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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G03C 1/498	A1	(11) International Publication Number: WO 97/48015
		(43) International Publication Date: 18 December 1997 (18.12.97)

(21) International Application Number: PCT/EP96/02580

(22) International Filing Date: 13 June 1996 (13.06.96)

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(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: PHOTOTHERMOGRAPHIC RECORDING MATERIAL

(57) Abstract

A photothermographic recording material comprising a photo-addressable thermally developable element coatable from aqueous media comprising a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the substantially light-insensitive organic silver salt and 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 mixture of a water-soluble polymer and a water-dispersible polymer and 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 ≤ 40 nm; and a recording process therefor.

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PHOTOTHERMOGRAPHIC RECORDING MATERIAL

DESCRIPTION

Field of the invention

The present invention relates to a photothermographic recording material with very fine uniformly distributed silver halide particles.

Background of the invention.

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

3. Imagewise transfer of an ingredient necessary for the chemical or physical process bringing about changes in colour or optical density to a receptor element containing other of the ingredients necessary for the chemical or physical process followed by uniform heating to bring about the changes in colour or optical density.

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 can be rendered photothermographic by incorporating a photosensitive agent 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.

US-P 3,457,075 discloses a sheet material useful in imaging by a process involving exposure to a light-image followed by uniform heating and including a stratum containing (a) photosensitive silver halide catalyst-forming means and (b) heat-sensitive reactant image-forming means including (1) a water-insoluble silver salt of a long chain fatty acid as an oxidizing agent, and (2) a reducing agent for silver ion, the oxidation-reduction reaction of which to produce a visible change is accelerated by the catalyst; the stratum being further characterized in that a sufficient quantity, of at least about one-fourth mol percent based on the fatty acid silver salt, of

the photosensitive means is in cataytic proximity with a sufficient proportion of the heat-sensitive means to provide a gamma infinity value of at least about 0.5 when the stratum is exposed image-wise to the light-image and the image is then developed by uniform heating and wherein the manufacture method for the sheet material comprises mixing with the fatty acid silver salt a source of halide ions under conditions permitting reaction therebetween with formation of the silver halide catalyst-forming means. As sources of halide ions for the conversion of organic silver salts to silver halides GB 1,547,326 lists: inorganic halides, halogen-containing metal complexes, onium halides (for example quaternary ammonium halides, quaternary phosphonium halides and ternary sulfonium halides), halogenated hydrocarbons, N-halo compounds and other halogen-containing compounds.

The standard teaching over such photothermographic materials based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt is that the organic silver salt is formed, optionally in the presence of ex situ formed silver halide, in an aqueous medium and is precipitated and dried before dispersion in an organic solvent medium from which the dispersion is coated, the silver halide either being prepared ex situ, and either added to a dispersion of the organic silver salt as described in US-P 3,080,254 or being present during the formation of the organic silver salt as disclosed in US-P 3,839,049, or being prepared in situ from the organic silver salt by reaction with a halide ion source as disclosed in US-P 3,457,075. In the latter case reaction of organic silver salt with a halide ion source, which can be inorganic or organic, occurs after the dispersion of the organic silver salt in a solvent medium and hence the reaction takes place in a non-aqueous medium. Photothermographic materials using silver behenate/silver halide dispersions produced by forming silver behenate in the present of 50nm particles of silver halide as disclosed in US-P 3,839,049 require about 10mol% of silver halide for optimal photosensitivity.

This production method is very inefficient as the organic silver salt after formation in water has to be separated and dried before dispersion in a solvent medium, is environmentally unsound as evaporation of solvent takes place during the coating process and it involves lengthy utilization of plant during the preparation of the organic silver salt dispersion and coating requires costly plant due

to the need for solvent explosion prevention measures and solvent recovery to prevent solvent emission to the environment.

Furthermore, it is desirable spectrally to sensitize photosensitive silver halide in aqueous media as this permits the use of a broader range of spectrally sensitizing dyes.

Despite forty years of continuous research in this area, a production method for photothermographic materials based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt which dispenses with these disadvantages of the current teaching, has to our knowledge not yet been developed.

WO 94/16361 discloses a multilayer heat-sensitive material for direct thermal recording for which no intermediate drying of organic noble metal salts is necessary and which is coatable from aqueous dispersions. This material comprises: a colour-forming amount of finely divided, solid colourless noble metal or iron salt of an organic acid distributed in a carrier composition; a color-developing amount of a cyclic or aromatic organic reducing agent, which at thermal copy and printing temperatures is capable of a colour-forming reaction with the noble metal or iron salt; and an image toning agent; characterized in that (a) the carrier composition comprises a substantially water-soluble polymeric carrier and a dispersing agent for the noble metal or iron salt and (b) the material comprises a protective overcoating layer for the colour-forming layer. However, this material suffers from poor stability both before and after image formation.

A further desirable aim is to reduce the amount of photosensitive silver halide necessary to achieve the required photosensitivity in photothermographic materials based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt. This would increase the intrinsic stability of such materials and hence their photosensitivity (or the amount of silver halide necessary to attain the same photosensitivity), since this reduces the amount of stabilizer necessary to achieve acceptable pre- and post-exposure stability and hence the degree of stabilizer-induced photo-sensitivity loss.

Objects of the invention.

It is therefore a first object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element for a photothermographic material with excellent image-forming properties.

