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(54) Recording material and process for producing the same

(57) A recording material which comprises a support having provided thereon at least a recording layer comprising (a) a heat-responsive microcapsule having encapsulated therein an organic silver salt, (b) a developer for the organic silver salt and (c) a water-soluble binder. A process for producing the recording material is further disclosed. The recording material of the present invention can be prepared without adversely affecting the working environment, has a remarkably prolonged shelf life, and is capable of recording a high density image thereon.

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Description

The present invention relates to a recording material which undergoes a dry process to form an image thereon and a process for producing the same. More particularly, the present invention relates to a dry recording material which can use an organic silver salt to form a silver image thereon and a process for producing the same.

A well known, practicable dry process photographic light-sensitive material which is not susceptible to the disadvantages of silver halide wet processing and which maintains the photosensitivity, gradation and good image quality of silver halide is the "dry silver" material developed by 3M Inc. of the U.S.A.

Organic silver salts for use as one of essential components of the dry silver material include a light-fast colorless or white silver salt such as silver behenate which is heated to a temperature of not lower than 100°C with a reducing agent. The silver salt undergoes a redox reaction that produces a silver image.

A dry silver light-sensitive material is typically prepared by a process which comprises adding a silver halide-forming agent to a polymer dispersion of an organic silver salt. The organic silver salt dispersion is obtained by dispersing an organic silver salt in a binder such as a polymer to convert a part of the organic silver salt to a silver halide to prepare a coating solution, or by mixing a silver halide which has been separately prepared, a reducing agent (developing agent) and various additives to prepare a coating solution, applying the coating solution to a support, and then drying the coated material to form a photosensitive layer thereon.

However, the photosensitive layer in such a light-sensitive material merely comprises an organic silver salt, and a reducing agent coated with a polymer in the form of a dispersion. Therefore, if the concentration of the organic silver salt is increased, a high density image can be obtained. However, when the concentration of the organic silver salt is increased, the reduction reaction can easily proceed at room temperature, to thereby reduce shelf life. Thus, this type of structure is disadvantageous in that it is difficult to obtain a recording material which has a prolonged shelf life and which can record a high density image thereon.

Furthermore, the preparation process of this type of light-sensitive material is disadvantageous in that a coating solution comprising an organic silver salt dispersed in an organic solvent normally must be used. However, use of the organic solvent is detrimental to the working environment.

The present inventors have extensively studied the foregoing problems. As a result, it was found that if the organic silver salt is encapsulated, a high concentration of the organic silver salt can be contained in the microcapsule. This makes it possible to record a high density image. It was also found that the organic silver salt incorporated in the microcapsule is isolated from the reducing agent at room temperature. However, the microcapsule wall becomes permeable to the reducing agent arranged outside the microcapsules at higher temperatures such that the organic silver salt reacts with the reducing agent. This makes it possible to inhibit the progress of the reduction reaction at room temperature to thereby provide prolonged shelf life. It was further found that the combined use of such microcapsules with a water-soluble binder provides a recording layer coating solution in an aqueous form that dispenses with the need of an organic solvent in the production process of the recording material. The present invention has been achieved based on the above described findings.

A first object of the present invention is to provide an organic silver salt-based recording material which has a prolonged shelf life and which can record a high density image thereon.

A second object of the present invention is to provide a recording material employing an organic silver salt that can be prepared without using an organic solvent to thereby provide a safe and healthful manufacturing environment.

A third object of the present invention is to provide a safe and healthful process for preparing a recording material, which recording material has a prolonged shelf life and can record a high density image thereon.

The foregoing objects of the present invention have been accomplished by providing a recording material comprising a support having provided thereon a recording layer comprising a heat-responsive microcapsule having encapsulated therein at least an organic silver salt, a developer for said organic silver salt and a water-soluble binder, and a process for preparing the same.

The organic silver salt for use in the present invention is a light-fast colorless or white silver salt which, regardless of whether an exposed silver halide is present or not, undergoes a redox reaction to produce silver when heated with a reducing agent. The organic silver salt is a silver salt of an organic compound having an imino group, a mercapto group or a carboxyl group. Specific examples of the organic silver salt are given below.

1) Silver salt of an organic compound having an imino group

Saccharin silver, phthalazinone silver, benzotriazole silver.

2) Silver salt of an organic compound having a mercapto group or a thione group

Silver salt of 3-(2-carboxyethyl)-4-oxymethyl-4-thiazoline-2-thione, silver salt of 3-mercapto-4-phenyl-1,2,4-triazole.

3) Silver salt of an organic compound having a carboxyl group

Silver stearate, silver behenate.

Most preferred among these organic silver salts is silver behenate, which is white and fast to light and exhibits excellent moisture resistance. Furthermore, silver behenate can be combined with a mild reducing agent, and can be used with known excellent color toners.

In a preferred embodiment, the recording material of the present invention comprises a desalted and purified organic silver salt. A desalted and purified organic silver salt is advantageously used when a high concentration of the organic silver salt is used to record a high density image. The desalting purification of the organic silver salt can be accomplished by the method described below.

In the present invention, the-organic silver salt is incorporated in the microcapsule described below to prevent a reduction reaction of the organic silver salt with the developer at room temperature and to thereby prolong the shelf life of the recording material.

Furthermore, a spectral sensitizer may be used in the present invention. Useful spectral sensitizers are described in U.S. Patent No. 4,584,267 (claims 26 and 27) and Research Disclosure (1989).

If the recording layer of the recording material of the present invention comprises a silver halide which is adjacent to the organic silver salt and which is sufficiently photosensitive to form a latent image when exposed to light while enabling a rapid reduction reaction, i.e., development with the organic silver salt, the recording material of the present invention acts as a photographic light-sensitive material. The silver halide contained in the recording layer may be a known silver halide such as silver chloride, silver bromide or silver chlorobromide.

When a silver halide is incorporated in the recording layer adjacent to the organic silver salt, a silver halide-forming agent is preferably added to convert a part of the organic silver salt to a silver halide.

