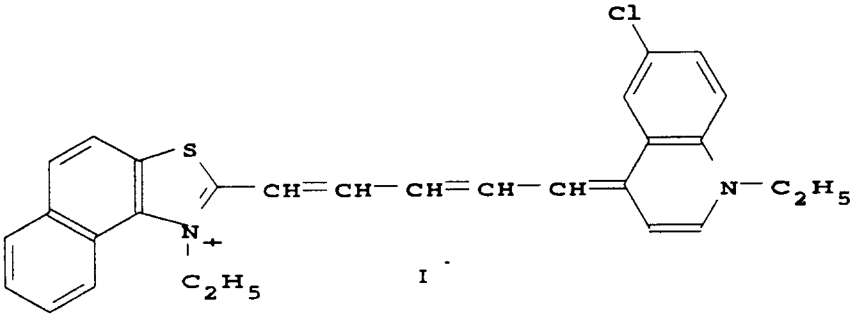
N
C2H5
Cl
O
+N
C2H5
I-

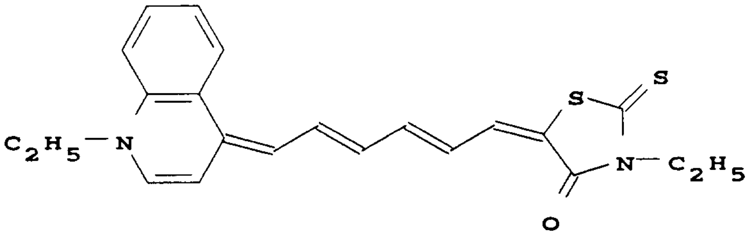
D·4



D - 5



D - 6



D - 7

Conventional silver halide photothermographic chemistry is used as the photothermographic chemistry in the system of the present invention. Such chemistry is well described in U.S. Patents 3,457,075; 3,839,049; 3,985,565; 4,022,617 and 4,460,681. These can be either black-and-white or color chemistries. Either in situ halidization (e.g., 3,457,075) or preformed silver halide sources (e.g., 3,839,049) may be used. Any of the various photothermographic media, such as full soaps, partial soaps, full salts, and the like may be used in the photothermographic chemistry.

Conventional photothermographic chemistry comprises a photosensitive silver halide catalyst, an essentially light-insensitive silver compound capable of being reduced to form a metallic silver image (e.g., silver salts, both organic or inorganic, and silver complexes, usually light sensitive silver materials), a developing agent for silver ion (a mild reducing agent for silver ion), and a binder. Color photothermographic systems additionally have a leuco dye or dye forming developer (alone or in combination with a developer for silver ion), or a color photographic coupler which would require a color photographic developer to be used as the developing agent for silver ion. Thus both negative and positive systems can be used.

In particular, the dyes listed in Japanese Kohyo National Publication No. 500352/82, published February 25, 1982 are preferred. Naphthols and arylmethyl-1-naphthols are generally preferred.

Conventional photothermographic chemistry is usually constructed as one or two layers on a substrate. Single layer constructions must contain the silver source material, the silver halide, the developer and binder as well as optional additional materials such as toners, coating aids and other adjuvants. Two-layer constructions must contain silver source and silver halide in one emulsion layer (usually the layer adjacent to the substrate) and the other ingredients in the second layer or both layers. In the present invention it is preferred to use two layer chemistry.

The silver source material, as mentioned above, ordinarily may be any material which contains a reducible source of silver ions. Silver salts or organic acids, particularly long chain (10 to 30, preferably 15 to 28 carbon atoms) fatty carboxylic acids are preferred in the practice of the present invention. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 and 10.0 are also useful in the present invention. The silver source material should constitute from about 20 to 70 percent by weight of the imaging layer. Preferably it is present as 30 to 55 percent by weight.