It is therefore a second object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt, which is produceable without necessitating intermediate drying of the organic silver salt.

It is therefore another object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt, which is coatable from an aqueous medium.

It is a further object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the organic silver salt and a reducing agent for the organic silver salt requiring lower quantities of silver halide to achieve an acceptable photosensitivity.

It is a still further object of the invention to provide a recording process for a thermographic 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

Despite the general rule in silver halide photography that photosensitivity of a photographic material increases with increasing size of the silver halide crystals (as disclosed for example by A.P.H. Trivelli and W.F. Smith in 1939 in Photographic Journal, volume 79 in papers beginning on pages 330, 463 and 609 and in 1940 in Photographic Journal, volume 80 in a paper beginning on

page 361 as cited on page 100 of "The Theory of the Photographic Process", Fourth Edition, edited by T.H. James and published in 1977 by Macmillan Publishing Co., Inc., New York) it has been surprisingly found that the photosensitivity of photothermographic materials of the present invention has been found to increase with decreasing silver halide crystal size at least down to diameters of 10nm as shown by the reduced quantity of silver halide needed to obtain an acceptable image density under the same exposure and development conditions.

According to the present invention a photothermographic recording material is provided 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 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 mixture of a water soluble polymer and a water-dispersible polymer and particles of the photosensitive silver halide which 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.

According to the present invention a recording process is also provided comprising the steps of: (i) providing 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 a reducing agent in thermal working relationship with the substantially light-insensitive organic silver salt and a binder; (ii) bringing the recording material into the proximity of a source of actinic radiation to which it is sensitive; (iii) image-wise exposing the recording material to the actinic radiation; (iv) bringing the image-wise exposed recording material into proximity with a heat source; (v) thermally developing the image-wise exposed recording material; and (vi) removing the thermally developed image-wise exposed recording material from the heat source, characterized in that the binder comprises a water soluble polymer, a water-

dispersible polymer or a mixture of a water soluble polymer and a water-dispersible polymer and 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.

Detailed description of the invention.

The invention is described hereinafter by way of examples with reference to the accompanying figures wherein :

FIGURE 1: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of invention example 1;

FIGURE 2: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of invention example 3;

FIGURE 3: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 4;

FIGURE 4: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 6;

FIGURE 5: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 17;

FIGURE 6: shows a transmission electron micrograph at a magnification of 150,000x of the silver behenate/silver iodide dispersion produced in the course of the

preparation of the material of invention example 6; and

FIGURE 7: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of comparative example 1.

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.

Photosensitive silver halide particles

According to the present invention, the photo-addressable thermally developable element comprises a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association with the substantially light-insensitive organic silver salt and a reducing agent in thermal working relationship with the substantially light-insensitive organic silver salt and a binder, characterized in that particles of the photosensitive silver halide are non-aggregated and are uniformly distributed over and between particles of the substantially light-insensitive organic silver salt, with at least 80% of the particles having a diameter, determined by transmission electron microscopy, of ≤40nm.

In a preferred embodiment of the present invention at least 80% by number of the photosensitive silver halide particles have a diameter, determined by transmission electron microscopy, of ≤25nm.

In another preferred embodiment of the present invention at least 90% by number of the photosensitive silver halide particles have a diameter, determined by transmission electron microscopy, of ≤40nm.

In a particularly preferred embodiment of the present invention at least 90% by number of the photosensitive silver halide particles have a diameter, determined by transmission electron microscopy, of ≤25nm.

One method of achieving particles of the photosensitive silver halide which are non-aggregated and are uniformly distributed over and between particles of the substantially light-insensitive organic silver salt with at least 80% by number of the particles having a diameter, determined by transmission electron microscopy, of ≤40nm is 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. By onium salts is meant, according to the definition given in "McGraw-Hill Dictionary of Scientific and Technical Terms, Fourth Edition, edited by SP Parker, McGraw-Hill Book Company, New York (1989)": "chemical suffix indicating a complex cation". The halide or polyhalide onium salts, according to the present invention, may be added as solids or solutions or may be formed in the aqueous dispersion of particles of the substantially light-insensitive silver salt by metathesis between a salt with halide or polyhalide anions and onium salts with anions other than halide or polyhalide.

Preferred oniums according to the present invention are organo-phosphonium, organo-sulphonium and organo-nitrogen onium cations, with heterocyclic nitrogen onium (e.g. pyridinium), quaternary phosphonium and ternary sulphonium cations being preferred. Preferred halide anions, according to the present invention, are chloride, bromide and iodide. Preferred polyhalide anions, according to the present invention, consist of chlorine, bromine and iodine atoms.