Examples of the silver halide-forming agent include halogen donating compounds such as inorganic halogen compounds, e.g., KBr, KCl and HBr, onium halides, e.g., NH_4Br and NH_4Cl, carbon halides, and N-halogeno compounds, e.g., N-bromosuccinimide.

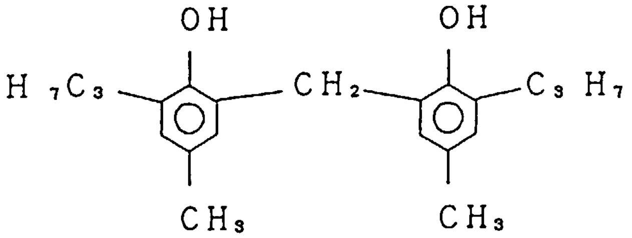
The silver halide is preferably used in an amount of from 1 mol% to 30 mol%, more preferably from 2 mol% to 20 mol%, based on the amount of the organic silver salt. The silver halide is preferably incorporated in the microcapsule together with the organic silver salt.

If the above described photosensitive silver halide is not added to the recording layer, the recording material of the present invention acts as a heat-sensitive recording material.

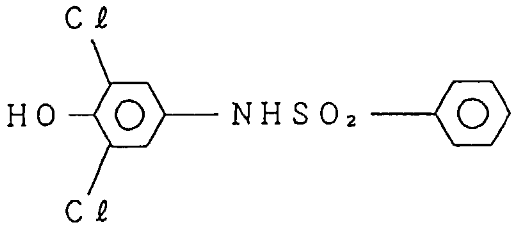
The developer for use in the present invention is a reducing agent. When heated, the reducing agent reduces the organic silver salt to produce silver.

The reducing agent for use in the present invention must be able to undergo a rapid reduction reaction at the desired development temperature. Furthermore, it must not adversely affect the color tone of the developed image.

Examples of useful reducing agents include hydroxycoumarones, hydroxycoumarans, sulfoamidephenols, sulfoamidenaphthols, hydradones, hydroxaminic acids, bis-β-naphthols, indane-1,3-diones, aminophenols, aminonaphthols, pyrazolidine-5-ones, hydroxylamines, reductones, hydrazines, hydroquinones, polyphenols such as bisphenol A, bisphenol B and gallates, phenylenediamines, hydroxyindanes, 1,4-dihydroxypyridines, amidoxims, hydroxy-substituted aliphatic carboxylic acid arylhydrazides, N-hydroxyureas, phosphonamidephenols, phosphonamidanilines, α-cyanophenylacetic esters and sulfonamideanilines. Among these reducing agents, compounds represented by the following formulae (I) to (IV), octyl gallate, propyl gallate, etc. are preferred.



(I)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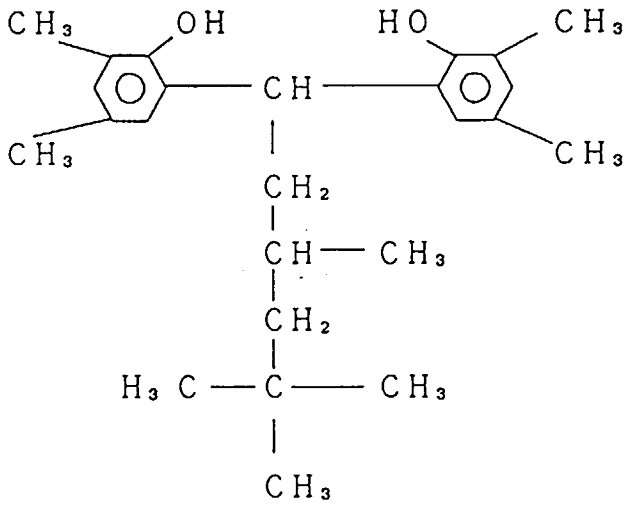
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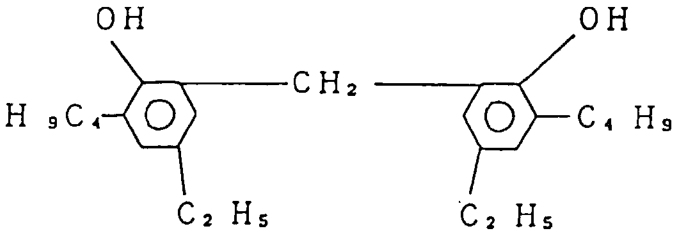

(IV)

A color toner is preferably used when it is desirable to form a high density image, particularly a black image. The addition amount of the color toner is from about 0.0001 mol to about 2 mol, preferably from about 0.0005 mol to about 1 mol, per mol of the organic silver salt. The type of color toner depends on the kind of the organic silver salt and reducing agent that is used. A widely used color toner is a heterocyclic organic compound containing at least two hetero atoms and containing at least one nitrogen atom in its heterocyclic ring.

Useful color toners are described in U.S. Patent No. 3,080,254. Specific examples of the color toner include phthalazone (phthalazinone), phthalic anhydride, 2-acetylphthalazinone, 2-phthalylphthalazinone and substituted phthalazinone as described in JP-A-50-67132 (The term "JP-A" as used herein means an "unexamined published Japanese patent application"). These color toners are preferably used in the present invention.

Other useful examples of color toners include pyrazoline-5-ones, cyclic imides and quinazolinone as described JP-A-46-6077. Specific examples of these color toners include phthalimide, N-hydroxyphthalimide, N-potassiumphthalimide and phthalimide silver. Furthermore, phthalazinones are useful as color toners.

Still other useful examples of color toners include the mercapto compounds as described in JP-A-49-5019 and JP-A-49-5020. Still further useful examples of color toners include the mercapto compounds as described in JP-A-49-5019. Besides these compounds, oxazinediones as described in JP-A-50-2542, phthalazinediones as described in JP-A-50-67641, uracils as described in JP-A-58-114217, N-hydroxynaphthalimides as described in U.S. Patent No. 3,782,941, substituted phthalimides as described in West German Patent Publication Nos. 2,140,406, 2,141,063 and 2,220,597, and phthalazinone derivatives as described in West German Patent Application Publication No. 2,220,618 may be similarly used.