Suitable organic silver salts include silver salts of organic compounds having a carboxy group. Preferred 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 laurate, silver caprate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartarate, silver furoate, silver linoleate, silver butyrate and silver camphorate or mixtures thereof. Silver salts which are substituted with a halogen atom of 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 or silver p-phenylbenzoate, silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, a silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione or the like as described in U.S. Pat. No. 3,785,830, and silver salt of an aliphatic carboxylic acid containing a thioether group as described in U.S. Pat. No. 3,330,633.

Silver salts of compounds containing mercapto or thione groups and derivatives thereof can 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-(S-ethylglycolamido) benzothiazole, a silver salt of thioglycolic acid such as a silver salt of a S-alkyl thioglycolic 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-2-phenyl-4-thiopyridine, a silver salt of mercaptotriazine, a silver salt of 2-mercaptobenzoxazole, a silver salt as described in U.S. Pat. No. 4,123,274, for example, a silver salt of a 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. Pat. No. 3,301,678.

Furthermore, a silver salt of a compound containing an imino group can be used. Preferred examples of these compounds include a silver salt of benzotriazole and a derivative thereof as described in Japanese Patent Publication Nos. 30270/69 and 18146/70, for example, a silver salt of benzotriazole such as silver salt of methylbenzotriazole, such as a silver salt of a halogen substituted benzotriazole, such as a silver salt of 5-chlorobenzotriazole, . silver salt of carboimidobenzotriazole, a silver salt of 1,2,4-triazole, of 1-H-tetrazole as described in U.S. Pat. No. 4,220,709, a silver salt of imidazole and an imidazole derivative, and the like.

The light sensitive silver halide used in the present invention can be employed in a range of 0.0005 mole to 5 mole and, preferably, from 0.005 mole to 1.0 mole per mole of organic silver salt.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide, etc.

The silver halide may be added to the emulsion layer in any fashion which places it in catalytic proximity to the silver source.

The silver halide and the organic silver salt which are separately formed in a binder can be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them in a ball mill for a long period of time. Further, it is effective to use a process which comprises adding a halogen-containing compound in the organic silver salts prepared 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 Disclosures, No. 170-29, Japanese Patent Application Nos. 32928/75 and 42529/76, U.S. Pat. No. 3,700,458, and Japanese Patent Application Nos. 13224/74 and 17216/75.

The use of preformed silver halide emulsions 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 Hewitson, et al., U.S. Pat. No. 2,618,556; Yutzy et al., U.S. Pat. No. 2,614,928; Yackel, U.S. Pat. No. 2,565,418; Hart et al., U.S. Pat. No. 3,241,969; and Waller et al., U.S. Pat. No. 2,489,341. The silver halide grains may have any crystalline habit including, but not limited to cubic, tetrahedral, orthorhombic, tabular, laminar or platelet.

Photothermographic emulsions containing preformed silver halide in accordance with this invention can be sensitized with chemical sensitizers, such as with reduction agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds, or combinations of these. Suitable chemical sensitation procedures are described in Shepard, U.S. Pat. No. 1,623,499; Waller, U.S. Pat. No. 2,399,083; McVeigh, U.S. Pat. No. 3,297,447; and Dunn, U.S. Pat. No. 3,297,446.

The reducing agent for silver ion may be any material, preferably organic material, which will reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 20 percent by weight of the imaging layer. In a two-layer construction, if the reducing agent is in the second layer, slightly higher proportions, of from about 2 to 20 percent tend to be more desirable.

