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(71) Applicant: **KANZAKI PAPER MANUFACTURING CO., LTD.**
7, Kandaogawamachi 3-chome Chiyoda-ku
Tokyo 101(JP)

(72) Inventor: **Watanabe, Kazuo, C/o Kanzaki Paper Mfg. Co. Ltd.**
Kanzaki Works, 3-1, Jokoji 4-chome
Amagasaki-shi, Hyogo(JP)
Inventor: **Okimoto, Tomoyuki, C/o Kanzaki Paper Mfg. Co. Ltd.**
Kanzaki Works, 3-1, Jokoji 4-chome
Amagasaki-shi, Hyogo(JP)

(74) Representative: **Hoffmann, Klaus, Dr. rer. nat. et al**
Hoffmann . Eitle & Partner Patentanwälte
Postfach 81 04 20 Arabellastrasse 4
D-8000 München 81(DE)

(54) Heat-sensitive recording material.

(57) A heat-sensitive recording material is disclosed, comprising a support having thereon a recording layer containing a color former and a color developer which makes said color former produce a color upon heating and an overcoat layer in that order, said overcoat layer containing a water-soluble resin, a modified silicone oil, and a hardener which reacts with both of said water-soluble resin and modified silicone oil.

HEAT-SENSITIVE RECORDING MATERIAL

FIELD OF THE INVENTION

The present invention relates to a heat-sensitive recording material. More particularly, it relates to a heat-sensitive recording material which not only can record information at a high color density but has an excellent gloss as well as excellent running properties in recording.

BACKGROUND OF THE INVENTION

Heat-sensitive recording materials have conventionally been known which can produce a color by the action of heat energy generated by a heat-sensitive head. Such heat-sensitive recording materials are comparatively inexpensive and can be used on compact recording devices whose maintenance is relatively easy. Because of these advantages, heat-sensitive recording materials are used in a variety of fields not only as recording media for use in facsimile telegraphs or various types of computers but also as heat-sensitive labels and others. However, heat-sensitive recording materials are poor in fingerprint resistance and solvent resistance, so that if the recording layer comes in contact, for example, with a human sebum or a solvent, the color density of information recorded on such a recording material is decreased or an unwanted coloration ("background fog") occurs.

In order to eliminate the above problem, several methods have been proposed. In one method, a heat-sensitive recording layer is coated with an aqueous emulsion of a resin having both film-forming properties and chemical resistance (JP-A-54-128347); in another method, a heat-sensitive recording layer is coated with a water-soluble polymer such as polyvinyl alcohol (JP-A-U-56-125354). (The term "JP-A" and JP-A-U" as used herein mean an "unexamined published Japanese patent application" and "unexamined published Japanese utility model application", respectively.) However, the above-proposed improvements have resulted in new defects and satisfactory results have not always been obtained so far.

For example, in the method in which an aqueous resin coating is applied on the heat-sensitive recording layer, the temperature for drying has to be limited to a certain level in order to avoid unwanted coloration of the recording layer due to high-temperature drying, whereby curing of the resin layer inevitably becomes insufficient and this results in sticking of the resin layer to a recording head during recording. In order to avoid this problem, improved running properties in recording have been attained by incorporation of a pigment, lubricant, hardener, etc.

On the other hand, as various kinds of printers including video printers for providing photograph-like high-quality images have come into use recently, heat-sensitive recording materials for printing out are also required to have better color densities of recorded images and better tone gradation characteristics. For this reason, heat-sensitive recording materials which employ a plastic film, synthetic paper, or coated paper with high smoothness as a support and have excellent tone gradation characteristics are being developed. In preparing such heat-sensitive recording materials also, attempts have been made to form an overcoat layer of a water-soluble resin or the like on the recording layer in order to improve the preservability of recorded images.

However, if such a recording material having an overcoat layer comprising a water-soluble resin is subjected to recording on a video printer particularly under high-humidity conditions, the overcoat layer is prone to stick to the recording head or paper feed guides and this often causes a trouble that feeding and running of the recording material is stopped. Further, conventional overcoat layers cannot provide highly glossy surfaces, and recorded images on conventional recording materials of the above type cannot always have satisfactory color densities.