In the present invention, the developer and development accelerator are used in the form of a solid dispersion. The developer and development accelerator may be used in microcapsulized form separate from the organic silver salt. In this case, however, a prolonged heat development time is required.

In the recording material of the present invention, the following measures are preferably taken to prevent heat fog or stabilization of the background of the recorded image.

Firstly, it is well known that a mercury compound remarkably inhibits heat fog and stabilizes the background of the recorded image. However, it is undesirable to use a mercury compound from the standpoint of environmental pollution. In the present invention, N-halogeno compounds such as N-halogenosuccinimide, N-halogenoacetamide, N-halogenooxazolinone, N-halogenobenzotriazole and N-halogenobenzimidazole as described in JP-A-49-10724, JP-A-48-2842 and JP-A-48-8194 are preferably used.

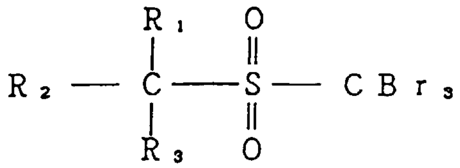
Furthermore, higher fatty acids as described in U.S. Patent No. 3,645,739, JP-A-49-125016, JP-A-49-130720, JP-A-50-57619, and JP-A-50-39264, tetrahalogenophthalic acid or the anhydride thereof, the salt of an arylsulfonic acid such as benzenesulfonic acid and p-toluenesulfonic acid, an arylsulfinic acid such as benzenesulfinic acid and p-toluenesulfinic acid or salts thereof, and lithium salts of higher fatty acids such as lithium myristate, lithium stearate, lithium behenate, lithium palmitate and lithium laurate, may be used as acid stabilizers.

Other useful examples of acid stabilizers include salicylic acid, an alkyl-substituted benzoic acid such as p-hydroxybenzoic acid, tetrabromobenzoic acid, tetrachlorobenzoic acid, p-acetamidebenzoic acid and p-t-butylbenzoic acid, phthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, dicitric acid and 5',5'-methylenebissalicylic acid. These acid stabilizers not only inhibit heat fog, but also inhibit photo discoloration of the background of the recorded image upon exposure to white light or improve the shelf life of the recording material.

Besides these materials, citric acid, tartaric acid, oxalic acid, boric acid, phosphoric acid, and pyrophosphoric acid may be added as acid stabilizers.

The addition amount of the acid stabilizer is preferably from 0.01 to 1.5 mol per mol of silver behenate.

Other examples of compounds which can be used to inhibit heat fog and photo discoloration include benzotriazole and derivatives thereof, thiouracils, mercapto compounds such as 1-phenyl-5-mercaptotetrazole, azolethioethers or blocked azolethiones as disclosed in JP-A-47-318, tetrazolylthio compounds as disclosed in U.S. Patent No. 3,700,457, photosensitive halogeno organic oxidizing agents as disclosed in U.S. Patent Nos. 3,707,377 and 4,108,455, polybromated organic compounds such as 2,4-bis(tribromomethyl)-s-triazine and polybromoalkylsulfonyl compounds as disclosed in U.S. Patent No. 3,874,946, trihalomethyltetrazole derivatives as disclosed in U.S. Patent No. 4,546,075, trihalomethylbenzimidazole, benzoxazole counterparts thereof or benzothiazole counterparts thereof, compounds represented by R^a-CX_2-R^b (in which X represents a halogen atom; and R^a and R^b each represent acyl, oxycarbonyl, oxysulfonyl, alkylsulfonyl, allylsulfonyl, aralkylsulfonyl, carboxyl, sulfo or sulfamoyl) as disclosed in JP-A-59-57234, organic halogen compounds as disclosed in U.S. Patent No. 4,465,761, 2-trihalomethyloxazole derivatives as disclosed in U.S. Patent No. 4,452,885, heterocyclic compounds having a trihalomethyl group as disclosed in U.S. Patent No. 4,756,999, and compounds represented by the following formula (V) as disclosed in European Patent No. 622,666:



$$R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CBr_3 \qquad (V)$$

wherein R_1, R_2 and R_3 each independently represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a thioalkyl group, a perhalogenated alkyl group or a cycloalkyl group.

When the above described heat fog/photo discoloration inhibitor is used in combination with a heat-responsive capsule, the effects of the present invention are remarkably enhanced.

The heat-responsive microcapsule for use in the present invention has a wall which isolates the substances incorporated therein from the exterior at room temperature, but becomes permeable without being destroyed when pressure is applied or when heated.

The microcapsule can be prepared by any of interfacial polymerization, internal polymerization and external polymerization. In particular, an interfacial polymerization process is preferably employed. This process comprises emulsifying a core substance comprising an organic silver salt that has been dissolved or dispersed in an organic solvent in an aqueous solution having a water-soluble polymer therein, and then forming a polymer wall around the emulsified oil droplets of the core substance.

The microcapsule can be prepared using a limited amount of an organic solvent in a small vessel. The evaporated organic solvent fumes can be collected easily, safely and inexpensively. Therefore, use of a limited amount of the organic solvent for producing a microcapsule is not detrimental to the working environment. On the other hand, coating and drying processes for producing a recording layer are conducted in a large space, during which an organic solvent contained in a coating solution evaporates from a support web which is in a large scale and which moves at high speed (i.e., a lot of danger of generating static electricity.) Thus, large facilities for collecting evaporated fumes and for safety are technically required.

The foregoing organic solvent preferably comprises a non-aqueous solvent having a boiling point of not higher than 150°C such as an ester carboxylate (e.g., ethyl acetate, butyl acetate), toluene, xylene and an ester phosphate.

The reactants for forming the polymer are added to the interior and/or exterior of the oil droplets.

Specific examples of the polymer include polyurethane, polyurea, polyamide, polyester, polycarbonate, urea-formaldehyde resin, polyamic acid, polystyrene, styrene methacrylate copolymer and styrene-acrylate copolymer. Preferred among these polymers are polyurethane, polyurea, polyamide, polyester, and polycarbonate. Particularly preferred among these polymers are polyurethane and polyurea, which can form a capsule that is difficult to destroy. Two or more of these polymers may be used in combination.

