(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 821 271 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.01.1998 Bulletin 1998/05

(51) Int. Cl.[6]: **G03C 1/498**, G03C 5/16, G03C 1/28

(21) Application number: **97201904.6**

(22) Date of filing: **21.06.1997**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

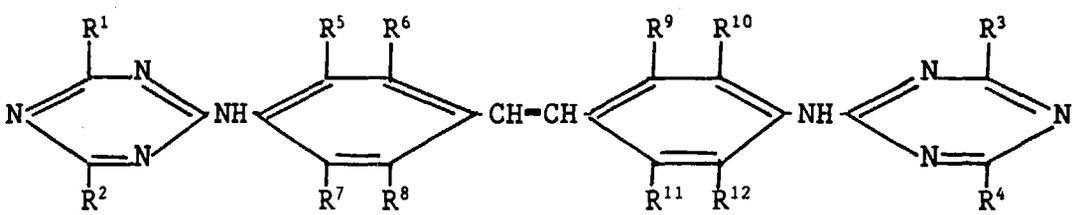
(30) Priority: **24.07.1996 EP 96202107**

(71) Applicant: **AGFA-GEVAERT N.V.**
2640 Mortsel (BE)

(72) Inventors:
- **Uytterhoeven, Herman**
  2640 Mortsel (BE)
- **Loccufier, Johan**
  2640 Mortsel (BE)
- **Deroover, Geert**
  2640 Mortsel (BE)
- **Callant, Paul**
  2640 Mortsel (BE)

(54) Infra-red photothermographic material comprising a spectral sensitizer and a stilbene derivative supersensitizer

(57) A photothermographic recording material comprising a photo-addressable thermally developable element comprising a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the substantially light-insensitive organic silver salt and spectrally sensitized to infra-red light with a dye, a supersensitizer for the dye, a reducing agent in thermal working relationship with the substantially light-insensitive organic silver salt and a binder, characterized in that the binder comprises a water soluble polymer, a water-dispersible polymer or a water soluble polymer and a water-dispersible polymer; the dye absorbs electromagnetic radiation in the wavelength range from 700 to 1100nm; and the supersensitizer is a stilbene compound represented by general formula (I):



wherein R^1, R^2, R^3 and R^4 are independently hydrogen or alkyl, aryl, aralkyl, alkaryl, alkoxy or aryloxy groups, which may all be substituted; and R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are independently hydrogen and alkyl, substituted alkyl, alkoxy, substituted alkoxy, carboxy or sulfo groups.

EP 0 821 271 A1

Description

Field of the invention

The present invention relates to a photothermographic recording material comprising a photo-addressable thermally developable element comprising a species which increases the infrared sensitivity thereof.

Background of the invention.

Thermal imaging or thermography is a recording process wherein images are generated by the use of thermal energy.

In thermography three approaches are known:

1. Direct thermal formation of a visible image pattern by imagewise heating of a recording material containing matter that by chemical or physical process changes colour or optical density;
2. Imagewise transfer of an ingredient necessary for the chemical or physical process bringing about changes in colour or optical density to a receptor element;
3. Thermal dye transfer printing wherein a visible image pattern is formed by transfer of a coloured species from an imagewise heated donor element onto a receptor element.

Thermographic materials of type 1 become photothermographic when a photosensitive agent is present which after exposure to UV, visible or IR light is capable of catalyzing or participating in a thermographic process bringing about changes in colour or optical density.

Examples of photothermographic materials are the so called "Dry Silver" photographic materials of the 3M Company, which are reviewed by D.A. Morgan in "Handbook of Imaging Science", edited by A.R. Diamond, page 43, published by Marcel Dekker in 1991.

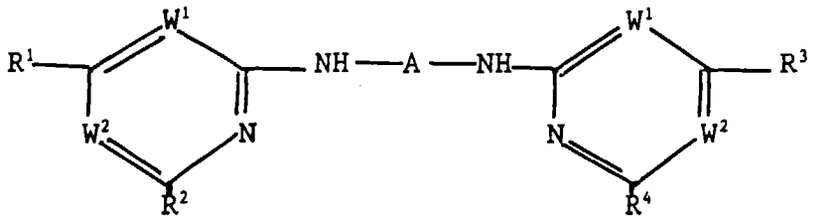
The most widely used radiation-sensitive salt in such materials is silver halide, which must be present in catalytic association with the organic silver salt so that the species formed on exposure can catalyze the thermal image forming process. Silver halide requires spectral sensitization with dyes to extend its sensitivity range into the infra-red region of actinic radiation.

In US-P 5,441,866 it is stated that: "While many of such dyes (dyes which impart spectral sensitivity to a gelatino silver halide element) provide spectral sensitization in photothermographic formulations the dye sensitization is often very inefficient and it is not possible to translate the performance of a dye in gelatino silver halide elements to photothermographic elements."

In the context of infra-red sensitization of "Dry Silver" materials, US 4,873,184 discloses a spectrally sensitized silver halide photothermographic emulsion layer comprising a reducible silver source material as 20 to 70% by weight of said emulsion layer, photosensitive silver halide, and a reducing agent for silver ion, said photosensitive silver halide having no latent image therein and being present as 1.5 to 7% by weight of said emulsion layer and said emulsion layer having a speed increasing effective amount of a metal complexing agent therein in an amount equal to 0.4 to 40% by weight of total silver in said emulsion.

Also in the context of infrared sensitization of "Dry Silver" materials, EP-A 559 228 discloses a photothermographic emulsion comprising a binder, a light insensitive silver salt, a reducing agent for silver ion, and silver halide, the silver halide being spectrally sensitized to radiation of from 750 to 1300 nm and the emulsion containing a supersensitizing amount of a compound selected from the group consisting of heteroaromatic mercapto compounds or heteroaromatic disulfide compounds. Furthermore, a comparative example is disclosed demonstrating an absence of supersensitization with a stilbene compound, Leucophor BCF from SANDOZ.

There is no teaching in the detailed description and examples in US-P 4,873,184 and EP-A 559 228 regarding the applicability of the particular invention described therein to photothermographic recording materials comprising a photo-addressable thermally developable elements coated from an aqueous medium. However, JP 63-23145 discloses a heat developable photosensitive material having at least one silver halide emulsion layer containing an infrared sensitizing dye and at least one compound of formula (A):



wherein A is a divalent aromatic residue; R^1, R^2, R^3 and R^4 are each H, OH, alkyl, alkoxy, aryloxy, halogen, heterocyclyl, heterocyclylthio, arylthio, amino, optionally substituted alkylamino, optionally substituted arylamino, optionally substituted aralkylamino, aryl or mercapto; at least one of the substituents A, R^1, R^2, R^3 and R^4 is substituted with a sulfo group; and each of W^1 and W^2 is -CH= or -N=, provided that at least one of them is -N=. according to the description and the invention examples of JP 63-23145 the heat developable photosensitive material may contain organic metal salts as oxidising agents in conjunction with the photosensitive silver halide in this invention; the divalent aromatic residue may be a 2,2'-disulfostilbene, a 4,4'-bis(benzoylamino)-2,2'-disulfostilbene residues; and water-soluble and water-dispersible polymers may be used with gelatin, a water-soluble polymer being used in the invention examples. No invention examples are disclosed in which in the compound (A) W^1 and W^2 are both N.

The extrapolation of materials technology for photothermographic materials based on organic silver salts/silver halide/reducing agent-systems coated from non-aqueous media to aqueous media is by no means self-evident as is borne out by the inventors' investigations and efficient supersensitizers are required for use in infra-red dye sensitized photothermographic materials coated from aqueous media.

Objects of the invention.

It is a first object of the invention to provide a photothermographic recording material with a high infra-red sensitivity and excellent image-forming properties.

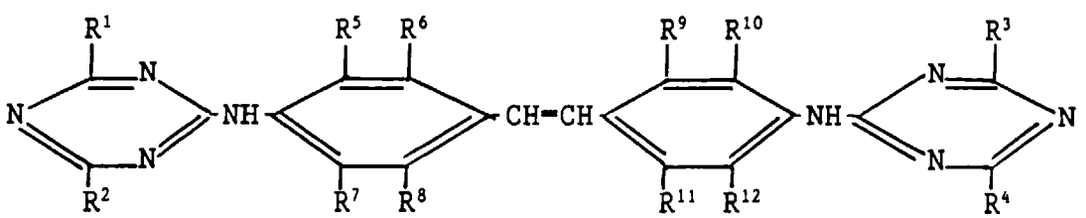
It is a second object of the invention to provide a photo-addressable thermally developable element with excellent image-forming properties, which can be coated from aqueous media.

It is a yet a still further object of the invention to provide a recording process for a photothermographic recording material with the above improved characteristics.

Further objects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention

According to the present invention a photothermographic recording material is provided comprising a support and a photo-addressable thermally developable element comprising a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the substantially light-insensitive organic silver salt and spectrally sensitized to infra-red light with a dye, a supersensitizer for the dye, a reducing agent in thermal working relationship with the substantially light-insensitive organic silver salt and a binder, characterized in that the binder comprises a water soluble polymer, a water-dispersible polymer or a water soluble polymer and a water-dispersible polymer; the dye absorbs electromagnetic radiation in the wavelength range from 700 to 1100nm; and the supersensitizer is a stilbene compound represented by general formula (I):



wherein R^1, R^2, R^3 and R^4 are independently hydrogen or alkyl, aryl, aralkyl, alkaryl, alkoxy or aryloxy groups, which may all be substituted; and R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are independently hydrogen and alkyl, substituted alkyl, alkoxy, substituted alkoxy, carboxy or sulfo groups.

A process is also provided producing a photothermographic recording material, as referred to above, comprising

the steps of; (i) producing an aqueous dispersion or aqueous dispersions comprising the substantially light-insensitive organic silver salt, the photosensitive silver halide spectrally sensitized to infra-red light with the dye, the supersensitizer for the dye, the reducing agent and the binder; (ii) coating the aqueous dispersion or aqueous dispersions onto a support.

A recording process for a photothermographic recording material us further provided comprising the steps of: imagewise exposing to infrared actinic radiation a photothermographic material as referred to above or produced according as referred to above; and overall heating of the photothermographic recording material.

Preferred embodiments of the present invention are disclosed in the detailed description of the invention.

Detailed description of the invention.