A wide range of reducing agents have been disclosed in dry silver systems including amidoximes such as phenylamidoxime, 2-thienylamidoxime and p-phenoxy-phenylamidoxime, azines, e.g., 4-hydroxy-3,5-dimethoxybenzaldehyde azine; a combination of aliphatic carboxylic acid aryl hydrazides and ascorbic acid, such as 2,2'-bis(hydroxymethyl)propionyl-beta-phenyl 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-methylphenyl hydrazine, hydroxamic acids such as phenylhydroxamic acid, p-hydroxyphenylhydroxamic acid, and beta-alanine hydroxamic acid; a combination of azines and sulphonamidophenols, e.g., phenothiazine and 2,6-dichloro-4-benzenesulphonamidophenol; alpha-cyanophenylacetic acid derivatives such as ethyl-alpha-cyano-2-methylphenylacetate, ethyl-alpha-cyanophenylacetate; bis-beta-naphthols as illustrated by 2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, and bis(2-hydroxy-1-naphthyl)-methane; a combination of bis-beta-naphthol and a 1,3-dihydroxybenzene derivative, e.g., 2,4-dihydroxy-benzophenone or 2'4'-dihydroxyacetophenone; 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones as illustrated by dimethylamino hexose reductone, anhydro dihydro amino hexose reductone, and anhydro dihydro piperidone hexose reductone; sulphonamido-phenol reducing agents such as 2,6-dichloro-4-benzenesulphonamidophenol, and p-benzenesulphonamidophenol; 2-phenylindane-1,3-dione and the like; chromans such as 2,2-dimethyl-7-t-butyl-6-hydroxychroman; 1,4-dihydro-pyridines such as 2,6-dimethoxy-3,5-dicarbethoxy-1,4-dihydropyridine; bisphenols e.g., bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-ethylidene-bis(2-tert-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 literature discloses additives or "toners", which improve the image. Toner materials may be present, for example, in amounts from 0.1 to 10 percent by weight of all silver bearing components. Toners are well known materials in the photothermographic art as shown in U.S. Pat. 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 a quinazolinone, 3-phenyl-2-pyrazoline-5-one, 1-phenylurazole, quinazoline, and 2,4-thiazolidinedione; naphthalimides, e.g., N-hydroxy-1,8-naphthalimide; cobalt complexes, e.g., 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)aryl dicarboximides, e.g. (N-dimethylaminomethyl)phthalimide, and N-(dimethylaminomethyl) naphthalene-2,3-dicarboximide; and a combination of blocked pyrazoles, isothiuronium derivatives and certian photobleach agents, e.g., a combination of N,N'-hexamethylene bis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis-(isothiuronium trifluoracetate) and 2-(tribromomethylsulphonyl)-(benzothiazole); and merocyanine dyes such as 3-ethyl-5[(3-ethyl-2-benzothiazolinylidene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione; 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 phthalazinone plus sulphinic 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 persulphates, e.g., ammonium peroxydisulphate 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.

A number of methods have been proposed for obtaining color images with dry silver systems. Such methods include incorporated coupler materials, e.g., a combination of silver benzotriazole, well known magenta, yellow and cyan dye-forming couplers, aminophenol developing agents, a base release agent such as guanidinium trichloroacetate and silver bromide in poly(vinyl butyral); a combination of silver bromoidodide, sulphonamidophenol reducing agent, silver behenate, poly(vinyl butyral), an amine such as n-octadecylamine and 2-equivalent or 4-equivalent cyan, magenta or yellow dye-forming couplers; incorporating leuco dye bases which oxidize to form a dye image, e.g., Malachite Green, Crystal Violet and pararosaniline; a combination of in situ silver halide, silver behenate, 3-methyl-1-phenylpyrazolone, and N,N'-dimethyl-p-phenylenediamine hydrochloride; incorporating phenolic leuco dye reducing agents such as 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,5-diphenylimidazole, and bis(3,5-di-tert-butyl-4-hydroxyphenyl)-

phenylmethane, incorporating azomethine dyes or azo dye reducing agents; silver dye bleach process, e.g., an element comprising silver behenate, behenic acid, poly(vinyl butyral), poly(vinylbutyral)peptized silver bromoidodide emulsion, 2,6-dichloro-4-benzenesulphonamidophenol, 1,8-(3,6-diazaoctane)bis-isothiuronium-p-toluene sulphonate and an azo dye was exposed and heat processed to obtain a negative silver image with a uniform distribution of dye which was laminated to an acid activator sheet comprising polyacrylic acid, thiourea and p-toluene sulphonic acid and heated to obtain well defined positive dye images; and incorporating amines such as aminoacetanilide (yellow dye-forming), 3,3'-dimethoxybenzidine (blue dye-forming) or sulphanilanilide (magenta dye-forming) which react with the oxidized form of incorporated reducing agents such as 2,6-dichloro-4-benzenesulphonamidophenol to form dye images. Neutral dye images can be obtained by the addition of amines such as behenylamine and p-anisidine.