Specific examples of the foregoing water-soluble polymer include gelatin, polyvinyl pyrrolidone and polyvinyl alcohol.

For example, if a polyurea or polyurethane is used as a capsule wall material, a polyisocyanate such as diisocyanate, triisocyanate, tetraisocyanate and polyisocyanate prepolymer, a polyamine such as diamine, triamine and tetramine, a prepolymer having two or more amino groups, piperazine or derivatives thereof, a polyhydric alcohol, or water are allowed to undergo reaction by interfacial polymerization in an aqueous solvent, to thereby easily form a microcapsule wall. The microcapsule thus formed is particularly desirable because of the microcapsule wall is dense.

Furthermore, a composite wall made of a polyurea and a polyamide can be prepared, e.g., by preparing an emulsified medium from a polyisocyanate such as an adduct of trimethylolpropane and xylylenediisocyanate, an acid chloride such as phthaloyl dichloride and a polyamine such as hexamethylenediamine as a reaction solution, adjusting the Ph value of the reaction solution, and then heating the reaction solution. A composite wall made of a polyurethane and a polyamide can be prepared, e.g., by preparing an emulsified medium from a polyisocyanate such as the adduct described above, an acid chloride such as phthaloyl dichloride, a polyamine such as hexamethylenediamine and a polyhydric alcohol such as trimethylolpropane as a reaction solution, adjusting the Ph value of the reaction solution, and then heating the reaction solution. The process for preparing this type of a composite wall made of a polyurea and a polyamide is further described in JP-A-58-66948. A capsule made of a polyamic acid can be formed, e.g., by interfacial reaction of a polystyrene-maleic anhydride copolymer with a polyamine.

Furthermore, in order to allow the microcapsule wall to swell upon heating, a sensitizer may be added in the form of an emulsion dispersion or solid dispersion.

The sensitizer exhibits a melting point of not lower than 50°C, preferably not higher than 150°C, but stays solid at room temperature. The sensitizer may be selected from commonly used polymer plasticizers of the microcapsule wall material. For example, if the wall material comprises a polyurea or polyurethane, a hydroxyl compound, ester carbaminate compound, aromatic alkoxy compound, organic sulfonamide compound, aliphatic amide-compound, or arylamide compound is preferably used as a sensitizer.

The water-soluble binder for use in the recording layer of the present invention is a compound which not only binds the developer and microcapsule contained in the recording layer, but also bonds the recording layer to the support. Examples of the water-soluble binder include water-soluble polymers such as gelatin, gelatin derivatives (e.g., phthalated gelatin), polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose and hydroxypropyl celulose, and various emulsions such as gum arabic, polyvinyl pyrrolidone, casein, styrene-butadiene latex, acrylonitrile-butadiene latex, polyvinyl acetate polyacrylic ester and ethylene-vinyl acetate copolymer.

The coated amount of the binder is preferably from 0.5 g/m^2 to 5 g/m^2 based on the solid content of the binder.

When the recording material of the present invention is prepared in the form of a photographic light-sensitive material, a preparation process is preferably used which comprises dispersing an organic silver salt represented by the formula RCOOAg in an organic solvent, adding a silver halide-forming agent to the dispersion to convert a part of said organic silver salt RCOOAg to a silver halide, adding a polyisocyanate to the dispersion simultaneously with or after conversion to obtain an oil phase component, adding said oil phase component to an aqueous solution containing a water-soluble polymer with stirring so that-it is dispersed in the aqueous solution, heating the dispersion to prepare a microcapsule solution containing microcapsules having said organic silver salt and silver halide incorporated therein, adding a developer for said organic silver salt to the microcapsule solution to prepare a recording layer coating solution, applying the coating solution thus obtained to a support, and then drying the coated material.

R in the above formula RCOOAg represents an alkyl group having from 6 to 23 carbon atoms, an aralkyl group having from 6 to 23 carbon atoms or an aryl group having from 6 to 23 carbon atoms. Among these groups, an alkyl group having from 6 to 23 carbon atoms is preferred.

When the recording material of the present invention is prepared in the form of a heat-sensitive recording material, it is not necessary to add the silver halide-forming agent in the above described preparation process.

The organic silver salt for use in the present invention is preferably a desalted and purified organic silver salt.

The term "desalting purification" as used herein means the removal of nitrates produced as a by-product by the addition- of silver nitrate to an organic acid salt which has been produced by the addition of an alkali to an organic acid. The desalting purification is preferably effected by a centrifugal separation process or an ultrafiltration process employing a semipermeable membrane which is permeable to organic silver salts but is impermeable to nitrates.

The support for use in the present invention may be transparent or opaque. Examples of such an opaque support include paper, synthetic paper, paper laminated with a polymer film, an aluminum-deposited base and a polymer film coated with a white pigment.

Examples of the transparent support include polyester films such as polyethylene terephthalate film and polybutylene terephthalate film, cellulose derivative films such as cellulose triacetate film, polyolefin films such as polystyrene film, polypropylene film and polyethylene film, polyimide film, polyvinyl chloride film, polyvinylidene chloride film, polyacrylic acid copolymer film and polycarbonate film. These films may be used singly or in laminated form. In particular, a polyester film which has been subjected to heat resisting treatment or antistatic treatment is desirable.

The thickness of the support is preferably from 20 μm to 200 μm, particularly from 50 μm to 100 μm.

In the present invention, if a polymer film or a paper laminated with such a polymer film is used as a support, or if a transparent support is used, a subbing layer is preferably provided which is interposed between the support and the recording layer to enhance the adhesion therebetween.

The subbing layer material may comprise gelatin, a synthetic polymer latex, or nitrocellulose. The coated amount of the subbing layer is preferably from 0.1 g/m^2 to 2.0 g/m^2, particularly from 0.2 g/m^2 to 1.0 g/m^2.

When the recording layer is applied to the subbing layer, the subbing layer can swell due to water contained in the recording layer. This swelling may deteriorate the quality of the image on the recording layer. Therefore, the subbing layer is preferably cured with a hardening agent.