Onium cations, according to the present invention, may be polymeric or non-polymeric. Suitable polymeric onium halides and polyhalides for partial conversion of particles of substantially light-insensitive organic silver salt into photo-sensitive silver halides according to the present invention are:

POLY01 = a polyurethane resin 50% quaternized with ethyl bromide;
POLY02 = a copolymer of 20.1mol% of a mixture of tributyl(3-vinyl-benzyl)phosphonium chloride and tributyl(4-vinylbenzyl)-phosphonium chloride, 45.5mol% of N-vinylimidazole and 34.4 mol% of acrylonitrile;
POLY03 = poly(2-vinylpyridine) quaternized with ethyl bromide;
POLY04 = poly(2-vinylpyridine) quaternized with ethyl iodide;
POLY05 = poly(4-vinylpyridine) hydrochloride
POLY06 = poly(4-vinylpyridine) hydrobromide perbromide
POLY07 = a copolymer of 83.5% by weight of acrylamide, 15% by weight

of 4-vinylpyridine and 1.5% by weight of N-vinylimidazole quaternized with ethyl bromide;

POLY08 = a copolymer of 8% by weight of styrene, 17% by weight of 4-vinylpyridine and 75% by weight of N-ethyl-4-vinyl-pyridinium bromide with 28% by weight of bromine;

POLY09 = a copolymer of 46% by weight of styrene, 19% by weight of 4-vinylpyridine and 35% by weight of N-ethyl-4-vinyl-pyridinium bromide with 13% by weight of bromine;

POLY10 = a copolymer of 62% by weight of styrene, 21% by weight of 4-vinylpyridine and 17% by weight of N-ethyl-4-vinyl-pyridinium bromide with 6.34% by weight of bromine;

POLY11 = a copolymer of 77% by weight of styrene, 17% by weight of 4-vinylpyridine and 6% by weight of N-ethyl-4-vinyl-pyridinium bromide with 2.24% by weight of bromine.

Preferred non-polymeric onium salts for partial conversion of particles of substantially light-insensitive organic silver salt into photo-sensitive silver halides according to the present invention are:

the nitrogen-onium polyhalides (NC):

NC01 = pyridinium hydrobromide perbromide
NC02 = pyridinium hydrobromide
NC03 = N-dodecyl-pyridinium iodide
NC04 = N-hexadecyl-pyridium bromide
NC05 = α, ω-bis-(N-pyridinium)decane dibromide
NC06 = 2-(2-[1-(3-nitrophenyl)ethenyl]-N-(2-phenylethyl)-pyridinium bromide
NC07 = tetrabutylammonium bromide
NC08 = tetrabutylammonium iodide
NC09 = tetramethylammonium bromide

the quaternary phosphonium polyhalides (PC):

PC01 = 3-(triphenyl-phosphonium)propionic acid bromide perbromide
PC02 = 3-(triphenyl-phosphonium)propionic acid bromide
PC03 = 3-(triphenyl-phosphonium)propionic acid iodide
PC04 = 3-(triphenyl-phosphonium)propionic acid iodide perchloride
PC05 = 3-(triphenyl-phosphonium)propionic acid iodide

perbromide
PC06 = 2-(triphenyl-phosphonium)ethanol bromide
PC07 = 2-(triphenyl-phosphonium)ethanol chloride
PC08 = methyl-triphenyl-phosphonium bromide
PC09 = methyl-triphenyl-phosphonium iodide
PC10 = tetraphenyl-phosphonium iodide perchloride

and the ternary sulfonium polyhalide:

SC01 = trimethylsulfonium iodide

According to the present invention, the photosensitive silver halide is preferably present in a concentration with respect to the substantially light-insensitive organic silver salt of between 0.1 and 35mol%, with quantities between 0.5 and 20mol% being particularly preferred and quantities between between 1 and 12mol% being especially preferred.

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 with the substantially light-insensitive organic silver salt and a 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 comprise a layer system with the silver halide in catalytic association with the substantially light-insensitive organic silver salt ingredients, 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.

Substantially light-insensitive organic silver salts

The substantially light-insensitive organic silver salt, according to the present invention, is present as rod-shaped particles with a preferred length of less than 3μm and a preferred diameter of less than 0.3μm.

Preferred substantially light-insensitive organic silver salts, according to the present invention, are silver salts of 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 dodecyl sulphonate described in US-P 4,504,575; and silver di-(2-ethylhexyl)-sulfosuccinate described in EP-A 227 141. Modified aliphatic carboxylic acids with thioether group as described e.g. in GB-P 1,111,492 and other organic silver salts as described in GB-P 1,439,478, e.g. silver benzoate and silver phthalazinone, may be used likewise to produce a thermally developable silver image. Further are mentioned silver imidazolates and the substantially light-insensitive inorganic or organic silver salt complexes described in US-P 4,260,677.

Particles of the silver salts of organic carboxylic acids are prepared by the reaction of a soluble silver salt with the organic carboxylic acid or a salt thereof.

A suspension of particles containing a substantially light-insensitive organic silver salt may be obtained by using a process, comprising simultaneous metered addition of a solution or suspension of an organic compound with at least one ionizable hydrogen atom or its salt; and a solution of a silver salt to a liquid, as described in the unpublished European patent application number 9501968.5.

Organic reducing agent

Suitable organic reducing agents for the reduction of said 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 substiuent is an amino-group.

In preferred reducing agents, the ring atoms of the non-sulfo-substituted 6-membered aromatic or heteroaromatic ring compound consist of nitrogen and carbon ring atoms and the non-sulfo-substituted 6-membered aromatic or heteroaromatic ring compound is annelated with an aromatic or heteroaromatic ring system.

In further preferred reducing agents, the non-sulfo-substituted 6-membered aromatic or heteroaromatic ring compound is substituted with one or more of the following substituents which may also be substituted: alkyl, alkoxy, carboxy, carboxy ester, thioether, alkyl carboxy, alkyl carboxy ester, aryl, sulfonyl alkyl, sulfonyl aryl, formyl, oxo-alkyl and oxo-aryl.