Furthermore, in the case where a heat-sensitive recording material has been formed into an adhesive label, the recording material is required to have a high degree of resistance to plasticizers contained in vinylidene chloride polymer films and various oils, so as to show good preservability of recorded images. However, heat-sensitive recording materials showing satisfactorily good preservability have not so far been obtained.

SUMMARY OF THE INVENTION

Under these circumstances, the present inventors have made intensive studies in order to eliminate the defects described above. As a result, they have found that a heat-sensitive recording material which is free from sticking to recording heads, has exceedingly good running properties and a high gloss, and also gives recorded images having a high color density and excellent preservability can be obtained by forming a specific overcoat layer on a heat-sensitive recording layer. The present invention has been accomplished based on this finding.

The present invention relates to a heat-sensitive recording material comprising a support having thereon a recording layer containing a color former and a color developer which makes the color former produce a color upon heating and an overcoat layer in that order, the overcoat layer containing a water-soluble resin, a modified silicone oil, and a hardener which reacts with both of the water-soluble resin and modified silicone oil.

DETAILED DESCRIPTION OF THE INVENTION

There is no particular limitation on the possible combination of color formers and color developers that are to be incorporated in a heat-sensitive recording layer of the heat-sensitive recording material of the present invention, and any combination that undergoes a coloring reaction by the action of heat energy generated by heat-sensitive heads may be employed. Illustrative combinations are those of colorless or pale-color basic dyes and inorganic or organic acidic substances, those of metal salts of higher fatty acids (e.g., ferric stearate) and phenols (e.g., gallic acid), and so-called photofixation-type heat-sensitive recording materials consisting of combinations of diazonium compounds, coupler compounds, and compounds that produce a basic atmosphere when fused upon heating.

Of these, the combination of a basic dye and an acidic substance is particularly preferred because a heat-sensitive recording material having especially good recording properties is obtained where the specific overcoat layer according to this invention is formed on a recording layer employing the combination of a basic dye and an acidic substance.

Various types of colorless or pale-color basic dyes are known. Examples thereof include triarylmethane-based dyes such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindol-3-yl)-6-dimethylaminophthalide, and 3-p-dimethylaminophenyl-3-(1-methylpyrrol-3-yl)-6-dimethylaminophthalide; diphenylmethane-based dyes such as 4,4′-bisdimethylaminobenzhydrylbenzyl ether, N-halophenyl-leucoauramines, and N-2,4,5-trichlorophenyl-leucoauramine; thiazine-based dyes such as benzoyl leucomethylene blue and p-nitrobenzoyl-leucomethylene blue; spiro-based dyes such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methylnaphtho(6′-methoxybenzo)spiropyran, and 3-propyl-spiro-dibenzopyran; lactam-based dyes such as rhodamine-B-anilinolactam, rhodamine(p-nitroanilino)lactam, and rhodamine(o-chloroanilino)lactam; and fluoran-based dyes such as 3-dimethylamino-7-methoxyfluoran, 3-diethylamino-6-methoxyfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-diethylamino-7-N-acetyl-N-methylaminofluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-N-methyl-N-benzylaminofluoran, 3-diethylamino-7-N-chloroethyl-N-methylaminofluoran, 3-diethylamino-7-N-diethylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran, 3-diethylamino-6-methyl-7-phenylaminofluoran, 3-diethylamino-7-(2-carbomethoxyphenylamino)fluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-phenylaminofluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-phenylaminofluoran, 3-piperi dino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-dibutylamino-7-(o-chlorophenylamino)fluoran, 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, 3-dibutylamino-6-methyl-7-phenylaminofluoran, and 3-dipentylamino-6-methyl-7-phenylaminofluoran.