Examples of the hardening agent include those described in JP-A-2-141279. The addition amount of the hardening agent may be properly selected from a range of from 0.20 wt% to 3.0 wt% depending on the coating method or desired degree of curing.

If necessary, caustic soda or citric acid or the like may be added to a coating solution for the subbing layer to adjust the pH value of the solution toward alkalinity or acidity, respectively, depending on the hardening agent that is used. Furthermore, an anti-foaming agent may be added to the system to eliminate foam that is generated upon coating. Alternatively, an activator may be added to the system to provide a solution having good leveling ability that inhibits the generation of coating lines.

Furthermore, application of the subbing layer is preferably preceded by activation of the surface of the support by a known method. The activation treatment may be accomplished by etching with an acid, flame treatment with a gas burner, corona discharge treatment, glow discharge treatment, etc. A corona discharge treatment as described in U. S. Patent Nos. 2,715,075, 2,846,727, 3,549,406 and 3,590,107 is most desirable from the standpoint of cost and convenience.

In the present invention, a protective layer comprising a pigment incorporated therein is preferably provided on the recording layer to protect the recording layer against sticking or solvents.

Examples of useful pigments include mica, calcium carbonate, zinc oxide, titanium oxide, aluminum hydroxide, kaolin, talc, agalmatolite, synthetic silicate, amorphous silica and urea-formalin resin powder. Particularly preferred among these pigments are calcium carbonate, aluminum hydroxide, kaolin, amorphous silica, mica and talc.

The protective layer of the present invention preferably comprises as a binder a completely-saponified polyvinyl alcohol, a carboxy-modified polyvinyl alcohol, or a silica-modified polyvinyl alcohol in view of pigment-retention as well as transparency.

The coating solution for the protective layer (hereinafter referred to as a "protective layer solution") of the present invention can be obtained by mixing the above described binder solution with a pigment. The protective layer solution may further comprise various auxiliary agents such as a lubricant and a dispersant (e.g., zinc stearate, calcium stearate, paraffin wax, polyethylene wax), a fluorescent brightening agent, a crosslinking agent, an alkaline metal salt of sulfosuccinic acid and a fluorine-containing surfactant.

The recording material of the present invention can be prepared, e.g., by preparing a coating solution for a recording layer comprising a heat-responsive microcapsule having an organic silver salt incorporated therein, a developer, a water-soluble binder and other additives and a protective layer coating solution, applying the recording layer coating solution to a support and applying the protective layer coating solution to the recording layer by a coating method such as bar coating, blade coating, air knife coating, gravure coating, roll coating, spray coating and dip coating, and then drying the coated material to form a recording layer having a solid content of from 2.5 to 25 g/m^2 and a protective layer having a solid content of from 0.2 to 7 g/m^2.

The coated amount of the organic silver salt and the developer are each preferably from 0.5 to 7.0 g/m^2, particularly preferably from 0.8 to 5.0 g/m^2.

The coating solution for use in the present invention may properly comprise a pigment dispersant, a thickening agent, a fluidity modifier, an anti-foaming agent, a foam-inhibitor, a release agent, a coloring agent, etc. as needed so long as the properties of the recording material are not impaired.

In the present invention, an organic silver salt is incorporated in a heat-responsive microcapsule so that it is isolated from other substances, to thereby inhibit the reduction reaction at room temperature. Accordingly, the recording material of the present invention has a remarkably prolonged shelf life as compared with prior art recording materials. Furthermore, images recorded on the recording material of the present invention have a high density.

Furthermore, the preparation process of the present invention employs a coating solution in aqueous form that is not detrimental to the working environment in the production of the recording material. Moreover, the preparation process does not pollute air with exhaust fumes of an organic solvent which are expelled from a factory.

The present invention will be further described in the following Examples, but the present invention should not be construed as being limited thereto. The parts and percentages as used herein are by weight unless otherwise specified.

EXAMPLE 1

Preparation of silver behenate

8.53 g of behenic acid was added to 200 g of water. The aqueous solution of behenic acid was then heated to a temperature of 90°C. To the aqueous solution was then added an aqueous solution obtained by dissolving 1.0 g of NaOH in 25 g of water. The mixture was then cooled to a temperature of 50°C.

Subsequently, to the resulting solution was added dropwise an aqueous solution obtained by dissolving 4.3 g of $AgNO_3$ in 25 g of water over a period of 1.5 hours to effect a reaction.

The resulting reaction solution was then added to a 1/1 (by weight) mixture of water and isopropanol. The mixture was stirred, and then subjected to centrifugal separation. This procedure was repeated three times. The resulting solid content was then air-dried at room temperature over the course of two days and two nights to obtain silver behenate having a water content of 0.5%. In this procedure, the resulting solid may be subjected to dehydration over isopropanol/butyl acetate followed by centrifugal separation instead of air drying.

Preparation of recording layer coating solution

(Preparation of capsule solution having silver behenate incorporated therein)

7.6 g of the silver behenate thus prepared, 20.0 g of n-butyl acetate, 5.0 g of an isopropyl alcohol and 2.0 g of a polyvinyl butyral were homogeneously mixed, and then subjected to dispersion at 10,000 rpm over a period of 2 hours by means of a homogenizer.

To the dispersion thus obtained was then added 8.0 g of Takenate D-110N (a capsule wall-forming agent, available from Takeda Chemical Industries, Ltd).

The resulting silver behenate solution was then added to a mixture (aqueous phase) of 40 g of a 6% aqueous solution of a polyvinyl alcohol (PVA217E, available from Kuraray Co., Ltd.) and 0.3 g of a 2% aqueous solution of dioctyl sodium sulfosuccinate. The mixture was then subjected to emulsion dispersion at 8,000 rpm for 10 minutes by means of a homogenizer.

To the resulting emulsion dispersion was then added 15 g of water. The mixture was then homogeneously mixed. The dispersion was then heated with stirring to a temperature of 40°C where it was allowed to undergo capsulization reaction for 3 hours so that the average grain diameter of the capsule reached 10 μm. As a result, a capsule solution having silver behenate incorporated therein was obtained.