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.

Reducing agent incorporation

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 heavy metal salt particles so that reduction of the organic heavy metal salt can take place.

Molar ratio of reducing agent : organic silver salt

The silver image density depends on the coverage of the above defined reducing agent(s) and organic silver salt(s) and has to be preferably such that, on heating above 80°C, an optical density of at least 1.5 can be obtained. Preferably at least 0.10 moles of reducing agent per mole of organic heavy metal salt is used.

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.

Spectral sensitizer

The photo-addressable thermally developable element of the photothermographic recording material, according to the present invention, may contain a spectral sensitizer, optionally together with a supersensitizer, for the silver halide. The silver halide may be spectrally sensitized with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol and xanthene dyes optionally, particularly in the case of sensitization to infra-red radiation, in the presence of a so-called supersensitizer. Useful cyanine dyes include those having a basic nucleus, such as a thiazoline nucleus, an oxazoline nucleus, a pyrroline nucleus, a pyridine nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and an imidazole nucleus. Useful merocyanine dyes which are preferred include those having not only the above described basic nuclei but also acid nuclei, such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidinedione nucleus, a thiazolidinedione nucleus, a barbituric acid nucleus, a thiazolinone nucleus, a málononitrile nucleus and a pyrazolone nucleus. In the above described cyanine and merocyanine dyes, those having imino groups or carboxyl groups are particularly effective. Suitable sensitizers of silver halide to infra-red radiation include those

disclosed in the EP-A's 465 078, 559 101, 616 014 and 635 756, the JN's 03-080251, 03-163440, 05-019432, 05-072662 and 06-003763 and the US-P's 4,515,888, 4,639,414, 4,713,316, 5,258,282 and 5,441,866. Suitable supersensitizers for use with infra-red spectral sensitizers are disclosed in EP-A's 559 228 and 587 338 and in the US-P's 3,877,943 and 4,873,184.

Water-dispersible and water-soluble binders

According to the present invention the photo-addressable thermally developable element comprises a binder comprising 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.

In a preferred embodiment of the present invention the binder is a polymer latex.

In a particularly preferred embodiment the binder is a polymer comprising monomer units selected from the group consisting of a diene-monomer and a methacrylate.

In another particularly preferred embodiment the binder is a polymer comprising monomer units selected from the group consisting of styrene and an acrylate.

An important prerequisite in the choice of binders 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. A particularly suitable polyvinyl butyral containing a minor amount of vinyl alcohol units is marketed under the trade name BUTVAR B79 of

Monsanto USA and provides a good adhesion to paper and properly subbed polyester supports. 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.

Weight ratio of binder to organic silver salt

The binder to organic heavy metal salt weight ratio is preferably in the range of 0.2 to 6, and the thickness of the photo-addressable thermally developable element is preferably in the range of 5 to 50 μm.

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.

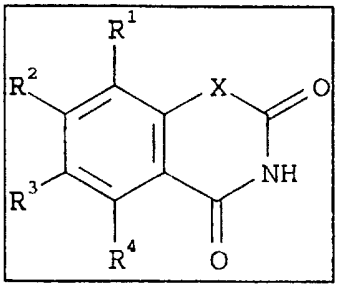
By the term "heat solvent" in this invention is meant a non-hydrolyzable organic material which is in solid state in the recording layer at temperatures below 50°C but becomes a plasticizer for the recording layer in the heated region and/or liquid solvent for at least one of the redox-reactants, e.g. the reducing agent for the organic heavy metal salt, at a temperature above 60°C. Useful for that purpose are a polyethylene glycol having a mean molecular weight in the range of 1,500 to 20,000 described in US-P 3,347,675. Further are mentioned compounds such as urea, methyl sulfonamide and

ethylene carbonate being heat solvents described in US-P 3,667,959, and compounds such as tetrahydro-thiophene-1,1-dioxide, methyl anisate and 1,10-decanediol being described as heat solvents in Research Disclosure, December 1976, (item 15027) pages 26-28. Still other examples of heat solvents have been described in US-P 3,438,776, and 4,740,446, and in published EP-A 0 119 615 and 0 122 512 and DE-A 3 339 810.

Toning agent

In order to obtain a neutral black image tone in the higher densities and neutral grey in the lower densities the recording layer contains preferably in admixture with the organic heavy metal salts and reducing agents a so-called toning agent known from thermography or photo-thermography.

Suitable toning agents are succinimide and the phthalimides and phthalazinones within the scope of the general formulae described in US-P 4,082,901. Further reference is made to the toning agents described in US-P 3,074,809, 3,446,648 and 3,844,797. Other particularly useful toning agents are the heterocyclic toner compounds of the benzoxazine dione or naphthoxazine dione type within the scope of following general formula :



in which:
X represents O or N-alkyl;
each of R^1, R^2, R^3 and R^4 (same or different) represents hydrogen, alkyl, e.g. C1-C20 alkyl, preferably C1-C4 alkyl, cycloalkyl, e.g. cyclopentyl or cyclohexyl, alkoxy, preferably methoxy or ethoxy, alkylthio with preferably up to 2 carbon atoms, hydroxy, dialkylamino of which the alkyl groups have preferably up to 2 carbon atoms or halogen, preferably chlorine or bromine; or R^1 and R^2 or R^2 and R^3 represent the ring members required to complete a fused

aromatic ring, preferably a benzene ring, or R^3 and R^4 represent the ring members required to complete a fused aromatic aromatic or cyclohexane ring. Toners within the scope of the general formula are described in GB-P 1,439,478 and US-P 3,951,660.