Leuco dye oxidation in such silver halide systems are disclosed in U.S. Pat. Nos. 4,021,240; 4,374,821; 4,460,681 and 4,883,747.

Silver halide emulsions containing the supersensitizers of this invention can be protected further against the additional production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in Staud, U.S. Pat. No. 2,131,038 and Allen U.S. Pat. No. 2,694,716; the azaindenes described in Piper, U.S. Pat. No. 2,886,437 and Heimbach, U.S. Pat. No. 2,444,605; the mercury salts described in Allen, U.S. Pat. No. 2,728,663; the urazoles described in Anderson, U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard, U.S. Pat. No. 3,235,652; the oximes described in Carrol et al., British Patent No. 623,448; nitron; nitroindazoles; the polyvalent metal salts described in Jones, U.S. Pat. No. 2,839,405; the thiuronium salts described by Herz, U.S. Pat. No. 3,220,839; and palladium, platinum and gold salts described in Trivelli, U.S. Pat. No. 2,566,263 and Damschroder, U.S. Pat. No. 2,597,915.

Supersensitized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton, U.S. Pat. No. 2,960,404; fatty acids or esters such as those described in Robins, U.S. Pat. No. 2,588,765 and Duane, U.S. Pat. No. 3,121,060; and silicone resins such as those described in DuPont British Patent No. 955,061.

The photothermographic elements can include image dye stabilizers. Such image dye stabilizers are illustrated by U.K. Patent No. 1,326,889; Lestina et al. U.S. Pat. Nos. 3,432,300 and 3,698,909; Stern et al. U.S. Pat. No. 3,573,050; Arai et al. U.S. Pat. No. 3,764,337 and Smith et al. U.S. Pat. No. 4,042,394.

Photothermographic elements containing emulsion layers supersensitized according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey, U.S. Pat. No. 3,253,921; Gaspar U.S. Pat. No. 2,274,782; Carroll et al., U.S. Pat. No. 2,527,583 and Van Campen, U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones, U.S. Pat. No. 3,282,699.

Photothermographic elements containing emulsion layers supersensitized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al., U.S. Pat. No. 2,992,101 and Lynn, U.S. Pat. No. 2,701,245.

Emulsions supersenitized in accordance with this invention can 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. Pat. Nos. 2,861,056, and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Pat. No. 3,428,451.

The binder may be selected from any of the wellknown natural or synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and terpolymers are of course included in these definitions. The preferred photothermographic silver containing polymer is polyvinyl butyral, but ethyl cellulose, methacrylate copolymers, maleic anhydride ester copolymers, polystyrene, and butadiene-styrene copolymers are also useful.

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. As a guide in the case of carrying at least an organic silver salt, it can be said that a preferred ratio of the binder to the organic silver salt ranges from 15:1 to 1:2, and particularly from 8:1 to 1:1.

Photothermographic emulsions containing the supersensitizer of the invention can be coated on a wide variety of supports. 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 alphaolefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The substrate with a backside resistive heating layer may also be used in photothermographic imaging systems such as shown in U.S. Pat. No. 4,460,681 and 4,374,921.

Photothermographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Benguin, U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Pat. No. 2,761,791 and Wynn, British Patent No. 837,095.

The present invention will be illustrated in detail in reference to the following examples.

EXAMPLES 1-13

A silver halide-silver behenate dry soap was prepared by the procedures described in U.S. Pat. No. 3,839,049. The silver halide totalled 9% of the total silver while silver behenate comprised 91% of the total silver. The silver halide was a 50/50 mixture of preformed silver halide grains. Both had a composition of 2% iodide and 98% bromide and were monodispersed. The two silver bromoiodide emulsions had grain sizes of 0.055 and 0.07 microns.