(Preparation of emulsion dispersion of developer)

0.5 g of bisphenol B, 5 g of propyl gallate, 3 g of phthalazinone (development accelerator), 0.2 g of benzoxazinedione, 2 g of tribromomethylbenzimidazole, 4 g of ethyl acetate, 3 g of methyl cellosolve, 3 g of tetrahydrofuran, and 0.5 g of tricresyl phosphate were homogeneously mixed.

The resulting developer solution was then added to a mixture of 15 g of a 10% aqueous solution of a polyvinyl alcohol (PVA217E, available from Kuraray Co., Ltd.), 1 g of a 1% aqueous solution of sodium benzenethiosulfonate and 3 g of a 6% aqueous solution of sodium dodecylbenzenesulfonate. The mixture was then subjected to emulsion dispersion at 10,000 rpm for 10 minutes by means of a homogenizer.

Ethyl acetate, methyl cellosolve and tetrahydrofuran were then evaporated from the resulting emulsion dispersion under reduced pressure to obtain an emulsion dispersion of a developer having a grain diameter of 0.6 μm.

(Preparation of coating solution)

30 g of the capsule solution having silver behenate incorporated therein and 10 g of the emulsion dispersion of the developer were then mixed to obtain a coating solution.

Preparation of support having a subbing layer

An SBR latex was applied to one side of a 175-µm thick antistatically-treated transparent polyethylene terephthalate film in an amount of 0.3 g/m^2 in terms of its solid content. The subbing layer coating solution described below was then applied to the support on the same side in an amount of 0.1 g/m^2 as calculated in terms of solid content to obtain a support having a subbing layer.

Preparation of subbing layer coating solution

200 g of a 5% aqueous solution of gelatin (#810, available from Nitta Gelatin Co., Ltd.), 0.5 g of a 5% gelatin dispersion of a particulate polymethyl methacrylate resin having a grain diameter of 2 µm, 1.0 g of a 3% aqueous solution of 1,2-benzothiazoline-3-one and 10 g of a 2% aqueous solution of sodium di-octylsulfosuccinate were mixed to obtain a subbing layer coating solution.

Preparation of protective layer coating solution

To a mixture of 32 g of water, 32 g of a 10% aqueous solution of a carboxy-modified polyvinyl alcohol (PVA-KL-318, available from Kuraray Co., Ltd.) and 3 g of a 30% dispersion of an epoxy-modified polyamide (FL-71, available from Toho Chemical Industry Co., Ltd.) were then added 5 g of a 2% aqueous solution of a polyoxyethylene (surfactant) and 4 g of a 20% dispersion of zinc stearate (Hydrin Z, available from Chukyo Yushi Co., Ltd.) to obtain a protective layer coating solution.

Preparation of recording material

The recording layer coating solution thus obtained was applied to the support on the subbing layer side thereof in an amount of 0.8 g/m^2 as calculated in terms of silver, and then dried.

A protective layer coating solution was then applied to the recording layer thus formed in an amount of 2.0 g/m^2 as calculated in terms of solid content, and then dried.

Thermal recording and evaluation of shelf life

The recording material thus obtained was then subjected to the following recording test immediately after preparation and after 3 days of storage (deterioration test) under conditions of 40°C and 80%RH (relative humidity).

An image was recorded on the recording material thus obtained at a recording heat energy per unit area of 60 mJ/mm^2 by means of a Type KST thermal head (available from Kyocera Corp.) with the applied voltage and pulse width properly adjusted. The density of the image thus formed was then measured on the maximum color-developed area and the minimum color-developed area by means of a Macbeth densitometer. The results are set forth in Table 1.

Table 1

Sample No.	Immediately after preparation of recording material			After accelerated deterioration test		
	Minimum color density	Maximum color density	Relative sensitivity	Minimum color density	Maximum color density	Relative sensitivity
Example 1	0.06	1.93	--	0.07	1.83	--
Example 2	0.05	1.90	2.10	0.06	1.80	2.15
Example 3	0.06	1.93	--	0.07	1.83	--
Example 4	0.05	1.93	2.10	0.06	1.83	2.15
Example 5	0.06	1.93	--	0.07	1.83	--
Example 6	0.07	1.75	2.00	0.08	1.75	2.12
Example 7	0.08	1.93	2.21	0.09	1.83	2.40
Example 8	0.08	1.93	2.32	0.10	1.83	2.38
Example 9	0.09	1.93	2.25	0.14	1.84	2.40
Example 10	0.09	1.92	2.25	0.14	1.84	2.40
Comparative Example 1	0.06	1.92	--	0.81	1.95	--
Comparative Example 2	0.08	1.95	2.10	0.95	1.95	2.8*

The symbol * indicates that the relative sensitivity value was inaccurate because the minimum color density was too high.

EXAMPLE 2

The procedure of Example 1 was followed to prepare a recording material, except that 0.5 g of N-bromosuccinimide was added to the dispersion which was then allowed to stand for 1 hour at 50°C with stirring, 1 hour before the addition of Takenate D110N. Subsequently, the resulting recording material was exposed to light through an optical wedge over an EG&G sensitometer to effect optical recording. The image thus formed was then heat-developed. The image thus developed was then evaluated for shelf life in the same manner as in Example 1. The results are set forth in Table 1.

In this example, the shelf life was evaluated by measuring relative sensitivity in the manner described below in addition to measuring the image density on the maximum color-developed area.

Measurement of relative sensitivity

The recording material is exposed to light through an optical wedge, and then heated to a temperature of 130°C for 16 seconds to develop the same. The density of various image areas is measured by means of a Macbeth densitometer. The relative sensitivity is represented by the logarithm of the amount of light (candela) at which the fog density plus 0.2 is obtained. The smaller the logarithmic value, the higher the sensitivity.