A toner compound particularly suited for use in combination with polyhydroxy benzene reducing agents is 3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine described in US-P 3,951,660.

Anti-halation dyes

In addition to the ingredients, the photothermographic recording material of the present invention may contain anti-halation or acutance dyes which absorb 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 anti-halation dye may also be bleached either thermally during the thermal development process, as disclosed in the US-P's 4,033,948, 4,088,497, 4,153,463, 4,196,002, 4,201,590, 4,271,263, 4,283,487, 4,308,379, 4,316,984, 4,336,323, 4,373,020, 4,548,896, 4,594,312, 4,977,070, 5,258,274, 5,314,795 and 5,312,721, or photo-bleached after removable after the thermal development process, as disclosed in the US-P,s 3,984,248, 3,988,154, 3,988,156, 4,111,699 and 4,359,524. Furthermore the anti-halation layer may be contained in a layer which can be removed subsequent to the exposure process, as disclosed in US-P 4,477,562 and EP-A 491 457. Suitable anti-halation 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.

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 silver salt of an organic carboxylic acid in aqueous media and to disperse water-dispersible binders, such as polymer latexes, in aqueous media. A mixture of non-ionic and anionic surfactacts, of non-ionic and cationic surfactants, of cationic and anionic surfactants or of non-ionic, cationic and anionic surfactants may also be used, according

to the present invention.

In one embodiment of the present invention the surfactant is an anionic surfactant. In a preferred embodiment of the present invention the anionic 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

In a further embodiment of the present invention the ionic surfactant is a non-ionic surfactant for example alkyl, aryl, alkaryl or aralkyl polyethoxy ethanols. Preferred non-ionic surfactants, according to the present invention, are alkoxy-polyethoxy ethanols and alkaryloxy-polyethoxy ethanols.

Other additives

In addition to the ingredients the photo-addressable thermally developable element may contain other additives such as free fatty 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 Öl A (tradename of BAYER AG - GERMANY), ultraviolet light absorbing compounds, white light reflecting and/or ultraviolet radiation reflecting pigments, silica, colloidal silica, fine polymeric particles [e.g. of poly(methylmethacrylate)] and/or optical brightening agents.

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, polypropylene, polycarbonate or polyester, e.g. polyethylene terephthalate. 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

need be to improve the adherence to the thereon coated thermosensitive recording layer. The support may be made of an opacified resin composition, e.g. polyethylene terephthalate opacified by means of pigments and/or micro-voids and/or coated with an opaque pigment-binder layer, and may be called synthetic paper, or paperlike film; information about such supports can be found in EP's 194 106 and 234 563 and US-P's 3,944,699, 4,187,113, 4,780,402 and 5,059,579. Should a transparent base be used, the base may be colourless or coloured, e.g. having a blue colour.

One or more backing layers may be provided to control physical properties such as curl or static.

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 to avoid local deformation of the photo-addressable thermally developable element, to improve its resistance against abrasion and to prevent its direct contact with components of the apparatus used for thermal development.

This protective layer may have the same composition as an anti-sticking coating or slipping layer which is applied in thermal dye transfer materials at the rear side of the dye donor material or protective layers used in materials for direct thermal recording.

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 polyvinylalcohol being particularly preferred.

A protective layer according to the present invention may be crosslinked. Crosslinking can be achieved by using crosslinking agents such as described in WO 95/12495 for protective layers, e.g. tetra-alkoxysilanes, polyisocyanates, zirconates, titanates, melamine resins etc., with tetraalkoxysilanes such as tetramethylorthosilicate and tetraethylorthosilicate being preferred.

A protective layer according to the present invention may comprise 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. Examples of suitable lubricating materials are surface active agents, liquid lubricants, solid lubricants which do not melt during thermal development of the recording material, solid lubricants which melt (thermomeltable) during thermal development of the recording material or mixtures thereof. The lubricant may be applied with or without a polymeric binder. The surface active agents may be any agents known in the art such as carboxylates, sulfonates, aliphatic amine salts, aliphatic quaternary ammonium salts, polyoxyethylene alkyl ethers, polyethylene glycol fatty acid esters, fluoroalkyl C_2-C_{20} aliphatic acids. Examples of liquid lubricants include silicone oils, synthetic oils, saturated hydrocarbons and glycols. Examples of solid lubricants include various higher alcohols such as stearyl alcohol and fatty acids. Suitable slipping layer compositions are described in e.g. EP 138483, EP 227090, US-P 4,567,113, 4,572,860 and 4,717,711 and in EP-A 311841.

A suitable slipping layer being a layer comprising as binder a styrene-acrylonitrile copolymer or a styrene-acrylonitrile-butadiene copolymer or a mixture hereof and as lubricant in an amount of 0.1 to 10 % by weight of the binder (mixture) a polysiloxane-polyether copolymer or polytetrafluoroethylene or a mixture hereof.

Other suitable protective layer compositions that may be applied as slipping (anti-stick) coating are described e.g. in published European patent applications (EP-A) 0 501 072 and 0 492 411.