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 poly(vinylbutyral) (B-76, Monsanto).

The homogenized photothermographic emulsion (500 g) and 100 g 2-butanone were cooled to 55°F with stirring. Additional poly(vinylbutyral) (75.7 g B-76) was added and stirred for 20 minutes. Pyridinium hydrobromide perbromide (0.45 g) was added and stirred for 2 hours. The addition of 3.25 ml of a calcium bromide solution (l g of $CaBr_2$ and 10 ml of methanol) was followed by 30 minutes of stirring. The temperature was raised to 70°F and the following were added in 15 minute increments with stirring: 3 g 2-(4-chlorobenzoyl)benzoic acid, IR dye solution (D-1 dye; 8.8 mg D-1 in 7.1 g DMF) and 16.6 g 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane.

The photothermographic emulsion was divided into 40 g portions. The control was coated at this stage without additional additives. The remaining aliquots were treated with 3 levels of heteroaromatic mercapto compounds added as 1% solutions in methanol (w/v). The results are reported in Table 1 for the levels of heteroaromatic mercapto compound listed as dry weight per 40 g aliquots giving the best balance of low fog and high speed.

The silver photothermographic emulsions were coated and clear 3 mil (0.76×10^{-4}m) polyester by means of a knife coater and dried at 175°F for four minutes. The dry coating weight was 23 g/m^2.

An active, protective topcoat solution was prepared with the following ingredients:

256 g acetone
123 g 2-butanone
50 g methanol
20.2 g cellulose acetate
2.89 g phthalazine
2.02 g 4-methylphthalic acid
0.69 g tetrachlorophthalic acid
0.90 g tetrabromophthalic anhydride
1.50 g tetrachlorophthalic anhydride
0.45 g 4-tribromomethylpyrimidine

The topcoat solution was coated over the silver layer at a dry weight of 3.0 g/m^2. The layer was dried at 165°F for four minutes.

The coated materials were then exposed with a continuous wedge and an EK 101 sensitometer through a 780 nm narrow band filter for 30.2 seconds. After exposure, the film strips were processed at 260°F for ten seconds. The images obtained were evaluated by a densitometer. Sensitometric results include Dmin, speed (Spd: measured at 0.D = 1.0), ergs (power to reach optical density of 1.0), change in speed from emulsion without heteroaromatic mercapto compound (dSpd) and the percent that speed change (dSpd) represented (%Spd). In all coatings, the maximum density ranged from only 3.2 to 3.5 and was not tabulated.

TABLE 1

Ex.	Mercapto Compound		Dmin	Spd	Ergs	dSpd	%Spd
	Number	mg/40g split					
A	None	---	0.10	1.46	364	---	100
1	M-1	3.6	0.10	1.97	107	0.51	323
2	M-2	1.2	0.10	1.91	123	0.45	282
3	M-2	3.6	0.10	1.89	129	0.43	269
4	M-3	1.2	0.10	1.90	126	0.44	275
5	M-4	10.8	0.11	2.02	95	0.56	363
6	M-5	1.2	0.09	1.82	151	0.36	229
7	M-6	1.2	0.09	1.85	141	0.39	245
8	M-7	10.8	0.10	1.55	282	0.11	129
9	M-8	10.8	0.10	1.81	155	0.35	224
10	M-9	3.6	0.09	1.96	110	0.50	316
11	M-10	1.2	0.10	1.68	209	0.22	166
12	M-11	1.2	0.10	1.93	117	0.47	295
13	M-12	10.8	0.10	1.60	252	0.14	138

A set of experiments were run to determine the scope of the present invention. Table 2 contains a list of sulfur compounds and silver halide, infrared supersensitizers tested in the formula described for Examples 1-13. The compounds were tested at the three levels described in Examples 1-13 with the best level listed in Table 2. The results show that thioethers, thioureas and thiones do not supersensitize the infrared photothermographic system. The thioureas and also benzotriazole and Leucophor BCF (Sandoz, sulfonated triazenyl stilbene) did not supersensitize the photothermographic system although they are used extensively as silver halide, infrared supersensitizers.