EXAMPLE 3

The procedure of Example 1 was followed to prepare a recording material, except that Takenate D-110 (a capsule wall-forming agent) contained in the capsule solution comprising silver behenate was replaced by Burnock D750 (a capsule wall-forming agent, available from Dainippon Ink & Chemicals, Inc.). The recording material was then subjected to thermal recording to record an image thereon in the same manner as in Example 1. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

EXAMPLE 4

The procedure of Example 2 was followed to prepare a recording material, except that Takenate D-110 (a capsule wall-forming agent) contained in the capsule solution comprising silver behenate was replaced by Burnock D750 (a capsule wall-forming agent, available from Dainippon Ink & Chemicals, Inc.). The recording material was then subjected to imagewise optical recording to record an image thereon, and the image thus formed was then heat-developed in the same manner as in Example 2. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

EXAMPLE 5

The procedure of Example 1 was followed to prepare a recording material, except that propyl gallate contained in the emulsion dispersion of the developer was replaced by bisphenol A. The recording material was then subjected to thermal recording to record an image thereon in the same manner as in Example 5. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

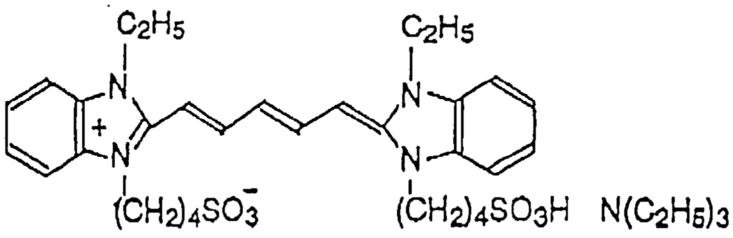
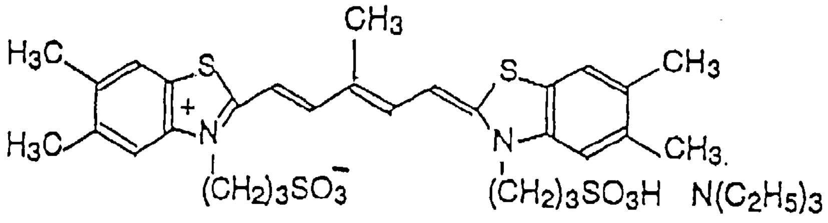
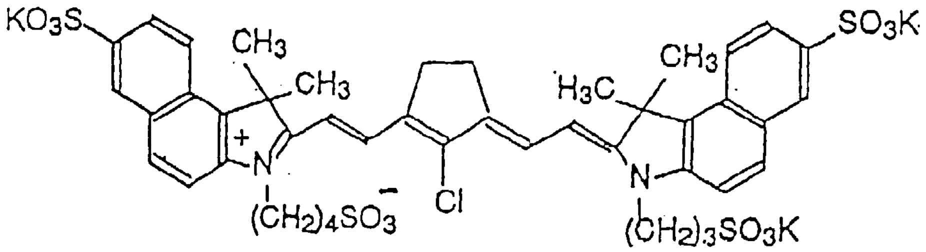
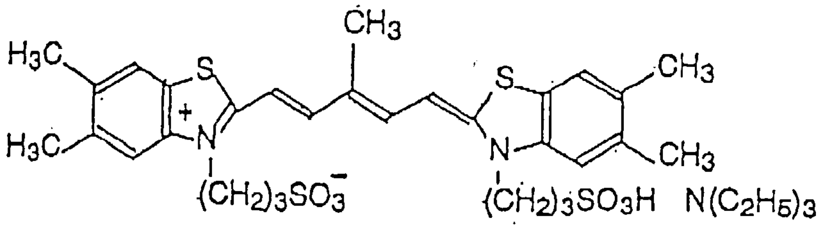
EXAMPLE 6

The procedure of Example 2 was followed to prepare a recording material, except that a capsule solution containing encapsulated silver behenate was prepared by adding 0.3 g of KBr to the aqueous phase 5 minutes after the beginning of the capsulization reaction instead of adding N-bromosuccinimide to the silver behenate solution. The recording material was subjected to imagewise optical recording, and then heat-developed in the same manner as in Example 2. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

EXAMPLES 7 to 10

The procedure of Example 2 was followed to prepare recording materials, except that the spectral sensitizers (Examples 7 to 10) set forth in Table 2 were added to silver behenate before the capsulization step in an amount of 10 cc in the form of 0.1% chloroform solution. The recording material was then irradiated with a 780 μm beam from a semiconductor laser to form a latent image therein. The latent image thus formed was then heat-developed in the same manner as in Example 2. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

Table 2

Example No.	Spectral sensitizer
Example 7	
Example 8	
Example 9	
Example 10	

COMPARATIVE EXAMPLE 1

The procedure of Example 1 was followed to prepare a recording material, except that the capsule solution comprising silver behenate was replaced by an emulsion dispersion of silver behenate prepared in the manner described below. The recording material thus obtained was then subjected to thermal recording to record an image thereon in the same manner as in Example 1. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

(Preparation of dispersion of silver behenate)

7.6 g of silver behenate (containing free stearic acid in an amount of 5 mol%), 40 g of a 6% polyvinyl alcohol and

50 g of water were homogeneously mixed. The mixture was then subjected to dispersion at 10,000 rpm by means of a homogenizer for 5 minutes to obtain a dispersion of silver behenate.

COMPARATIVE EXAMPLE 2

The procedure of Comparative Example 2 was followed to prepare a recording material, except that the capsule solution comprising silver behenate was replaced by a solution obtained by adding 0.5 g of N-bromosuccinimide to the dispersion of silver behenate that was used in Comparative Example 1. The recording material was subjected to imagewise optical recording, and then heat-developed in the same manner as in Example 2. The recording material thus prepared was evaluated for shelf life. The results are set forth in Table 1.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A recording material comprising a support having provided thereon at least a recording layer comprising (a) a heat-responsive microcapsule having encapsulated therein an organic silver salt, (b) a developer for the organic silver salt and (c) a water-soluble binder.

2. The recording material according to Claim 1, wherein the recording layer further comprises a color toner.

3. The recording material according to either Claim 1 or 2, wherein the heat-responsive microcapsule further comprises a silver halide encapsulated therein in an amount of from 1 to 30 mol% based on the amount of the encapsulated organic silver salt, and the silver halide is adjacent to the organic silver salt.