Such protective layers may also comprise 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

The coating of any layer of the recording material 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 radiation of wavelength between an X-ray wavelength and a 5 microns wavelength with the image either being obtained by pixel-wise exposure with a finely focussed light source, such as a CRT light source; a UV, visible or IR wavelength laser, such as a He/Ne-laser or an IR-laser diode, e.g. emitting at 780nm, 830nm or 850nm; or a light emitting diode, for example one emitting at 659nm; or by direct exposure to the object itself or an image therefrom with appropriate illumination e.g. with UV, visible or 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.

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.

While the present invention will hereinafter be described in connection with a preferred embodiment thereof, it will be understood that it is not intended to limit the invention to that embodiment. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included in the spirit and scope of the invention as defined by the appending claims.

The invention is illustrated hereinafter by way of invention examples and comparative examples. The percentages given in these examples are by weight unless otherwise indicated.

INVENTION EXAMPLE 1

In situ preparation of a silver behenate/silver halide-emulsion

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 to a predispersion 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.

The following ingredients were then added with stirring to 1.5g of the silver behenate dispersion: 1g of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, butadiene and itaconic acid in a weight ratio of 45:45:10), 0.013g of succinimide, 0.1g of a 11% by weight

solution of saponin in a mixture of deionized water and methanol and 2.4g of a 1.28% by weight aqueous solution of 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01), corresponding to a concentration of 8 mol% of PC01 with respect to silver behenate, to accomplish in situ conversion of part of the silver behenate to silver bromide.

Transmission electron micrograph of the resulting silver behenate/silver bromide dispersion

The transmission electron micrograph of the resulting dispersion produced at a magnification of 50,000x (1cm = 200nm) is shown in figure 1. The large rod-shaped particles are silver behenate. The very small black particles, ≤40nm in diameter, uniformly distributed over these silver behenate particles and also uniformly distributed between these particles are silver bromide particles.

Coating and drying of the thermographic 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 60µm. After drying for several minutes at 40°C on the coating bed, the emulsion layer was then doctor blade-coated with a 2.44% by weight aqueous solution of 3-(3,4-dihydroxyphenyl)propionic acid at a blade setting of 30µm. The resulting thermographic material was first allowed to dry on the coating bed for several minutes at 40°C and then was dried for 1 hour in a hot air oven at 50°C.

Image-wise exposure and thermal processing

The thermographic material was then exposed to ultra-violet light through a test original in contact with the material in an Agfa-Gevaert™ DL 2000 exposure apparatus followed by heating on a heated metal block for 10s at 95°C to produce a very good image with a high contrast and good sharpness. The quality of the image obtained was assessed qualitatively and awarded a numerical score between 0 and 5 where these values correspond to:

0 = no image
1 = a very weak image

2 = a weak image
3 = a moderate image quality
4 = a good image
5 = a very good image with high contrast and good sharpness

This material was awarded a score of 5 for image quality.

INVENTION EXAMPLES 2 to 28

The materials of invention examples 2 to 28 were prepared as described for invention example 1 except that the aqueous solution of the onium polyhalide, 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01), was replaced by aqueous solutions of the onium polyhalides given in table 1 and different molar concentrations of these onium polyhalides with respect to silver behenate were used.

Transmission electron micrographs were produced at a magnification of 50,000x (1cm = 200nm) for the silver behenate/silver halide dispersions produced in the course of the preparation of the materials of invention examples 3, 4, 6 and 17 and these are shown in figures 2, 3, 4 and 5 respectively. As in figure 1, in all these figures the very small silver halide (black) particles are exclusively distributed over the large rod-shaped silver behenate particles with the silver halide particles being uniformly distributed over these particles and also uniformly distributed between these particles. These silver halide particles were particularly small in the cases of figures 4 and 6 (invention examples 6 and 17 respectively) having diameters of ≤15nm and ≤20nm respectively. In the case of figure 4 (invention example 6), the silver iodide particles are so small that most of them are not visible at a magnification of 50,000x. At a magnification of 150,000x they are, however, clearly visible, see figure 6. The maximum particles sizes and the uniformity of distribution of the silver halide particle distribution are also given in table 1.

From table 1 it can be seen that in the case of the phosphonium halide PC03, invention examples 4 to 7, a good image was obtainable at PC03 concentrations of between 8 and 0.5mol% with respect to silver behenate, indicating a surprising constancy of photosensitivity with decreasing molar concentration of PC03 and hence of the silver iodide formed therefrom. This result enables photothermographic recording materials to be produced with lower

silver halide contents and hence enhanced intrinsic stabilities without sacrificing photosensitivity.

Table 1:

Invention Example number	Onium polyhalide Compound(s) used	mol% vs. AgBeh	AgX particles size (nm)	distrib-ution	Image quality assessment
1	PC01	8	≤40	uniform	5
2	PC01	4			5
3	PC02	8	≤20	uniform	5
4	PC03	8	≤20	uniform	4
5	PC03	4			4
6	PC03	1	≤15	uniform	4
7	PC03	0.5			4
8	PC02 + PC03	3 + 1			5
9	PC02 + PC03	1 + 3			5
10	PC04	4			4
11	PC05	8			4
12	PC06	4			5
13	PC07	4			5
14	PC08	4			5
15	PC09	4			4
16	PC10	8			5
17	SC01	8	≤20	uniform	5
18	SC01	4			4
19	NC01	8			5
20	NC01	4			5
21	NC02	4			5
22	NC03	4			3
23	NC04	4			5
24	NC05	4			4
25	NC06	4			3
26	NC07	8			4
27	NC08	8			4
28	NC09	8			3

COMPARATIVE EXAMPLES 1 to 6

The materials of comparative examples 1 to 6 were prepared as

described for invention example 1 except that the aqueous solution of the onium polyhalide, 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01) was not added (comparative example 1) or that the aqueous solution of the onium polyhalide, 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01) was replaced by aqueous solutions of the inorganic halides given in table 2 and different molar concentrations of these inorganic halides with respect to silver behenate were used (comparative examples 2 to 5).