TABLE 2

Ex.	--------------Sulfur Compound------------- Name	mg/40g Split	Dmin	Spd	Ergs	dSpd	%Spd
A	-------	----	0.10	1.46	364	---	100
B	2-(Methylmercapto)benzimidazole	1.2	0.10	1.46	364	0	100
C	1,1,3,3-Tetramethyl-2-thiourea	1.2	0.10	1.41	390	-0.05	93
D	1,3-Dibenzyl-2-thiourea	1.2	Black				
E	3-Methylbenzothiazole-2-thione	1.2	0.10	1.42	381	-0.04	96
F	Benzotriazole	1.2	0.10	1.26	552	-0.20	66
G	Leucophor BCF	1.2	0.10	1.42	381	-0.04	96

EXAMPLES 14-26

The same silver and topcoat formulas were used in these examples as those given in Examples 1-13 except that a pure silver bromide grain of 0.055 microns was used instead of the 50/50 mixture of preformed, 0.055 and 0.07 micron silver bromoiodine grains used in Examples 1-13.

These examples were again run as 40 g aliquots with a control coated without addition of heteroaromatic mercapto compound. The heteroaromatic mercapto compounds used in Examples 14-17 were evaluated at 3 levels while Examples 18-26 were examined at 2 levels. The coated film strips were exposed with a laser sensitometer incorporating a 780 nm laser diode. After exposure, the film strips were processed at 260 ° F for ten seconds. The results are compiled in Table 3.

TABLE 3

Mercapto Compound							
Ex.	Number	mg/40g Split	Dmin	Spd	Ergs	dSpd	%Spd
A	None	----	0.11	1.25	565	----	100
14	M-1	3.6	0.11	1.93	117	0.68	479
15	M-13	10.8	0.11	1.79	162	0.54	347
16	M-14	3.6	0.11	1.54	289	0.29	195
17	M-15	1.2	0.11	1.64	230	0.39	245
18	M-16	7.2	0.11	1.59	258	0.34	219
19	M-17	1.2	0.11	1.42	381	0.17	148
20	M-18	7.2	0.11	1.41	390	0.16	144
21	M-19	7.2	0.11	1.39	409	0.14	138
22	M-20	1.2	0.11	1.49	324	0.24	174
23	M-21	1.2	0.11	1.39	409	0.14	138
24	M-22	1.2	0.11	1.63	235	0.38	240
25	M-23	7.2	0.11	1.56	276	0.31	204
26	M-24	1.2	0.11	1.47	340	0.22	166

Experiments were run to determine the necessity of having a heteroaromatic system for the mercapto supersensitizers. The silver and topcoat formulas were the same as in Examples 14-26. The results are listed in Table 4 and show the importance of having a heteroaromatic system attached to the mercapto group in order to supersensitize the infrared, photothermographic film.

TABLE 4

Ex.	Name	mg/40g Split	Dmin	Spd	Ergs	dSpd	%Spd
	----------Non Aromatic Mercapto----------						
A	--------	----	0.11	1.25	565	---	100
H	3,4,5,6-Tetrahydro-2-pyrimidinethiol	1.2*	0.11	0.88	1330	-0.37	42
I	2-Mercaptothiazoline	1.2*	No Image				

*Higher levels desensitized further.

EXAMPLES 27-33

The supersensitization effects of mercapto heteroaromatic compounds on infrared sensitized photothermographic systems were evaluated for other infrared sensitizing dyes. The formula was the same as in

Examples 14-26. The infrared dyes were examined with and without M-1 (2-mercaptobenzimidazole). The sensitivity maximum of the infrared dyed photothermographic film was found by exposing with a series of narrow band filters and an EK 101 sensitometer. The speed and supersensitization effect was evaluated on a laser sensitometer incorporating a 780 nm laser diode. The Dmin values were unaffected by the addition of M-1. The results are listed in Table 5 and show clearly that mercapto heteroaromatic compounds supersensitize all infrared dye classes in photothermographic compositions.