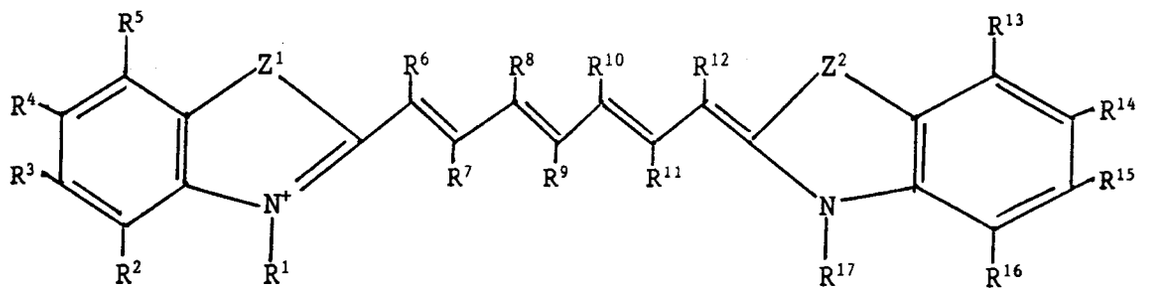
Aqueous

The term aqueous for the purposes of the present invention includes mixtures of water with water-miscible organic solvents such as alcohols e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones e.g. 2-propanone and 2-butanone etc.

Spectral sensitizer

According to the present invention a dye is provided which spectrally sensitizes photosensitive silver halide to infra-red light, wherein the dye absorbs electromagnetic radiation in the wavelength range from 700 to 1100nm and preferably in the wavelength range from 750 to 950nm.

In a preferred embodiment, according to the present invention, the dye corresponds to the general formula (II):

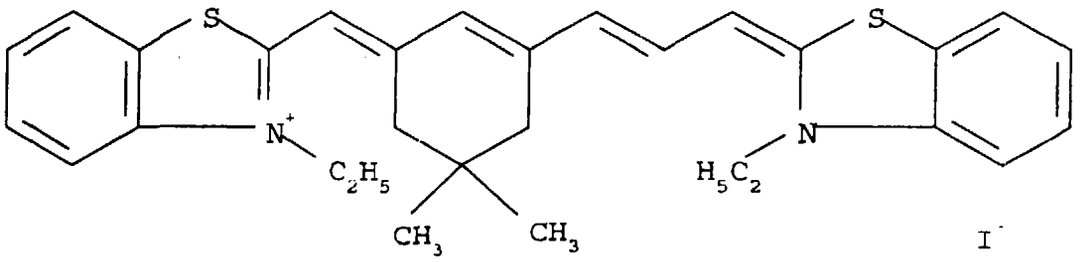


wherein Z^1 and Z^2 independently represent S, O or Se; R^1 and R^{17} are independently each an alkyl or substituted alkyl group; R^2, R^3, R^4, R^5, R^{13}, R^{14}, R^{15} and R^{16} are independently each hydrogen, chlorine, bromine, fluorine or a keto-, sulfo-, carboxy-, ester-, sulfonamide-, amide-, dialkylamino, nitro-, cyano-, alkyl-, alkenyl-, hetero-aromatic, aryl-, alkoxy- or aryloxy- group, which groups may be substituted; or each of R^2 together with R^3, R^3 together with R^4, R^4 together with R^5, R^{13} together with R^{14}, R^{14} together with R^{15} and R^{15} together with R^{16} may independently constitute the atoms necessary to complete a benzene ring which may be substituted; R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} independently each represent hydrogen, an alkyl group, a substituted alkyl group, chlorine, fluorine, bromine, iodine, a disubstituted amino group, wherein said substituents may constitute the atoms necessary to form a 5-ring atom or 6-ring atom heterocyclic ring, or each of R^6 together with R^8, R^8 together with R^{10}, R^{10} together with R^{12}, R^7 together with R^9 and R^9 together with R^{11} may independently constitute the atoms necessary to complete a 5-atom or 6-atom carbocyclic or heterocyclic ring which may be substituted; each of R^1 together with R^6 and R^{12} together with R^{17} may independently constitute the atoms necessary to complete a 5-atom or 6-atom heterocyclic ring which may be substituted; and X^- represents an anion.

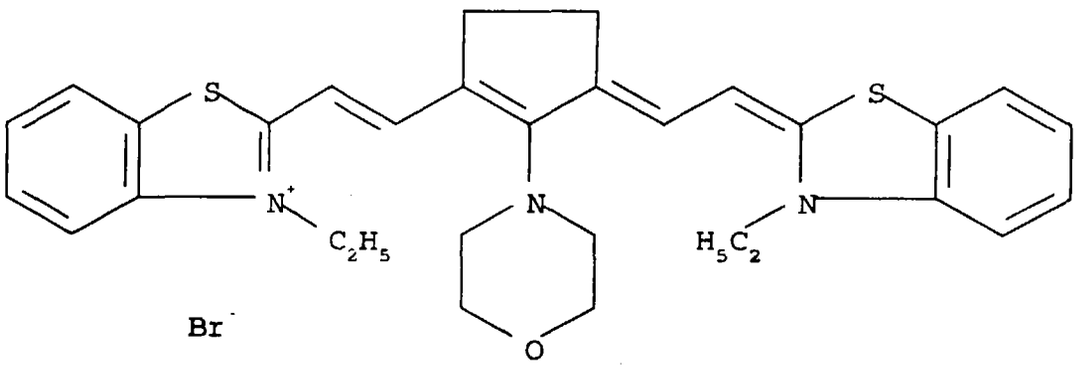
In a particularly preferred embodiment, according to the present invention, in formula (II) R^1 and R^{17} each independently represent an alkyl group consisting of 1 to 6 carbon atoms which may be substituted with a sulfo- or a carboxy-group.

Suitable infra-red sensitizing dyes for photosensitive silver halide, according to the present invention, are the N-alkyl benzothiazole heptamethine cyanine dyes:

* SENSI 01

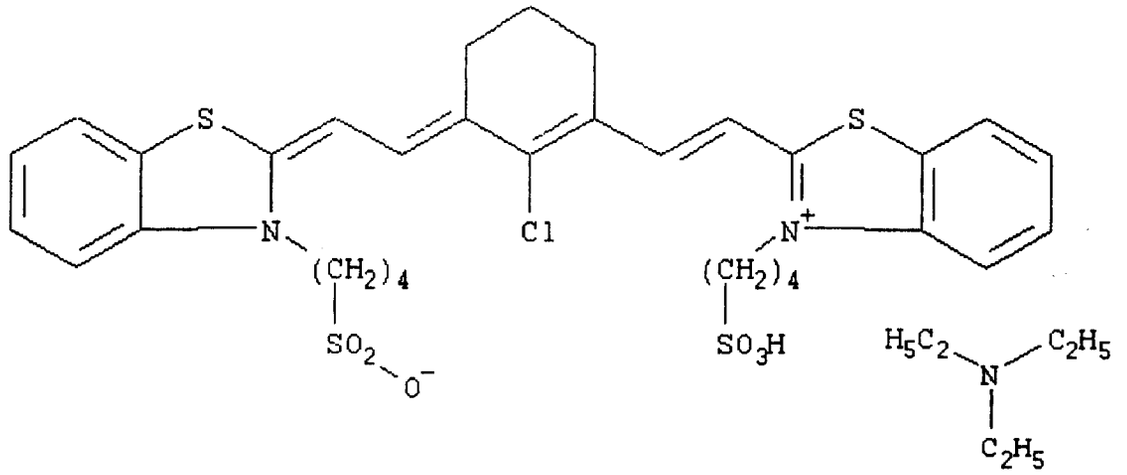


* SENSI 02

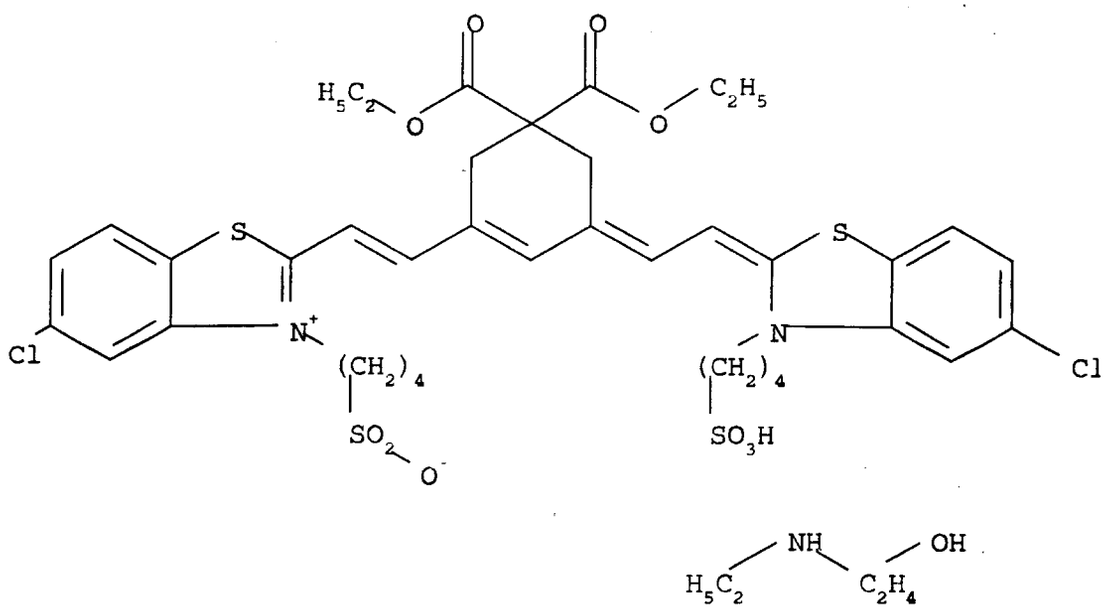


the N-alkylsulfo benzothiazole heptamethine cyanine dyes:

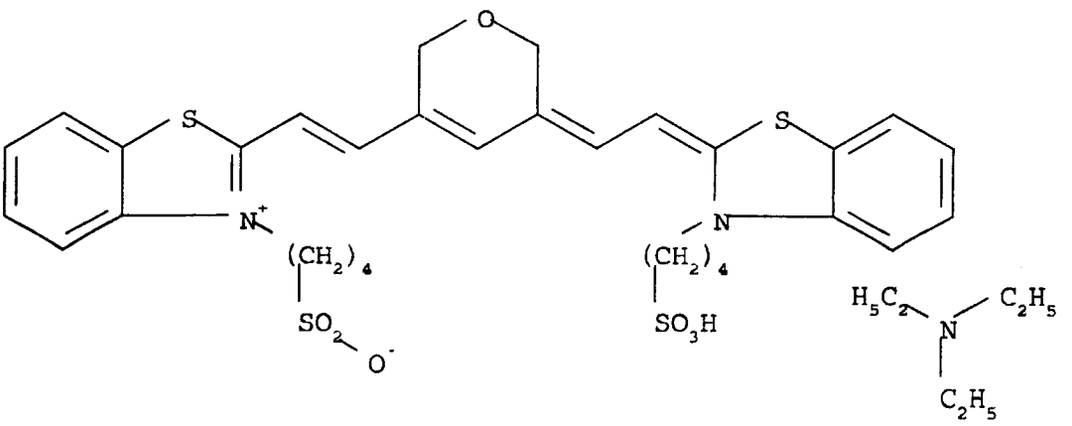
* SENSI 03



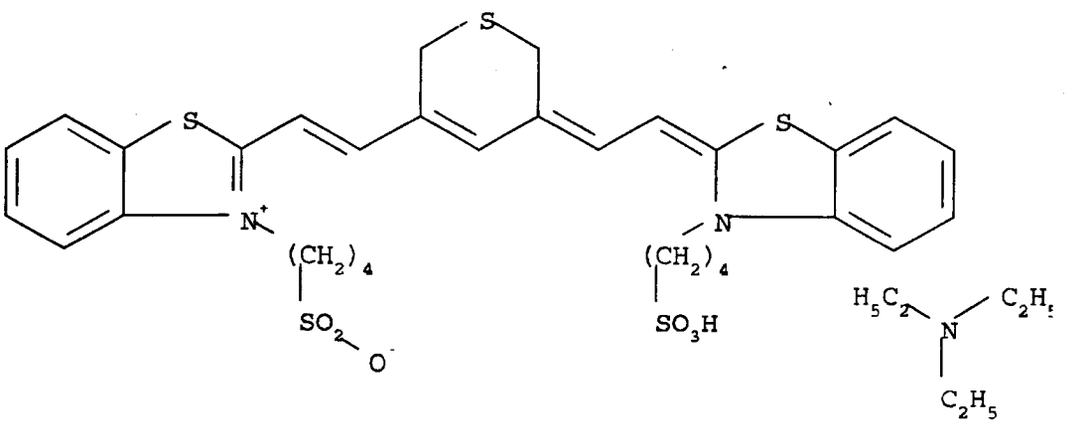
* SENSI 04



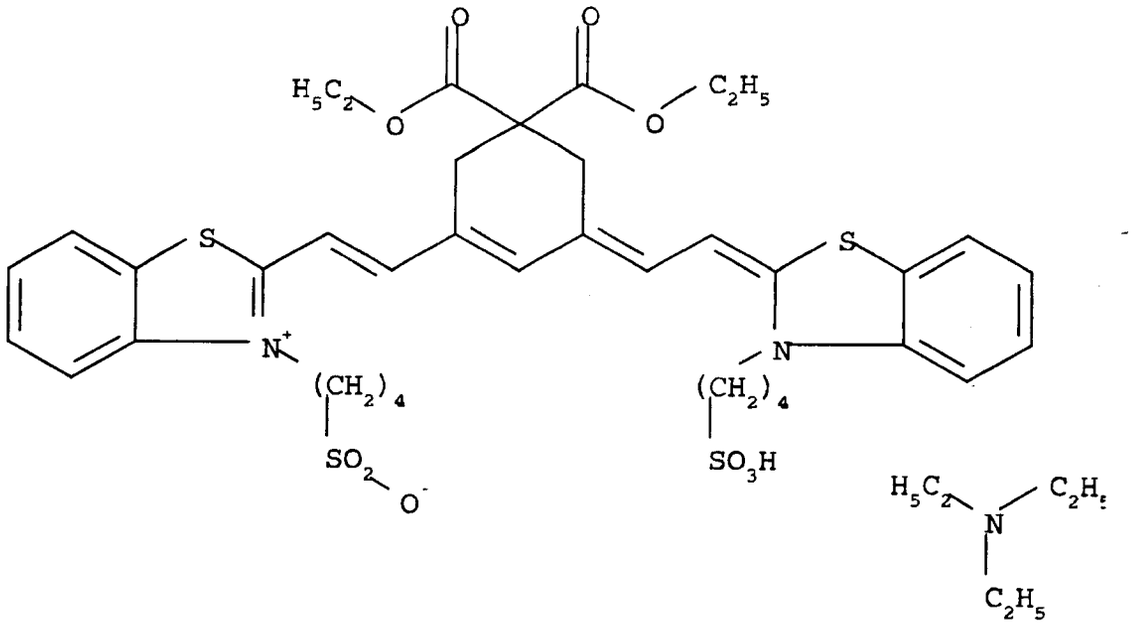
* SENSI 05



* SENSI 06

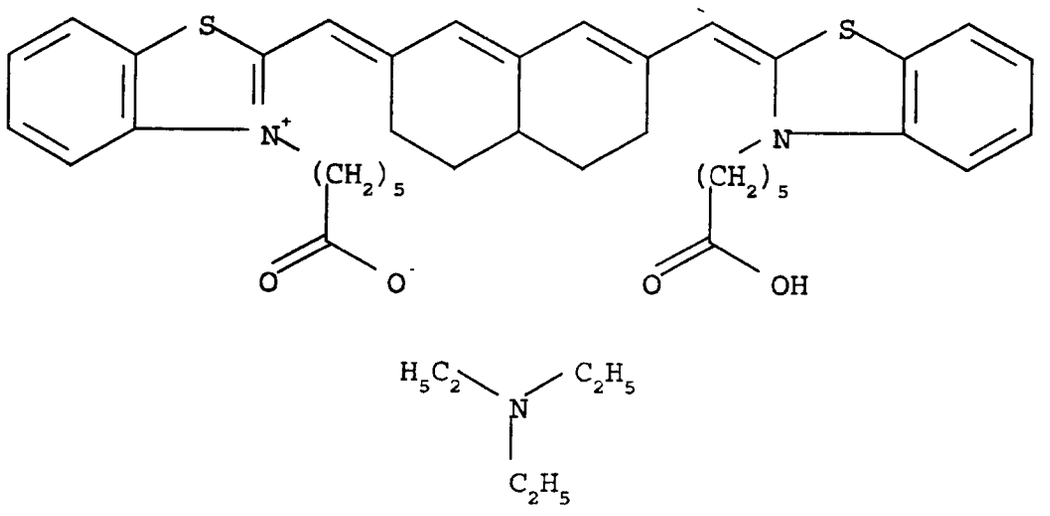


* SENSI 07

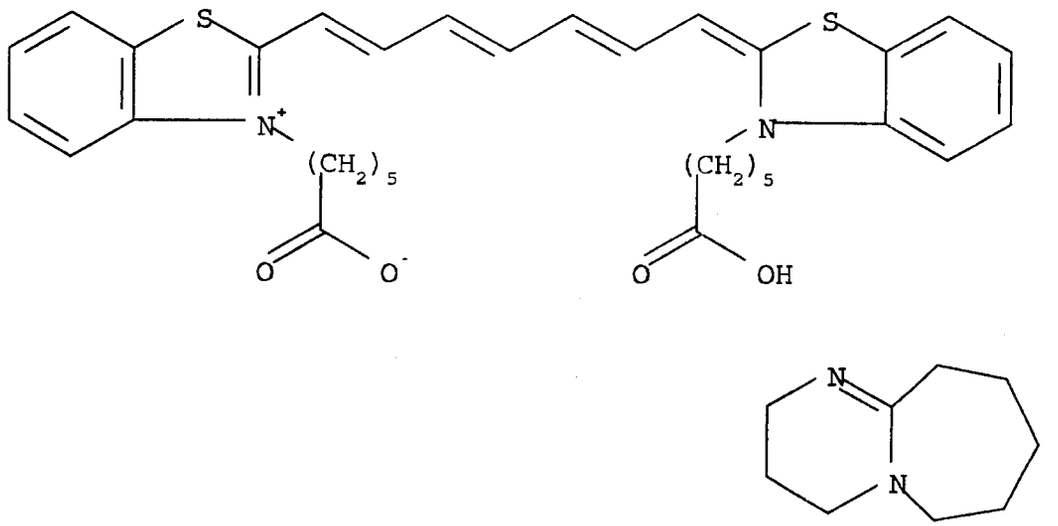


the N-alkylcarboxy benzothiazole heptamethine cyanine dyes:

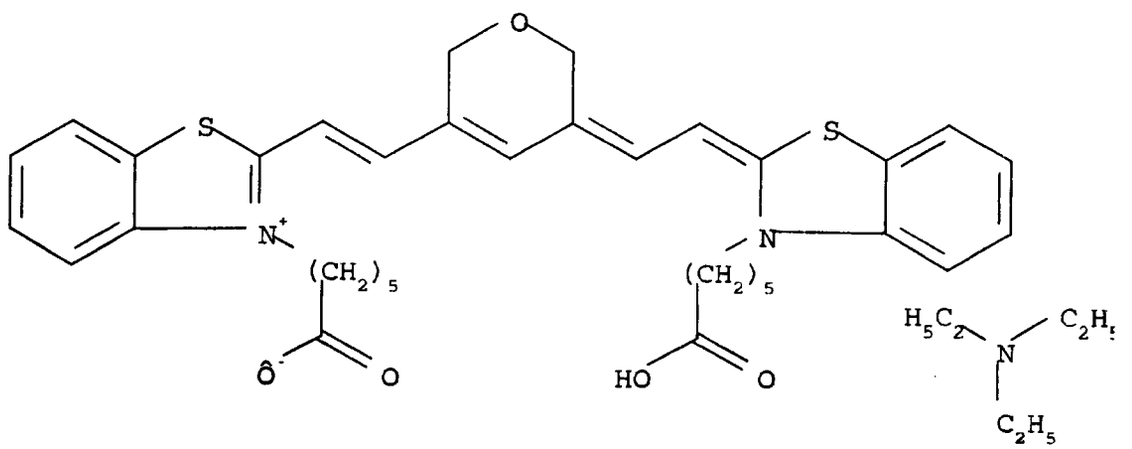
* SENSI 08



* SENSI 09



* SENSI 10

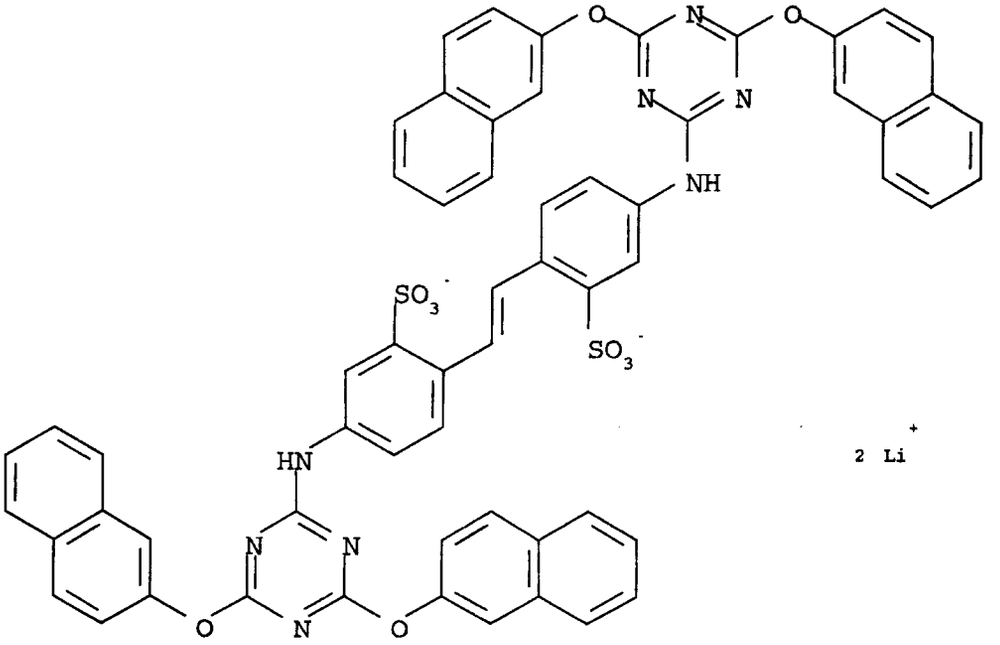


Supersensitizers

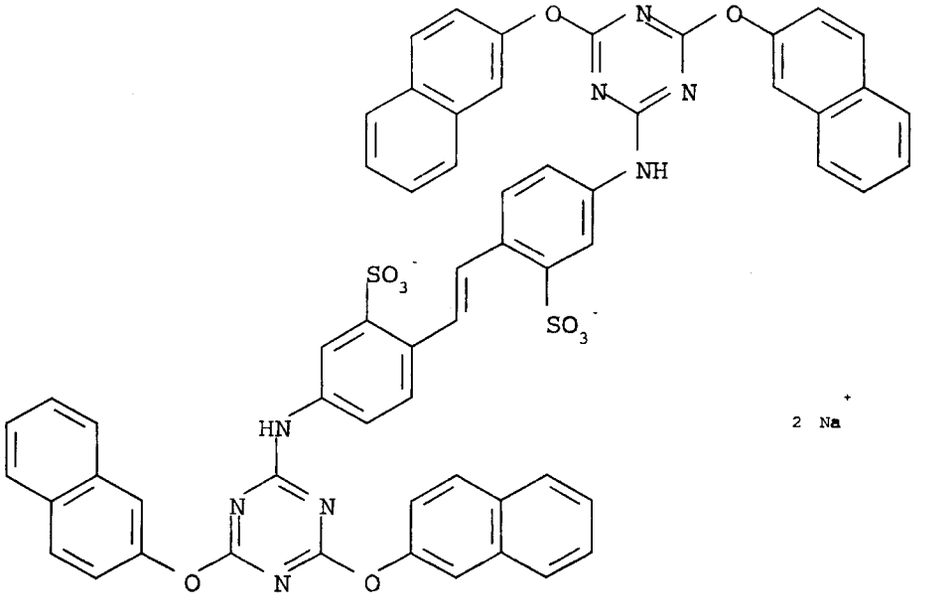
In the supersensitizer compounds represented by general formula (I) the term carboxy-group represents -COOH and its salts and the term sulfo-group represents $-SO_3H$ and its salts. In a preferred embodiment of the stilbene compound used in the present invention at least two of R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} in general formula (I) are sulfo- or carboxy-groups. In a particularly preferred embodiment of the present invention the compound represented by general formula (I) is a 2,2'-disulfo-4,4'-bis(triazinylamino)stibene compound.

Particularly preferred supersensitizers used according to the present invention, are:

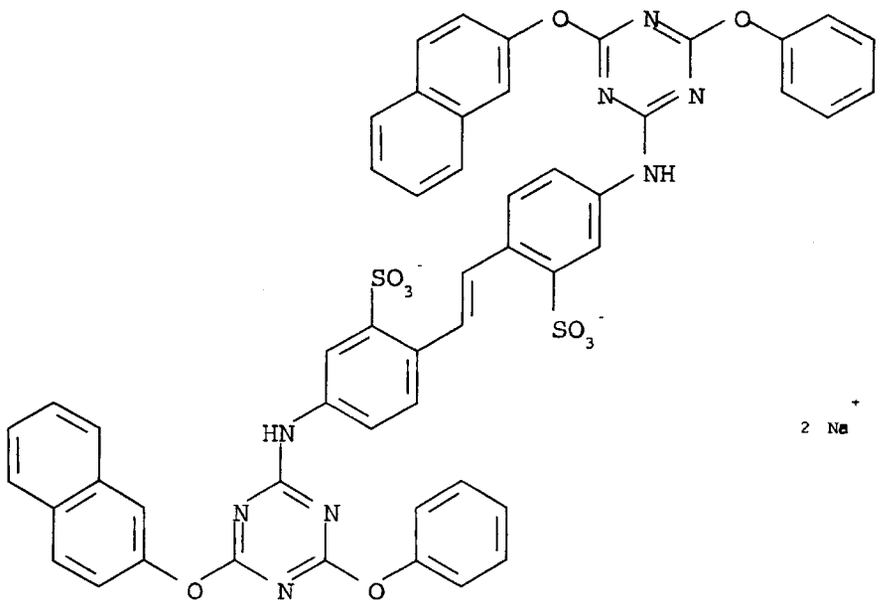
* SS-01:



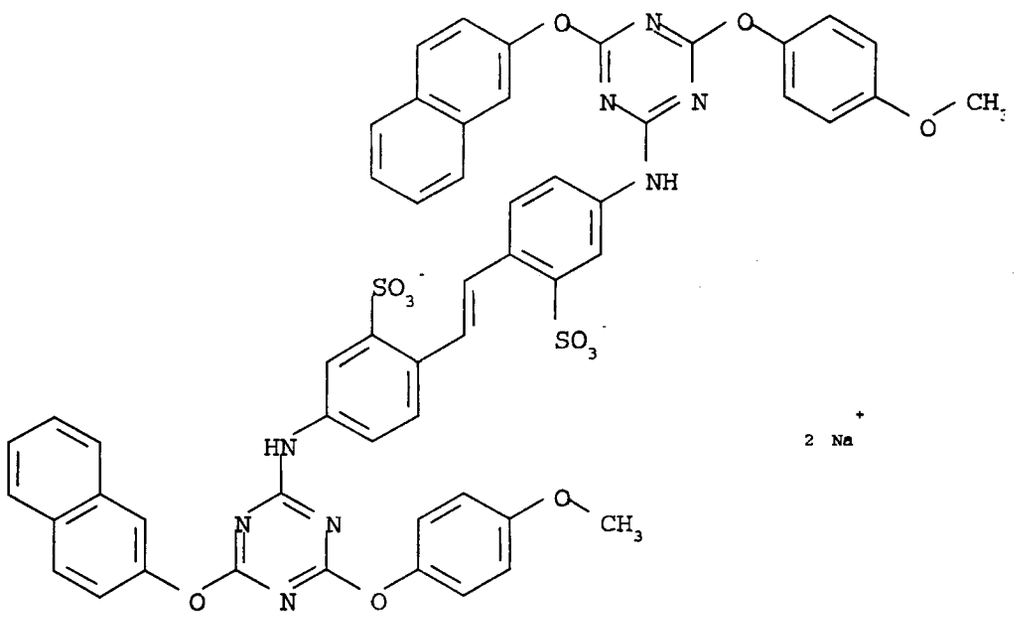
* SS-02:



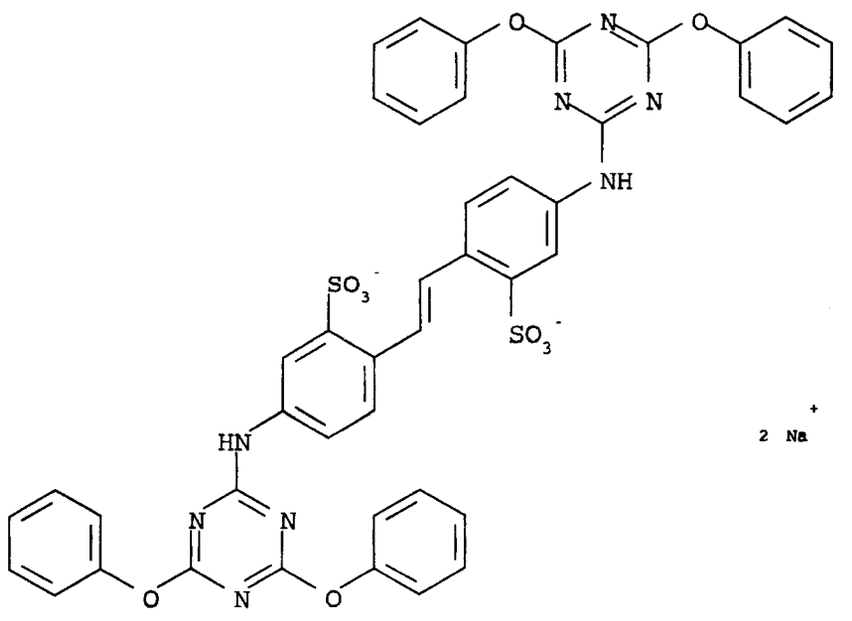
* SS-03:



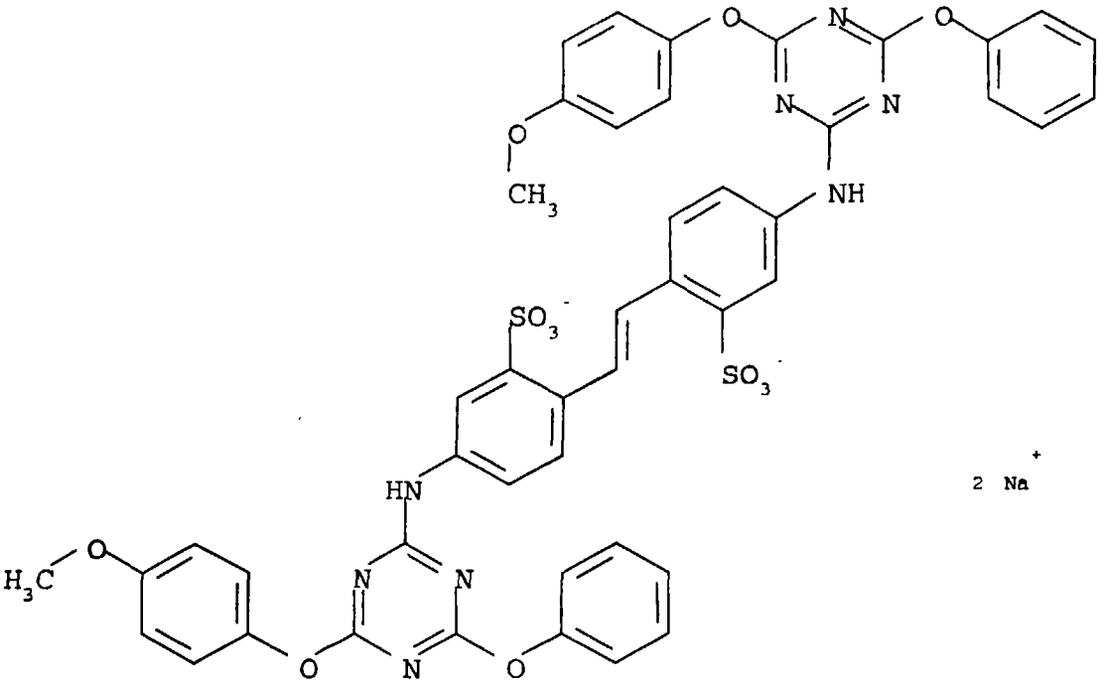
* SS-04:



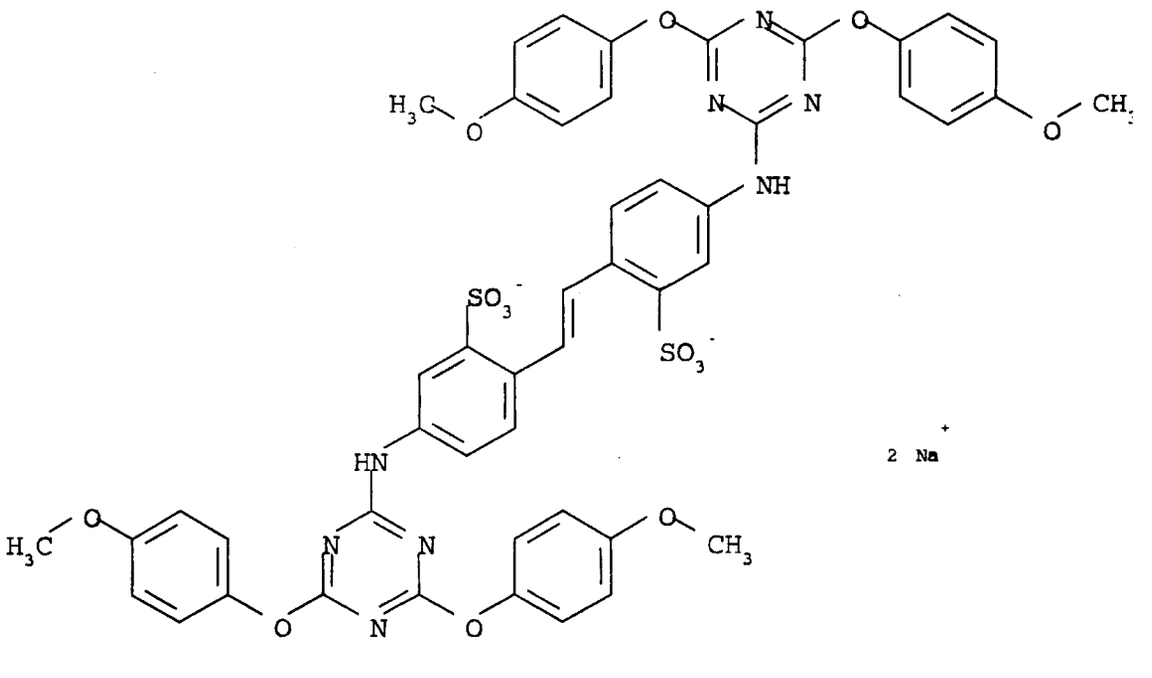
* SS-05:



* SS-06:



* SS-07:



Water-dispersible and water-soluble binders

According to the present invention the photo-addressable thermally developable element includes a binder containing a water-soluble binder, a water-dispersible binder or a mixture of a water soluble binder and a water-dispersible binder. An important prerequisite in the choice of binders and binder-mixtures is their ability to form a continuous layer with the other ingredients present.

The water-dispersible binder can be any water-insoluble polymer e.g. water-insoluble cellulose derivatives, polymers derived from α,β-ethylenically unsaturated compounds such as polyvinyl chloride, after-chlorinated polyvinyl chloride, copolymers of vinyl chloride and vinylidene chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate and partially hydrolyzed polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals that are made from polyvinyl alcohol as starting material in which only a part of the repeating vinyl alcohol units may have reacted with an aldehyde, preferably polyvinyl butyral, copolymers of acrylonitrile and acrylamide, polyacrylic acid esters, polymethacrylic acid esters, polystyrene and polyethylene or mixtures thereof. It should be noted that there is no clear cut transition between a polymer dispersion and a polymer solution in the case of very small polymer particles resulting in the smallest particles of the polymer being dissolved and those slightly larger being in dispersion.

Suitable water-soluble polymers, according to the present invention, are: polyvinyl alcohol, polyacrylamide, polyacrylic acid, polymethacrylic acid, polyethyleneglycol, proteins, such as gelatin and modified gelatins such as phthaloyl gelatin, polysaccharides, such as starch, gum arabic and dextran and water-soluble cellulose derivatives.

To improve the layer-forming properties of water-soluble and water-dispersible polymers, plasticizers can be incorporated into the polymers, water-miscible solvents can be added to the dispersion medium and mixtures of water-soluble polymers, mixtures of water-dispersible polymers, or mixtures of water-soluble and water-dispersible polymers may be used.

Photo-addressable thermally developable element

The photo-addressable thermally developable element, according to the present invention, comprises a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association therewith and an organic reducing agent in thermal working relationship with the substantially light-insensitive organic silver salt and a water soluble or water-dispersible binder. The element may include a layer system with the silver halide in catalytic association with the substantially light-insensitive organic silver salt, spectral sensitizer optionally together with a supersensitizer in intimate sensitizing association with the silver halide particles and the other ingredients active in the thermal development process or pre- or post-development stabilization of the element being in the same layer or in other layers with the proviso that the organic reducing agent and the toning agent, if present, are in thermal working relationship with the substantially light-insensitive organic silver salt i.e. during the thermal development process the reducing agent and the toning agent, if present, are able to diffuse to the substantially light-insensitive organic silver salt.

Light-insensitive organic silver salts

Preferred substantially light-insensitive organic silver salts produced using the process according to the present invention and used in the photothermographic materials, according to the present invention, are silver salts of organic carboxylic acids having as their organic group: aryl, aralkyl, alkaryl or alkyl. For example aliphatic carboxylic acids known as fatty acids, wherein the aliphatic carbon chain has preferably at least 12 C-atoms, e.g. silver laurate, silver palmitate, silver stearate, silver hydroxystearate, silver oleate and silver behenate, which silver salts are also called "silver soaps". Silver salts of modified aliphatic carboxylic acids with thioether group, as described e.g. in GB-P 1,111,492, may likewise be used to produce a thermally developable silver image.

In a preferred embodiment, according to the present invention, the substantially light-insensitive organic silver salt is a silver salt of a fatty acid.

The term substantially light-insensitive organic silver salt for the purposes of the present invention also includes mixtures of organic silver salts.

Binder to organic silver salt ratio

The binder to organic silver salt weight ratio is preferably in the range of 0.2 to 6, and the thickness of the recording layer is preferably in the range of 1 to 50 μm.

Photosensitive silver halide

The photosensitive silver halide used in the present invention may be employed in a range of 0.1 to 35 mol percent

of substantially light-insensitive organic silver salt, with the range of 0.5 to 20 mol percent being preferred and the range of 1 to 12 mol percent being particularly preferred.

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 in any form which is photosensitive including, but not limited to, cubic, orthorhombic, tabular, tetrahedral, octagonal etc. and may have epitaxial growth of crystals thereon.

The silver halide used in the present invention may be employed without modification. However, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulphur, selenium, tellurium etc., or a compound containing gold, platinum, palladium, iron, 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, Macmillan Publishing Co. Inc., New York (1977), Chapter 5, pages 149 to 169.

According to a preferred embodiment used in the present invention, particles of the photosensitive silver halide are non-aggregating in the photo-addressable thermally developable element and are uniformly distributed over and between particles of the substantially light-insensitive organic silver salt, at least 80% by number of the particles having a diameter, determined by transmission electron microscopy, of ≤40nm.

Emulsion of organic silver salt and photosensitive silver halide

According to a process, according to the present invention, the suspension of particles of a substantially light-insensitive organic silver salt may be produced by simultaneous metered addition of an aqueous solution or suspension of an organic carboxylic acid, or its salt, and an aqueous solution of a silver salt to an aqueous liquid and the metered addition of the aqueous solution or suspension of the organic carboxylic acid or its salt; and/or the aqueous solution of the silver salt is regulated by the concentration of silver ions or the concentration of anions of the silver salt in the aqueous liquid as disclosed in EP-A 754 969.

The silver halide may be added to the photo-addressable thermally developable element in any fashion which places it in catalytic proximity to the substantially light-insensitive organic silver salt. Silver halide and the substantially light-insensitive organic silver salt which are separately formed, i.e. ex-situ or "preformed", in a binder can be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them for a long period of time. Furthermore, it is effective to use a process which comprises adding a halogen-containing compound to the organic silver salt to partially convert the substantially light-insensitive organic silver salt to silver halide as disclosed in US-P 3,457,075.

The aqueous emulsion of the organic silver salt optionally including photosensitive silver halide can, according to the present invention, also be produced from particles of the organic silver salt optionally containing photosensitive silver halide by dispersing the particles in water in the presence of non-ionic or anionic surfactants or a mixture of non-ionic and anionic surfactants using any dispersion technique known to one skilled in the art such as ball milling, dispersion in a impingement mill (rotor-stator mixer), dispersion in a microfluidizer etc. A combination of dispersion techniques may also be used, for example using a first technique to produce a predispersion and a second technique to produce a fine dispersion.

Onium halides and polyhalides

According to the present invention photosensitive silver halide particles produced by reacting an aqueous dispersion of particles of the substantially light-insensitive organic silver salt with at least one onium salt with halide or polyhalide anions may be present. Onium cations, according to the present invention, may be polymeric or non-polymeric. Preferred non-polymeric onium salts for partial conversion of particles of substantially light-insensitive organic silver salt into photosensitive silver halides according to the present invention are:

PC01 = 3-(triphenyl-phosphonium)propionic acid bromide perbromide
PC02 = 3-(triphenyl-phosphonium)propionic acid bromide
PC03 = 3-(triphenyl-phosphonium)propionic acid iodide

The onium salts are present in quantities of between 0.1 and 35mol % with respect to the quantity of substantially light-insensitive organic silver salt of organic, with quantities between 0.5 and 20mol% being preferred and with quantities between 1 and 12mol % being particularly preferred.