The transmission electron micrograph was produced at a magnification of 50,000x (1cm = 200nm) for the silver behenate/silver halide dispersion produced during the preparation of the material of comparative example 1 is shown in figure 7. In this case the far fewer (black), but larger, particles are clearly not exclusively distributed over the much larger rod-shaped silver behenate particles and the distribution of these particles over the silver behenate particles is far from uniform. The maximum particle size of the silver bromide particles together with the degree of uniformity of the distribution of these particles are given in table 2.

Image-wise exposure followed by thermal processing was carried out on the materials of comparative examples 1 to 6 as described for invention example 1 and the image quality assessment values obtained are given in table 2.

Table 2:

Comparative Example number	Inorganic halide Compound(s) used	mol% vs. AgBeh	AgX particle size (nm)	distribution	Image quality assessment
1	none	0			0
2	KBr	8	≤80	non-uniform	2
3	KBr	16			2
4	KI	8			2
5	NH_4Br	8			2
6	$CaBr_2$	8			2

In the absence of PC01 (comparative example 1) no image was obtained and hence a numerical score of 0 was assigned for image quality. Surprisingly only weak images were obtained when PC01 was replaced

by various inorganic halides and numerical scores of 2 were awarded. This is in marked variance with the performance of analogous materials prepared using solvent dispersions of silver behenate emulsions to which inorganic halides had been added, which produced very good images.

COMPARATIVE EXAMPLES 7 and 8

The materials of comparative examples 7 and 8 were prepared as described for invention example 1 except that the aqueous solution of the onium polyhalide, 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01) was replaced by an ex situ prepared silver halide emulsion of 50nm particles consisting of 96.3 mol% of silver bromide and 3.7mol% of silver iodide in an aqueous solution of gelatin in a quantity corresponding to 10mol % and 20mol% of silver halide with respect to the silver behenate present respectively.

Image-wise exposure followed by thermal processing as described for invention example 1 surprisingly produced only very weak images, which were awarded a numerical score of 1. This is again at variance with the performance of analogous materials prepared by mixing a similar ex situ prepared silver halide emulsion with an aqueous dispersion of silver behenate evaporating off the dispersant, redispersing in an organic solvent, adding appropriate quantities of appropriate reducing and toning agents and then coating and drying the resulting dispersion, with which very good images were obtained under the same exposure and thermal processing conditions.

COMPARATIVE EXAMPLES 9 and 10

The materials of comparative examples 9 and 10 were prepared using silver behenate/silver halide dispersions produced by producing the silver behenate in the presence of the same silver halide emulsion used in the silver behenate/silver halide dispersions of comparative examples 7 and 8 as described in US-P 3,839,049. Sodium behenate was first prepared by adding a stoichiometric quantity of sodium hydroxide to an aqueous dispersion of behenic acid, then silver halide emulsion was added in quantities such that 0.1moles of silver halide (comparative example 9) or 0.2moles of silver halide (comparative example 10) per mole of sodium behenate and finally the sodium behenate was stoichiometrically converted in the presence of silver halide into

silver behenate by adding aqueous silver nitrate as described in invention example 1. The resulting silver behenate/silver halide precipitate was then filtered off and 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/silver halide mixture was dispersed in deionized water with the anionic dispersion agents Ultravon™ W and Mersolat™ H to produce, after rapid mixing to a predispersion and homogenization with a microfluidizer, a finely divided and stable dispersion containing 20% by weight of silver behenate/silver halide mixture, 2.1% by weight of Ultravon™ W and 0.203% by weight of Mersolat™ H80. The pH of the resulting dispersion was adjusted to about 6.5.

The following ingredients were then added with stirring to 1.5g of the silver behenate/silver halide dispersion with 10mol% silver halide with respect to silver behenate (comparative example 9) or 1.5g of the silver behenate/silver halide dispersion with 20mol% silver halide with respect to silver behenate (comparative example 10): 1g of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, butadiene and itaconic acid in a weight ratio of 45:45:10), 0.013g of succinimide and 0.1g of a 11% by weight solution of saponin in a mixture of deionized water and methanol.

The resulting dispersions were coated and resulting thermographic materials dried as described for invention example 1. Image-wise exposure and thermal processing of these materials was also performed as described for invention example 1 and very weak images were obtained for both the materials of comparative examples 9 and 10, which were awarded a numerical score of 1 for image quality.

This is yet again at variance with the performance of analogous materials prepared by dispersing the dried silver behenate/silver mixtures in an organic solvent, adding appropriate quantities of appropriate reducing and toning agents and then coating and drying the resulting dispersion, with which very good images were obtained under the same exposure and thermal processing conditions.