TABLE 5

Ex.	IR DYE Number	IR DYE mg/40g Split	mg M-1 per 40g split	Sensitivity Max. (nm)	Spd	Ergs	dSpd	%Spd
A	D-1	0.52	0	800	1.25	565	---	100
27	D-1	0.52	3.6	800	1.90	126	0.65	447
J	D-2	2.10	0	780	1.26	552	---	100
28	D-2	2.10	3.6	780	1.83	148	0.57	372
K	D-3	2.10	0	800	0.95	1130	---	100
29	D-3	2.10	3.6	800	1.64	230	0.69	490
L	D-4	2.10	0	750	0.51	3200	---	100
30	D-4	2.10	3.6	750	1.49	324	0.98	955
M	D-5	1.05	0	820	0.86	1390	---	100
31	D-5	1.05	3.6	820	1.35	449	0.49	309
N	D-6	1.05	0	750	0.77	1700	---	100
32	D-6	1.05	3.6	750	1.36	438	0.59	389
O	D-7	0.52	0	820	no image			
33	D-7	0.52	3.6	820	trace			

EXAMPLE 34

An in situ halidized photothermographic system was examined for infrared supersensitization with mercapto heteroarmatic compounds. A photothermograhpic emulsion was prepared by combining 206 g of a silver behenate full soap dispersion (converted to 26% silver by weight) with the following ingredients, each added in its listed order with mixing:

40 g 2-butanone
0.54 g N-methylpyrrolidone
5.4 ml of $ZnBr_2$ solution (10 g $ZnBr_2$ and 100 ml of methanol)
The mixture was held for 4 hours before adding the following:
3.6 g poly(vinylbutyral) B-76
2.6 ml of pyridine solution (3.6 g pyridine and 71 g 2-butanone)
27.5 g poly(vinylbutyral) B-76
4.6 ml NBS solution (0.67 g N-bromosuccinimide and 40 g 2-butanone)
The mixture was held overnight before adding the following:
6.3 g 2,2'-methylenebis(4-ethyl-6-tertiarybutylphenol)
IR dye solution (6 mg D-1 and 4.0 g DMF)

The resulting composition was divided into 40 g portions. The control was coated without additional additives while M-1(2-mercaptobenzimidazole) was added to a second aliquot. The results are compiled in Table 6. The silver photothermographic emulsions were coated on clear 3 mil (0.76×10^{-4} m) polyester by means of a knife coater and dried at 185 ° F for three minutes. The dry coating weight was 17 g/m^2.

An active, protective topcoat solution was prepared with the following ingredients:

224 g 2-butanone
33.3 g acetone
13.8 g methanol
20.7 g cellulose acetate
2.64 g phthalazine
1.86 g 4-methylphthalic acid
1.23 g tetrachlorophthalic anhydride
0.57 g tetrachlorophthalic acid
1.80 g 2-(tribromomethylsulfone)benzothiazole

The topcoat solution was coated at 2.7 g/m^2 over the silver coating and dried at 185 ° F for three minutes. The coated material was exposed on a laser sensitometer with a 780 nm laser diode and then processed at 260 ° F for ten seconds. The results listed in Table 6 show that mercapto heteroaromatic compounds supersensitize in situ halidized photothermographic systems sensitized to the infrared.

TABLE 6

Ex.	mg M-1 per 40 g Split	Dmin	Spd	Ergs	dSpd	%Spd
P	None	0.23	0.57	2717	---	100
36	0.8	0.26	1.89	128	1.32	2090

EXAMPLES 35-40

The following coatings show that a combination of mercapto heteroaromatic compounds may give improved results as infrared supersensitizers for photothermographic systems. The same silver and topcoat formulas were used in these examples as those given in Examples 14-26 except that a higher infrared dye level was used (50% more IR dye, D-1) and a change was made in the tribromo antifoggant. Examples 14-26 had 0.45 g of 4-tribromomethylpyrimidine in the topcoat solution whereas Examples 35-40 contained 2.25 g of 2-(tribromomethylsulfone)benzothiazole in the same quantity of topcoat solution.