Organic reducing agent

Suitable organic reducing agents for the reduction of the substantially light-insensitive organic heavy metal salts

are organic compounds containing at least one active hydrogen atom linked to O, N or C. Particularly suitable organic reducing agents for the reduction of the substantially light-insensitive organic silver salt, an organic reducing agent for the substantially light-insensitive organic silver salt are non-sulfo-substituted 6-membered aromatic or heteroaromatic ring compounds with at least three substituents one of which is a hydroxy group at a first carbon atom and a second of which is a hydroxy or amino-group substituted on a second carbon atom one, three or five ring atoms removed in a system of conjugated double bonds from the first carbon atom in the compound, in which (i) the third substituent may be part of an annelated carbocyclic or heterocyclic ring system; (ii) the third substituent or a further substituent is not an aryl- or oxo-aryl-group whose aryl group is substituted with hydroxy-, thiol- or amino-groups; and (iii) the third substituent or a further substituent is a non-sulfo-electron withdrawing group if the second substituent is an amino-group.

Particularly preferred reducing agents are substituted catechols or substitued hydroquinones with 3-(3',4'-dihydroxyphenyl)-propionic acid, 3',4'-dihydroxy-butyrophenone, methyl gallate, ethyl gallate and 1,5-dihydroxy-naphthalene being especially preferred.

During the thermal development process the reducing agent must be present in such a way that it is able to diffuse to the substantially light-insensitive organic silver salt particles so that reduction of the substantially light-insensitive organic silver salt can take place.

Auxiliary reducing agents

The above mentioned reducing agents, regarded as primary or main reducing agents, may be used in conjunction with so-called auxiliary reducing agents. Auxiliary reducing agents that may be used in conjunction with the above mentioned primary reducing agents are sulfonyl hydrazide reducing agents such as disclosed in US-P 5,464,738, trityl hydrazides and formyl-phenyl-hydrazides such as disclosed in US-P 5,496,695 and organic reducing metal salts, e.g. stannous stearate described in US-P 3,460,946 and 3,547,648.

Thermal solvents

The above mentioned binders or mixtures thereof may be used in conjunction with waxes or "heat solvents" also called "thermal solvents" or "thermosolvents" improving the reaction speed of the redox-reaction at elevated temperature.

By the term "heat solvent" in this invention is meant a non-hydrolyzable organic material which is in a solid state in the recording layer at temperatures below 50°C, but becomes a plasticizer for the recording layer where thermally heated and/or a liquid solvent for at least one of the redox-reactants, e.g. the reducing agent for the substantially light-insensitive organic silver salt, at a temperature above 60°C.

Toning agents

In order to obtain a neutral black image tone in the higher densities and neutral grey in the lower densities, photothermographic materials according to the present invention may contain one or more toning agents. The toning agents should be in thermal working relationship with the substantially light-insensitive organic silver salts and reducing agents during thermal processing. Any known toning agent from thermography or photothermography may be used.

Suitable toning agents are succinimide and the phthalimides and phthalazinones within the scope of the general formulae described in US-P 4,082,901 and the toning agents described in US-P 3,074,809, US-P 3,446,648 and US-P 3,844,797. Particularly useful toning agents are the heterocyclic toner compounds of the benzoxazine dione or naphthoxazine dione type as described in GB-P 1,439,478 and US-P 3,951,660.

Stabilizers and antifoggants

In order to obtain improved shelf-life and reduced fogging, stabilizers and antifoggants may be incorporated into the photothermographic materials of the present invention. Examples of suitable stabilizers and antifoggants and their precursors, which can be used alone or in combination, include the thiazolium salts described in US-P 2,131,038 and 2,694,716; the azaindenes described in US-P 2,886,437 and 2,444,605; the urazoles described in US-P 3,287,135; the sulfocatechols described in US-P 3,235,652; the oximes described in GB-P 623,448; the thiuronium salts described in US-P 3,220,839; the palladium, platinum and gold salts described in US-P 2,566,263 and 2,597,915; the tetrazolyl-thio-compounds described in US-P 3,700,457; the mesoionic 1,2,4-triazolium-3-thiolate stablizer precursors described in US-P 4,404,390 and 4,351,896; the tribromomethyl ketone compounds described in EP-A 600 587; the combination of isocyanate and halogenated compounds described in EP-A 600 586; the vinyl sulfone and β-halo sulfone compounds described in EP-A 600 589; and those compounds mentioned in this context in Chapter 9 of "Imaging Processes and Materials, Neblette's 8th edition", by D. Kloosterboer, edited by J. Sturge, V. Walworth and A. Shepp, page 279, Van

Nostrand (1989); in Research Disclosure 17029 published in June 1978; and in the references cited in all these documents.

Surfactants

Non-ionic, cationic or anionic surfactants may be used, according to the present invention, to produce dispersions of particles of the substantially light-insensitive organic silver salt in aqueous media and to disperse water-dispersible binders, such as polymer latexes, in aqueous media. In a preferred embodiment used in the present invention the surfactant is a sulfonate e.g. alkyl, aryl, alkaryl or aralkyl sulfonate, with alkyl and alkaryl sulfonates being particularly preferred e.g.:

MERSOLAT™ H, a sodium salt of an alkyl sulfonate from BAYER
ULTRAVON™ W, a sodium salt of an aryl sulfonate from CIBA-GEIGY

Additional ingredients

In addition to the ingredients the photothermographic material may contain other additives such as free organic carboxylic acids, surface-active agents, antistatic agents, e.g. non-ionic antistatic agents including a fluorocarbon group as e.g. in $F_3C(CF_2)_6CONH(CH_2CH_2O)$-H, silicone oil, e.g. BAYSILONE ÖI A (tradename of BAYER AG - GERMANY), ultraviolet light absorbing compounds, white light reflecting and/or ultraviolet radiation reflecting pigments, silica, and/or optical brightening agents.

Antihalation dyes

According to a preferred embodiment of the present invention, the photothermographic recording material further comprises an antihalation or acutance dye which absorbs light which has passed through the photosensitive layer, thereby preventing its reflection. Such dyes may be incorporated into the photo-addressable thermally developable element or in any other layer comprising the photothermographic recording material of the present invention. The antihalation dye may also be bleached either thermally during the thermal development process or photo-bleached after removable after the thermal development process and it may be contained in a layer which can be removed subsequent to the exposure process. Suitable antihalation dyes for use with infra-red light are described in the EP-A's 377 961 and 652 473, the EP-B's 101 646 and 102 781 and the US-P's 4,581,325 and 5,380,635.

Support

The support for the photothermographic recording material according to the present invention may be transparent, translucent or opaque, e.g. having a white light reflecting aspect and is preferably a thin flexible carrier made e.g. from paper, polyethylene coated paper or transparent resin film, e.g. made of a cellulose ester, e.g. cellulose triacetate, corona and flame treated polypropylene, polystyrene, polymethacrylic acid ester, polycarbonate or polyester, e.g. polyethylene terephthalate or polyethylene naphthalate as disclosed in GB 1,293,676, GB 1,441,304 and GB 1,454,956. For example, a paper base substrate is present which may contain white reflecting pigments, optionally also applied in an interlayer between the recording material and the paper base substrate.

The support may be in sheet, ribbon or web form and subbed if needs be to improve the adherence to the thereon coated heat-sensitive recording layer.

Suitable subbing layers for improving the adherence of the thermosensitive element and the antistatic layer outermost backing layer of the present invention for polyethylene terephthalate supports are described e.g. in GB-P 1,234,755, US-P 3,397,988; 3,649,336; 4,123,278 and US-P 4,478,907 which relates to subbing layers applied from aqueous dispersion of sulfonated copolyesters, and further the subbing layers described in Research Disclosure published in Product Licensing Index, July 1967, p. 6.

Suitable pretreatments of hydrophobic resin supports are, for example, treatment with a corona discharge and/or attack by solvent(s), thereby providing a micro-roughening.

Protective layer

According to a preferred embodiment of the photothermographic recording material of the present invention, the photo-addressable thermally developable element is provided with a protective layer.

The protective layer preferably comprises a binder, which may be solvent soluble (hydrophobic), solvent dispersible, water soluble (hydrophilic) or water dispersible. Among the hydrophobic binders polycarbonates as described in

EP-A 614 769 are particularly preferred. Suitable hydrophilic binders are, for example, gelatin, polyvinylalcohol, cellulose derivatives or other polysaccharides, hydroxyethylcellulose, hydroxypropylcellulose etc., with hardenable binders being preferred and polyvinyl alcohol being particularly preferred.

A protective layer used in the present invention may be crosslinked. Crosslinking can be achieved by using crosslinking agents such as described in WO 95/12495 for protective layers.

A protective layer used in the present invention may include in addition at least one solid lubricant having a melting point below 150°C and at least one liquid lubricant in a binder, wherein at least one of the lubricants is a phosphoric acid derivative, further dissolved lubricating material and/or particulate material, e.g. talc particles, optionally protruding from the outermost layer. The lubricant may be applied with or without a polymeric binder.

Such protective layers may also include particulate material, e.g. talc particles, optionally protruding from the protective outermost layer as described in WO 94/11198. Other additives can also be incorporated in the protective layer e.g. colloidal particles such as colloidal silica.

Antistatic layer

In a preferred embodiment the recording material of the present invention an antistatic layer is applied to the outermost layer on the side of the support not coated with the photo-addressable thermally developable element. Suitable antistatic layers therefor are described in EP-A's 444 326, 534 006 and 644 456, US-P's 5,364,752 and 5,472,832 and DOS 4125758.

Coating techniques

The coating of any layer of the photothermographic materials of the present invention may proceed by any coating technique e.g. such as described in Modern Coating and Drying Technology, edited by Edward D. Cohen and Edgar B. Gutoff, (1992) VCH Publishers Inc. 220 East 23rd Street, Suite 909 New York, NY 10010, U.S.A.

Recording process

Photothermographic materials, according to the present invention, may be exposed with infrared radiation with the image either being obtained by pixel-wise exposure with a finely focussed light source, such as an IR wavelength laser or an IR-laser diode, e.g. emitting at 780nm, 830nm or 850nm; or by direct exposure to the object itself or an image therefrom with IR light.

For the thermal development of image-wise exposed photothermographic recording materials, according to the present invention, any sort of heat source can be used that enables the recording materials to be uniformly heated to the development temperature in a time acceptable for the application concerned e.g. contact heating, radiative heating, microwave heating etc.

According to the present invention a photothermographic recording process is also provided comprising the steps of: (i) image-wise exposing a photothermographic recording material, as referred to above, with actinic radiation to which the photothermographic recording material is sensitive; and (ii) thermally developing the image-wise exposed photothermographic recording material.

Applications

The photothermographic recording materials of the present invention can be used for both the production of transparencies and reflection type prints. This means that the support will be transparent or opaque, e.g. having a white light reflecting aspect. For example, a paper base substrate is present which may contain white reflecting pigments, optionally also applied in an interlayer between the recording material and the paper base substrate. Should a transparent base be used, the base may be colourless or coloured, e.g. has a blue colour.

In the hard copy field photothermographic recording materials on a white opaque base are used, whereas in the medical diagnostic field black-imaged transparencies are widely used in inspection techniques operating with a light box.