INVENTION EXAMPLE 29

The material of invention example 29 was prepared as described for invention example 1 except that the silver behenate dispersion was prepared by the process described in the unpublished European

patent application number 95201968.5. 60g of gelatin was dissolved in 1500g of deionized water in a reaction vessel and the resulting solution heated to 75°C. The UAg, defined as the potential difference between a silver electrode (of ≥99.99% purity) in the liquid and a reference electrode consisting of a Ag/AgCl-electrode in 3M KCl solution at room temperature connected to the liquid via a salt bridge consisting of a 10% KNO_3 salt solution, was adjusted to 400mV. To this solution were simultaneously metered into the reaction vessel a solution of sodium behenate in a mixture of deionized water and 2-propanol at 80°C and an aqueous solution of silver nitrate at room temperature such that the UAg remained constant at 400mV. The dissolved salts were then removed by ultrafiltration and the resulting dispersion of silver behenate and after pH adjustment to 6.5 the procedure described in invention example 1 was followed.

Image-wise exposure and thermal processing, as described in invention example 1, produced a very good image with a high contrast, which was awarded a score of 5 for image quality as in the case of the material of invention example 1.

INVENTION EXAMPLE 30

The material of invention example 30 was prepared as described for invention example 1 except that the binder used was changed, 1g of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, butadiene and itaconic acid in a weight ratio of 47.5:47.5:5) being used instead of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, butadiene and itaconic acid in a weight ratio of 45:45:10). Image-wise exposure and thermal processing of the resulting material, as described in invention example 1, produced a very good image with a high contrast which was awarded a score of 5 for image quality as in the case of the material of invention example 1.

INVENTION EXAMPLE 31

The material of invention example 31 was prepared as described for invention example 1 except that the binder used was changed, 1g of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, isoprene and itaconic acid in a

weight ratio of 47.5:47.5:5) being used instead of a 30% by weight concentration of a latex-copolymer (obtained by copolymerizing methyl methacrylate, butadiene and itaconic acid in a weight ratio of 45:45:10). Image-wise exposure and thermal processing of the resulting material, as described in invention example 1, produced a very good image with a high contrast which was awarded a score of 5 for image quality as in the case of the material of invention example 1.

INVENTION EXAMPLE 32

The material of invention example 32 was prepared as described for invention example 1 except that the aqueous solution of the onium polyhalide, 3-(triphenyl-phosphonium)propionic acid bromide perbromide (PC01), was replaced by the addition of an aqueous solution of 1-methoxy-2-(triphenyl-phosphonium)ethane tosylate followed by the addition of a solution of potassium bromide.

Image-wise exposure and thermal processing of the resulting material, as described in invention example 1, produced a good image which was awarded a score of 4 for image quality.

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.

FIGURES:

FIGURE 1: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of invention example 1.

FIGURE 2: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of invention example 3.

FIGURE 3: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 4.

FIGURE 4: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 6.

FIGURE 5: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 17.

FIGURE 6: Transmission electron micrograph at a magnification of 150,000x of the silver behenate/silver iodide dispersion produced in the course of the preparation of the material of invention example 6.

FIGURE 7: Transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of the material of comparative example 1.

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 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 mixture of a water soluble polymer and a water-dispersible polymer and particles of said photosensitive silver halide are non-aggregating in said 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 said particles having a diameter, determined by transmission electron microscopy, of ≤40nm.

2. A photothermographic recording material according to claim 1, wherein at least 80% by number of said silver halide particles have a diameter, determined by transmission electron microscopy, of ≤25nm.

3. A 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.

4. A photothermographic recording material according to any of the preceding claims, wherein said photosensitive silver halide is present in a concentration with respect to said substantially light-insensitive organic silver salt of between 0.1 and 35mol%.

5. A photothermographic recording material according to any of the preceding claims, wherein said photosensitive silver halide is present in a concentration with respect to said substantially light-insensitive organic silver salt of between 0.5 and 20mol%.

6. A photothermographic recording material according to any of the preceding claims, wherein said photo-addressable thermally developable element contains a spectral sensitizer, optionally

together with a supersensitizer, for the silver halide.

7. A photothermographic recording material according to any of the preceding claims, wherein said binder comprises a water-dispersible polymer latex.

8. A photothermographic recording material according to any of the preceding claims, wherein said photo-addressable thermally developable element contains a toning agent.

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

10. A recording process comprising the steps of: (i) providing a photothermographic recording material according to any of claims 1 to 9; (ii) bringing said recording material into the proximity of a source of actinic radiation to which it is sensitive; (iii) image-wise exposing said recording material to said actinic radiation; (iv) bringing said image-wise exposed recording material into proximity with a heat source; (v) thermally developing said image-wise exposed recording material; and (vi) removing said thermally developed image-wise exposed recording material from said heat source.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

INTERNATIONAL SEARCH REPORT

Inter. ...nal Application No
PCT/EP 96/02580

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03C1/498

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 725 534 A (KAGAMI ET AL.) 16 February 1988 see column 10, line 58 - line 66; example 10 -----	1,3-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
18 March 1997	18. 04. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Buscha, A

INTERNATIONAL SEARCH REPORT

information on patent family members

Inte. ional Application No
PCT/EP 96/02580

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4725534 A	16-02-88	JP 1580946 C	11-10-90
		JP 2004889 B	30-01-90
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