The examples were again run as 40 g aliquots. The coated film strips were exposed with a laser sensitometer incorporating a 780 nm laser diode. After exposure, the film strips were processed at 260 ° F for ten seconds. The results are compiled in Table 7.

Example 35 was the optimized level for M-1 (2-mercaptobenzimidazole) in terms of speed or sensitivity. Examples 36-38 show the optimized level of M-3 (2-mercaptobenzothiazole) to be slightly slower in speed than M-1 but higher in contrast (cont = contrast measured from a density of 0.25 to 2.0 above fog). The two mercapto heteroaromatic compounds were combined in Examples 39 and 40 to produce higher speed and contrast than when tested separately. The difference between Examples 39 and 40 was that in Example 39, M-1 was added first and M-3 was added 15 minutes later whereas in Example 40, M-3 was added first and M-1 was added 15 minutes later. Table 7 shows that the combination of mercapto heteroaromatic compounds produced higher speed and high contrast which would be useful for graphic arts applications.

TABLE 7

Mercapto Compounds						
Ex	mg M-1 Per 40 g Split	mg M-3 Per 40 g split	Dmin	Spd	Ergs	Cont
35	4.2	----	0.14	1.91	123	2.92
36	----	1.4	0.16	1.72	191	3.78
37	----	2.8	0.20	1.83	148	3.84
38	----	4.2	0.16	1.77	170	4.64
39	4.2	4.2	0.14	2.01	97	4.42
40	4.2	4.2	0.14	2.05	89	4.94

Claims

1. A photothermographic emulsion comprising a binder, a light insensitive silver salt, a reducing agent for silver ion, and silver halide, said silver halide being spectrally sensitized to radiation of from 750 to 1300 nm and said emulsion containing a supersensitizing amount of a compound selected from the group consisting of heteroaromatic mercapto compounds or heteroaromatic disulfide compounds.

2. The emulsion of claim 1 comprising a supersensitizing compound selected from either of the formulae:

   Ar-SM and
   Ar-S-S-Ar

   wherein M is hydrogen or an alkali metal, and Ar is a heteroaromatic ring group.

3. The emulsion of claim 1 or 2 wherein said supersensitizing compound is present in an amount of from 10^{-3} to 1 moles of said compound per mole of silver in said emulsion.

4. The emulsion of any one of claims 1 to 3 wherein said silver halide being spectrally sensitized comprises silver halide and a cyanine dye, carbocyanine dye, or tricarbocyanine dye.

5. The emulsion of any one of claims 2 to 4 wherein Ar is selected from the group consisting of benzimidazole, naphthimidazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, benzotellurazole, imidazole, oxazole, pyrazole, triazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine, pyrazine, pyridine, purine, quinoline, and quinazolinone.

6. The emulsion of any one of claims 1 to 5 wherein said light-insensitive silver salt comprises a silver salt of an organic acid.

7. The emulsion of claim 6 wherein said organic acid comprises a fatty carboxylic acid.

8. The emulsion of any one of claims 1 to 7 comprising at least two different compounds of said supersensitizing compounds.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 3608

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.5)
Y	EP-A-0 271 260 (3M) * page 6, line 6 - page 7, line 24 * * page 15, line 31 - page 16, line 1 *	1-8	G03C1/498
D,Y	US-A-4 910 129 (TAKAHASHI ET AL.) * column 1, line 66 - column 5, line 9 *	1-8	
Y	RESEARCH DISCLOSURE vol. 299, no. 63, March 1989, HAVANT GB pages 208 - 214 P.W.LAUF 'Photothermographic Silver Halide Systems' * page 211, right column, line 33 - page 212, left column, line 36 *	1-8	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 MAY 1993	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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