The following ingredients in addition to those mentioned above were used in the photothermographic recording materials of the examples and comparative examples illustrating this invention:

the following supersensitizers according to EP-A 559 228:

SS C01: 2-mercaptobenzimidazole;

SS C02: 2-mercaptobenzothiazole-5-[N-(4'-chlorophenyl)]sulfonamide;

and the latex binder:

BINDER 01: copolymer consisting of 45% by weight of methylmethacrylate, 45% by weight of butadiene and 10% by weight of itaconic acid.

The following examples and comparative examples illustrate the present invention. The percentages and ratios used in the examples are by weight unless otherwise indicated.

COMPARATIVE EXAMPLES 1 to 22

Extrapolation of the state of the art concerning photothermographic materials with IR-spectral sensitizers and heteroaromatic mercapto supersensitizers as disclosed in EP-A 559 228 to photothermographic recording materials comprising photo-addressable thermally developable elements coated from aqueous media:

Silver behenate dispersion

Silver behenate was prepared by dissolving 34g (0.1 moles) of behenic acid in 340mL of 2-propanol at 65°C, converting the behenic acid to sodium behenate by adding 400mL of 0.25M aqueous sodium hydroxide to the stirred behenic acid solution and finally adding 250mL of 0.4M aqueous silver nitrate the silver behenate precipitating out. This was filtered off and then washed with a mixture of 10% by volume of 2-propanol and 90% by volume of deionized water to remove residual sodium nitrate.

After drying at 45°C for 12h. the silver behenate was dispersed in deionized water with the anionic dispersion agents Ultravon™ W and Mersolat™ H to produce, after rapid mixing using a high speed impingement mill (rotor-stator mixer) to obtain a paste and homogenization with a microfluidizer, a finely divided and stable dispersion containing 20% by weight of silver behenate, 2.1% by weight of Ultravon™ W and 0.203% by weight of Mersolat™ H. The pH of the resulting dispersion was adjusted to about 6.5.

Photothermographic emulsion

The following ingredients were then added with stirring to 3.0g of the silver behenate dispersion: 2g of a 2.22% by weight aqueous solution of 3-(triphenyl-phosphonium)propionic acid bromide (PC02), corresponding to a concentration of 8 mol% of PC02 with respect to silver behenate, at a pH of 4 to accomplish in situ conversion of part of the silver behenate to silver bromide. After 10 minutes further stirring, the supersensitizer was added with stirring as a solution in water and/or methanol, as specified in table 1, immediately followed by the IR-spectral sensitizer as a solution or dispersion in water and/or methanol as specified in table 1. After stirring for a further 15 minutes 2g of a 30% by weight concentration of BINDER 01 at a pH of 4 was added with stirring followed by 2g of a 4.5% by weight aqueous solution of 3-(3',4'-dihydroxyphenyl)propionic acid.

Table 1

Comparative example number	IR-sensitizer			supersensitizer		
	code	Weight of solution [g]	Conc. of solution [% by wt]	code	Weight of solution [g]	Conc. of solution [% by wt]
1	SENSI 01	0.81	0.05 (MeOH)	-	-	-
2	SENSI 01	1.10	0.05 (MeOH)	SS-C01	0.3	2 (MeOH)
3	SENSI 01	1.20	0.05 (MeOH)	SS-C02	1.0	1 (MeOH)
4	SENSI 02	0.046	0.3 (MeOH)	-	-	-
5	SENSI 02	0.046	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
6	SENSI 02	0.110	0.3 (MeOH)	SS-C02	0.8	1 (MeOH)
7	SENSI 02	0.110	0.3 (MeOH)	-	-	-
8	SENSI 02	0.110	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
9	SENSI 02	0.180	0.3 (MeOH)	-	-	-
10	SENSI 02	0.180	0.3 (MeOH)	SS-C02	0.8	1 (MeOH)
11	SENSI 02	0.180	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
12	SENSI 03	0.046	0.3 (MeOH)	-	-	-
13	SENSI 03	0.046	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
14	SENSI 03	0.110	0.3 (MeOH)	-	-	-
15	SENSI 03	0.110	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
16	SENSI 07	0.046	0.3 (MeOH)	-	-	-
17	SENSI 07	0.046	0.3 (MeOH)	SS-C02	0.4	1 (MeOH)
18	SENSI 08	0.180	0.3 (MeOH)	-	-	-
19	SENSI 08	0.180	0.3 (MeOH)	SS-C01	0.2	2 (MeOH)
20	SENSI 09	0.270	0.2 (MeOH)	-	-	-
21	SENSI 09	0.270	0.2 (MeOH)	SS-C01	0.4	2 (MeOH)
22	SENSI 09	0.270	0.2 (MeOH)	SS-C02	0.8	1 (MeOH)

Coating and drying of the photothermographic material

A subbed polyethylene terephthalate support having a thickness of 100μm was doctor blade-coated with the silver behenate/silver bromide dispersion at a blade setting of 90μm. After drying for several minutes at 40°C on the coating bed, the emulsion layer was dried for 1 hour in a hot air oven at 40°C.

Image-wise exposure and thermal processing

The photothermographic materials of COMPARATIVE EXAMPLES 1 to 22 were exposed to a beam of a 836nm diode laser type HL 8318G from HITACHI with a nominal power of 12.8mW focussed to give a spot diameter ($1/e^2$) of 115μm, scanned at a speed of 5m/s with a pitch of 63μm and an overlap of 30% through a wedge filter with optical density varying between 0 and 3.3 in optical density steps of 0.15. The maximum exposure (filter optical density = 0) was about $50J/m^2$.

Thermal processing was carried out on a heated metal block for 5 to 30s at 105 to 115°C, as specified in table 2. The maximum and minimum optical densities, D_{max} and D_{min}, of the images were measured in transmission with a MacBeth™ TR924 densitometer through a visible filter.

The D_{max}- and D_{min}-values obtained upon the image-wise exposure and thermal processing of the photothermographic materials of COMPARATIVE EXAMPLES 1 to 22 together with the IR-sensitizer, supersensitizer, molar ratio of supersensitizer to IR-sensitizer and thermal processing conditions used are summarized in table 2.

The results obtained with 5 different IR-sensitizers and 2 different mercapto-sensitizers at molar ratios of supersensitizer to IR-sensitizer between 13 and 74 demonstrate at best only a moderate degree of supersensitization showing that an extrapolation of the state of the art to photothermographic recording materials comprising photo-addressable thermally developable elements coated from aqueous media is by no means evident.

Table 2

Comparative example number	IR-sensitizer code	supersensitizer code	moles supersensitizer/mol IR-sensitizer	thermal processing conditions			
				temperature [°C]	time [s]	D_{max}	D_{min}
1	SENSI 01	-	-	105	10	0.13	0.13
2	SENSI 01	SS-C01	45 : 1	105	10	0.13	0.13
3	SENSI 01	SS-C02	29 : 1	105	10	0.63	0.08
4	SENSI 02	-	-	105	15	0.27	0.27
5	SENSI 02	SS-C02	49 : 1	105	15	0.22	0.22
6	SENSI 02	SS-C02	41 : 1	105	15	0.49	0.14
7	SENSI 02	-	-	105	15	0.40	0.40
8	SENSI 02	SS-C02	21 : 1	105	15	0.40	0.21
9	SENSI 02	-	-	105	15	0.30	0.30
10	SENSI 02	SS-C02	25 : 1	105	15	0.89	0.12
11	SENSI 02	SS-C02	13 : 1	105	15	0.34	0.18
12	SENSI 03	-	-	105	15	0.15	0.15
13	SENSI 03	SS-C02	66 : 1	105	15	0.15	0.15
14	SENSI 03	-	-	105	15	0.15	0.15
15	SENSI 03	SS-C02	27 : 1	105	15	0.15	0.15
16	SENSI 07	-	-	105	15	0.25	0.25
17	SENSI 07	SS-C02	75 : 1	105	15	0.25	0.25
18	SENSI 08	-	-	105	15	0.20	0.20
19	SENSI 08	SS-C01	37 : 1	105	15	0.24	0.14
20	SENSI 09	-	-	105	15	0.25	0.25
21	SENSI 09	SS-C01	73 : 1	105	15	0.13	0.13
22	SENSI 09	SS-C02	31 : 1	105	15	0.65	0.12

INVENTION EXAMPLES 1 to 12 and COMPARATIVE EXAMPLES 23 to 25

Photothermographic recording materials comprising photo-addressable thermally developable elements with IR-sensitizers and stilbene supersensitizers coated from aqueous media:

The photothermographic emulsions of INVENTION EXAMPLES 1 to 12 and COMPARATIVE EXAMPLES 23 to 25 were prepared as described for COMPARATIVE EXAMPLES 1 to 22 except that the IR-sensitizer, IR-sensitizer solution or dispersion, weight of IR-sensitizer solution or dispersion, supersensitizer, supersensitizer solution and weight of supersensitizer solution used for each photothermographic emulsion is as given in table 3.

Table 3

Invention example number	IR-sensitizer			supersensitizer		
	code	Weight of solution [g]	Conc. of solution [% by wt]	code	Weight of solution [g]	Conc. of solution [% by wt]
1	SENSI 01	1.10	0.05 (MeOH)	SS-01	1.25	0.25 (MeOH)
2	SENSI 01	0.16	0.46 (H_2O*)	SS-01	1.3	0.25 (MeOH)
3	SENSI 01	1.10	0.05 (MeOH)	SS-02	1.3	0.25 (MeOH)
4	SENSI 01	1.10	0.05 (MeOH)	SS-03	1.3	0.25 (MeOH)
5	SENSI 01	1.10	0.05 (MeOH)	SS-04	1.3	0.25 (MeOH)
6	SENSI 01	1.10	0.05 (MeOH)	SS-06	0.36	0.9 (MeOH)
7	SENSI 01	1.10	0.05 (MeOH)	SS-07	0.46	0.7 (MeOH)
8	SENSI 02	0.18	0.3 (MeOH)	SS-01	1.2	0.25 (MeOH)
9	SENSI 03	0.18	0.3 (MeOH)	SS-01	1.2	0.25 (MeOH)
10	SENSI 07	0.046	0.3 (MeOH)	SS-01	1.2	0.25 (MeOH)
11	SENSI 09	0.070	0.2 (MeOH)	SS-01	1.2	0.25 (MeOH)
12	SENSI 10	0.046	0.3 (MeOH)	SS-01	1.2	0.25 (MeOH)
Comparative example number						
1	SENSI 01	0.81	0.05 (MeOH)	-	-	-
9	SENSI 02	0.18	0.3 (MeOH)	-	-	-
23	SENSI 03	0.18	0.3 (MeOH)	-	-	-
16	SENSI 07	0.046	0.3 (MeOH)	-	-	-
24	SENSI 09	0.070	0.2 (MeOH)	-	-	-
25	SENSI 10	0.046	0.3 (MeOH)	-	-	-

* dispersion with ULTRAVON™ W as surfactant

The photothermographic emulsions of INVENTION EXAMPLES 1 to 12 and COMPARATIVE EXAMPLES 23 to 25 were coated as described for COMPARATIVE EXAMPLES 1 to 22 and then image-wise exposed, thermally processed and the resulting images evaluated as also described for COMPARATIVE EXAMPLES 1 to 22.