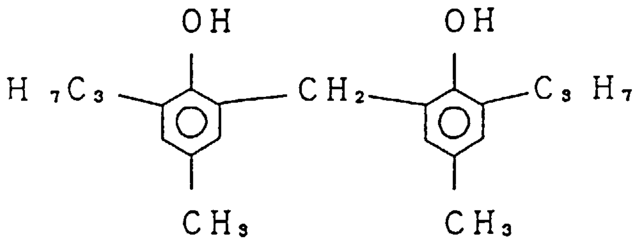
4. The recording material according to any preceding claim, wherein the organic silver salt has been subjected to desalting purification prior to encapsulating in the heat-responsive microcapsule.

5. The recording material according to any preceding claim, wherein the organic silver salt is a silver salt of an organic compound having an imino group, a silver salt of an orgnaic compound having a mercapto group or a thione group, or a silver salt of an organic compound having a carboxyl group.

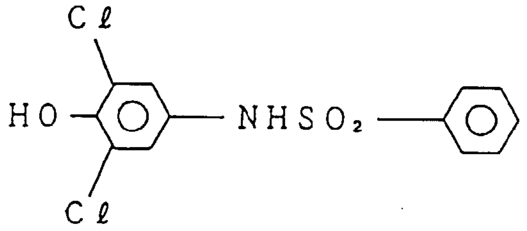
6. The recording material according to Claim 5, wherein the organic silver salt comprises silver behenate.

7. The recording material according to any preceding claim, wherein the developer and the water-soluble binder are arranged in the recording layer outside the heat-responsive microcapsule.

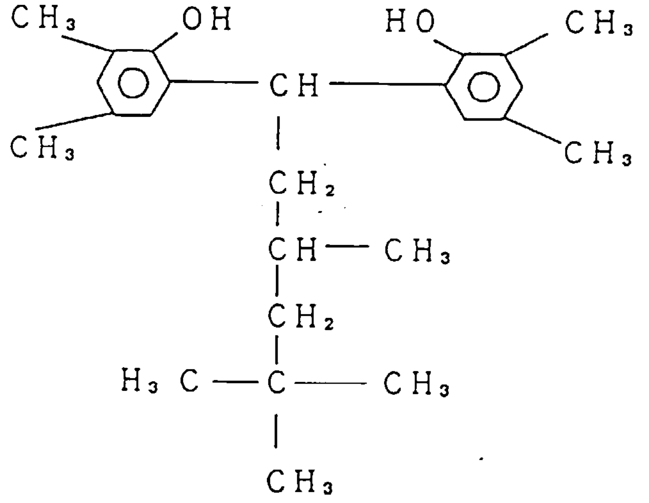
8. The recording material according to any preceding claim, wherein the developer comprises a compound represented by one of formulae (I) to (IV), octyl gallate or propyl gallate:



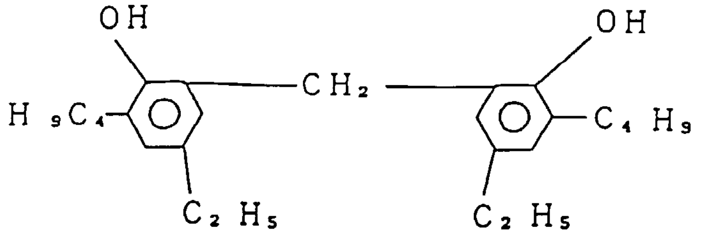
(I)



(II)



(III)



(IV)

9. The recording material according to any preceding claim, wherein the coated amount of the binder is from 0.5 g/m^2 to 5 g/m^2 based on the solid content of the binder.

10. The recording material according to any preceding claim, wherein the encapsulated organic silver salt is free of nitrates.

11. The recording material according to any preceding claim, further comprising a subbing layer disposed between the support and the recording layer.

12. A process for producing a recording material comprising a support having provided thereon at least a recording layer comprising (a) a heat-responsive microcapsule having encapsulated therein an organic silver salt, (b) a developer for the organic silver salt and (c) a water-soluble binder, wherein the heat-responsive microcapsule further comprises a silver halide encapsulated therein in an amount of from 1 to 30 mol% based on the amount of the encapsulated organic silver salt, and the silver halide is adjacent to the organic silver salt, said process comprising the steps of

dispersing an organic silver salt represented by the formula RCOOAg in an organic solvent, wherein R represents an alkyl group having from 6 to 23 carbon atoms;
then adding a silver halide-forming agent to the organic solvent to thereby convert a part of the organic silver salt to silver halide;

simultaneously with or after the conversion, adding a polyisocyanate to the solution to provide an oil phase component;
adding the oil phase component to an aqueous solution containing a water-soluble polymer, and stirring to thereby disperse the oil phase in the aqueous solution;
then heating and preparing a microcapsule solution containing a microcapsule having encapsulated therein the organic silver salt and the silver halide; and
further adding a developer for the organic silver salt to the solution to thereby prepare a coating solution for forming a recording layer; and
coating a support with the coating solution, and drying the coating solution.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 2324

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)
Y	US-A-5 380 644 (YONKOSKI ET AL.) * column 11, line 17 - line 24 * * column 11, line 31 - line 40 * * column 12, line 14 - line 15 * * column 15, line 1 - line 15 * * column 15, line 24 - line 26 * * column 18, line 36 - line 37 * * column 18, line 67 - column 19, line 2 * * column 23, line 59 - line 64 * ---	1-12	G03C1/498 G03C1/00
Y	US-A-4 708 928 (GEISLER) * column 6, line 43 - line 53 * * column 7, line 3 - line 24 * * column 7, line 55 - column 8, line 3; claim 1 * ---	1-12	
Y	DE-A-38 35 062 (FUJI) * page 3, line 58 - line 64 * * page 9, line 3 - line 8; claim 1 * ---	9,12	
Y	EP-A-0 452 853 (FUJI) * page 48, line 28 - line 32 * -----	4,10	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	18 June 1996	Magrizos, S

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document

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