The D_{max}- and D_{min}-values obtained upon the image-wise exposure and thermal processing of the photothermographic materials of INVENTION EXAMPLES 1 to 12 and COMPARATIVE EXAMPLES 23 to 25 together with the IR-sensitizer, supersensitizer, molar ratio of supersensitizer to IR-sensitizer and thermal processing conditions used are summarized in table 4. The corresponding data for COMPARATIVE EXAMPLES 1, 9 and 16 are included in table 4 for the sake of comparison.

Table 4

Invention example number	IR-sensitizer code	supersensitizer code	moles supersensitizer/mol IR-sensitizer	thermal processing conditions			
				temperature [°C]	time [s]	D_{max}	D_{min}
1	SENSI 01	SS-01	3 : 1	105	20	1.52	0.15
2	SENSI 01	SS-01	2.4:1	105	15	1.65	0.17
3	SENSI 01	SS-02	3 : 1	105	15	1.21	0.17
4	SENSI 01	SS-03	4 : 1	105	15	0.98	0.17
5	SENSI 01	SS-04	3 : 1	105	15	1.21	0.18
6	SENSI 01	SS-06	4 : 1	105	15	0.60	0.16
7	SENSI 01	SS-07	4 : 1	105	15	0.95	0.18
8	SENSI 02	SS-01	3 : 1	105	15	1.59	0.17
9	SENSI 03	SS-01	4 : 1	105	15	0.75	0.15
10	SENSI 07	SS-01	18 : 1	105	15	0.58	0.15
11	SENSI 09	SS-01	14 : 1	105	15	1.20	0.13
12	SENSI 10	SS-01	14 : 1	105	15	1.49	0.12
Comparative example number							
1	SENSI 01	-	-	105	10	0.13	0.13
9	SENSI 02	-	-	105	15	0.30	0.30
23	SENSI 03	-	-	105	15	0.15	0.15
16	SENSI 07	-	-	105	15	0.25	0.25
24	SENSI 09	-	-	105	15	0.21	0.21
25	SENSI 10	-	-	105	15	0.14	0.14

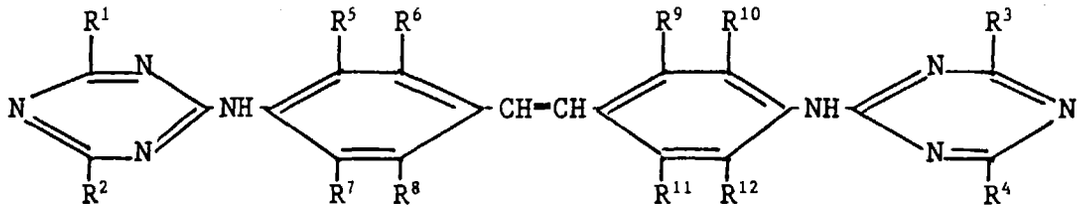
The results obtained with 6 different IR-sensitizers and 5 different stilbene-supersensitizers at molar ratios of supersensitizer to IR-sensitizer between 3 and 18 for photothermographic recording materials comprising photo-addressable thermally developable elements coated from aqueous media show a much superior supersensitization performance compared with corresponding materials using mercapto-supersensitizers. This is at total variance with the results cited in EP-A 559 228, which showed that mercaptosupersensitizers exhibited excellent supersensitizing properties in photothermographic materials, whereas a stilbene supersensitizer, Leucophor BCF from SANDOZ evaluated in COMPARATIVE EXAMPLE G exhibited an absence of supersensitization. This confirms the fundamental difference between supersensitization in photo-addressable thermally developable elements coated from aqueous media and supersensitization in photo-addressable thermally developable elements coated from organic solvent media.

Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the following claims.

Claims

1. A photothermographic recording material comprising a photo-addressable thermally developable element comprising a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with said substantially light-insensitive organic silver salt and spectrally sensitized to infrared light with a dye, a supersensi-

tizer for said dye, a reducing agent in thermal working relationship with said substantially light-insensitive organic silver salt and a binder, characterized in that said binder comprises a water soluble polymer, a water-dispersible polymer or a water soluble polymer and a water-dispersible polymer; said dye absorbs electromagnetic radiation in the wavelength range from 700 to 1100nm; and said supersensitizer is a stilbene compound represented by general formula (I):

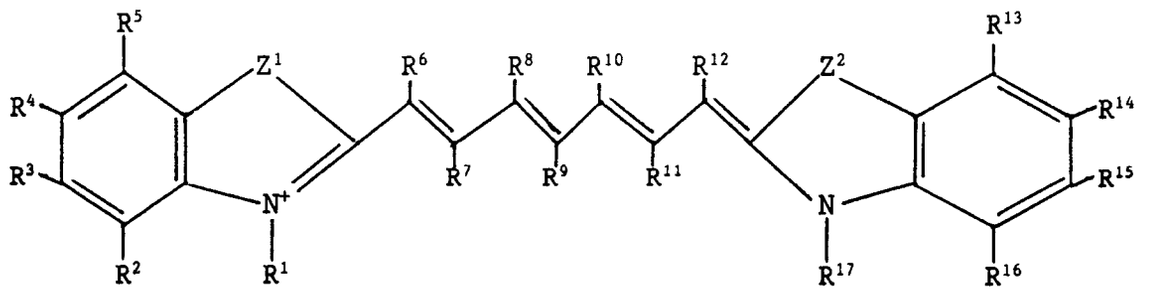


wherein R^1, R^2, R^3 and R^4 are independently hydrogen or alkyl, aryl, aralkyl, alkaryl, alkoxy or aryloxy groups, which may all be substituted; and R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are independently hydrogen and alkyl, substituted alkyl, alkoxy, substituted alkoxy, carboxy or sulfo groups.

2. Photothermographic recording material according to claim 1, wherein said stilbene is represented by general formula (I) in which at least two of R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are sulfo- or carboxy-groups.

3. Photothermographic recording material according to claim 1 or 2, wherein said dye is a near infrared dye which absorbs light in the wavelength range from 750 to 950nm.

4. Photothermographic recording material according to any of the preceding claims, wherein said dye corresponds to the general formula (II):



wherein Z^1 and Z^2 independently represent S, O or Se; R^1 and R^{17} are independently each an alkyl or substituted alkyl group; R^2, R^3, R^4, R^5, R^{13}, R^{14}, R^{15} and R^{16} are independently each hydrogen, chlorine, bromine, fluorine or a keto-, sulfo-, carboxy-, ester-, sulfonamide-, amide-, dialkylamino, nitro-, cyano-, alkyl-, alkenyl-, hetero-aromatic, aryl-, alkoxy- or aryloxy- group, which groups may be substituted; or each of R^2 together with R^3, R^3 together with R^4, R^4 together with R^5, R^{13} together with R^{14}, R^{14} together with R^{15} and R^{15} together with R^{16} may independently constitute the atoms necessary to complete a benzene ring which may be substituted; R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} independently each represent hydrogen, an alkyl group, a substituted alkyl group, chlorine, fluorine, bromine, iodine, a disubstituted amino group, wherein said substituents may constitute the atoms necessary to form a 5-ring atom or 6-ring atom heterocyclic ring, or each of R^6 together with R^8, R^8 together with R^{10}, $R^{1\circ}$ together with R^{12}, R^7 together with R^9 and R^9 together with R^{11} may independently constitute the atoms necessary to complete a 5-atom or 6-atom carbocyclic or heterocyclic ring which may be substituted; each of R^1 together with R^6 and R^{12} together with R^{17} may independently constitute the atoms necessary to complete a 5-atom or 6-atom heterocyclic ring which may be substituted; and X^- represents an anion.

5. Photothermographic recording material according to claim 4, wherein in said general formula (II) R^1 and R^{17} each independently represent an alkyl group consisting of 1 to 6 carbon atoms which may be substituted with a sulfo- or a carboxy-group.

6. Photothermographic recording material according to any of the preceding claims, wherein said photothermographic recording material further comprises an antihalation dye.

7. Photothermographic recording material according to any of the preceding claims, wherein said photo-addressable thermally developable element is provided with a protective layer.

8. Photothermographic recording material according to any of the preceding claims, wherein said substantially light-insensitive organic silver salt is a silver salt of a fatty acid.

9. A process for producing a photothermographic recording material, according to any of claims 1 to 8, comprising the steps of: (i) producing an aqueous dispersion or aqueous dispersions comprising said substantially light-insensitive organic silver salt, said photosensitive silver halide spectrally sensitized to infra-red light with said dye, said super-sensitizer for said dye, said reducing agent and said binder; (ii) coating said aqueous dispersion or aqueous dispersions onto a support.

10. A recording process for a photothermographic recording material comprising the steps of: imagewise exposing to infrared actinic radiation a photothermographic material according to any of claims 1 to 8 or produced according to claim 9; and overall heating of said photothermographic recording material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 1904

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,X	DATABASE WPI Section PQ, Week 8810 Derwent Publications Ltd., London, GB; Class P83, AN 88-068085 XP002043732 & JP 63 023 145 A (FUJI PHOTO FILM CO LTD) , 30 January 1988 * abstract * ---	1-10	G03C1/498 G03C5/16 G03C1/28
D,A	EP 0 559 228 A (MINNESOTA MINING & MFG) 8 September 1993 * page 2, line 38 - page 6, line 25 * * page 11, line 55 - line 58 * ---	1-10	
A	DATABASE WPI Section PQ, Week 8641 Derwent Publications Ltd., London, GB; Class P83, AN 86-267419 XP002024492 & JP 61 193 142 A (KURARAY KK) , 27 August 1986 * abstract * ---	1,10	
A	JP 58 028 737 A (KONISHIROKU PHOTO KK) 19 February 1983 * the whole document * & Derwent Abstract AN83-30920K ---	1,10	
A	J.A. VERDONE ET AL: "POLYMERIC BINDERS FOR PHOTOTHERMOGRAPHIC MATERIALS" RESEARCH DISCLOSURE, no. 186, October 1979, HAVANT GB, page 573 XP002024491 * the whole document * --- -/--	1,10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 October 1997	Bolger, W

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

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 1904

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)
A	EP 0 609 571 A (AGFA GEVAERT NV) 10 August 1994 * page 3, line 51 - page 4, line 11; claims 1-5 * -----	1,5,6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 October 1997	Bolger, W

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

EPO FORM 1503 03.82 (P04C01)