Various types of inorganic or organic acidic substances are also known as a color developer which makes the colorless or pale-color basic dye produce a color upon contact therewith. Examples thereof include inorganic acidic substances such as activated clay, acid clay, attapulgite, bentonite, colloidal silica, and aluminum silicate; and organic acidic substances including phenolic compounds such as 4-tert-butylphenol, 4-hydroxydiphenoxide, α-naphthol, β-naphthol, 4-hydroxyacetophenol, 4-tert-octylcatechol, 2,2′-dihydroxydiphenol, 2,2′-methylenebis(4-methyl-6-tert-isobutylphenol), 4,4′-isopropylidenebis(2-tert-butylphenol), 4,4′-sec-butylidenediphenol, 4-phenylphenol, 4-hydroxy-4′-isopropoxydiphenyl sulfone, 4,4′-isopropylidenephenol (bisphenol A), 2,2′-methylenebis(4-chlorophenol), 4,4′-(1,3-dimethylbutylidene)-bisphenol, hydroquinone, 4,4′-cyclohexylidenediphenol, benzyl 4-hydroxybenzoate, dimethyl 4-hydroxyphthalate, hydroquinone monobenzyl ether, novolak type phenol resins, and phenol polymers; aromatic carboxylic acids such as benzoic acid, p-tert-butylbenzoic acid, trichlorobenzoic acid, terephthalic acid, 3-sec-butyl-4-hydroxybenzoic acid, 3-cyclohexyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, salicylic acid, 3-isopropylsalicylic acid, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-(α-methylbenzyl)-salicylic acid, 3-chloro-5-(α-methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-(α,α-dimethylbenzyl)salicylic acid, and 3,5-di-α-methylbenzylsalicylic acid; salts of such phenolic compounds or aromatic carboxylic acids with polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin, and nickel; organic acidic compounds; and the like.

The proportion of the color former to the color developer used in the recording layer of the heat-sensitive recording material of the present invention is not particularly limited and may be appropriately selected according to the kinds of the color former and developer employed. For example, in the case where a colorless or pale-color basic dye and an acidic substance are employed, the latter may generally be used in an amount from 1 to 50 parts by weight, preferably from 1 to 10 parts by weight, per part by weight of the former.

A coating composition containing these substances may be prepared by dispersing the color former and developer, either together or separately, in a dispersion medium, which is typically water, by means of a suitable stirrer/pulverizer such as a ball mill, an attritor, or a sand mill.

Such a coating composition may contain a binder in an amount from about 10 to 40 wt%, preferably from about 15 to 30 wt%, of the total solids content of the coating composition. Examples of the binder include starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, gum arabic, polyvinyl alcohol, diisobutylene/maleic anhydride copolymer salts, styrene/maleic anhydride copolymer salts, ethylene/acrylic acid copolymer salts, styrene/acrylic acid copolymer salts, and styrene/butadiene copolymer emulsions.

The coating composition may further contain a variety of additives such as dispersants (e.g., sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salts of lauryl alcohol sulfuric acid esters, alginic acid salts, and metal salts of fatty acids), ultraviolet light absorbers (e.g., benzophenone- and triazole-based compounds), defoaming agents, fluorescent dyes, and coloring dyes.

Other additives that may be incorporated according to need in the coating composition include: lubricants such as zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, and ester waxes; inorganic pigments such as kaolin, clay, talc, calcium carbonate, calcined clay, titanium oxide, diatomaceous earth, fine granular anhydrous silica, and activated clay; and heat-fusible substances of various known kinds including stearic acid amide, stearic acid methylenebisamide, oleic acid amide, palmitic acid amide, sperm oleic acid amide, coconut fatty acid amide, hindered phenols such as 2,2′-methylenebis(4-methyl-6-tert-butylphenol) and 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, ethers such as 1,2-bis(phenoxy)ethane, 1,2-bis(4-methylphenoxy)ethane, 1,2-bis(3-methylphenoxy)ethane, 2-naphthyl benzyl ether, and benzyl 4-methylthiophenyl ether, and esters such as phenyl 1-hydroxy-2-naphthoate and dibenzyl terephthalate.

As the support for use in the heat-sensitive recording material of this invention, paper, plastic films, and synthetic paper can be employed. Of these, plastic films and synthetic paper provide recording layers having high smoothness. Although there is a tendency for such highly smooth recording layers to be more apt to stick to recording heads, the poor running properties of such a heat-sensitive recording material employing a plastic film or synthetic paper support can be greatly improved according to the present invention.

Examples of plastic films include films of polyethylene, polyesters, polyvinyl chloride, polystyrene, and nylons. Examples of synthetic paper include one produced by a film method or a fiber method. Examples of the film method include the internal paper-making process in which a synthetic resin, a filler, and additives are melt-kneaded and then formed into a film by extrusion, the surface-coating process in which a pigment coating layer is formed, and the surface-treating process in which an anchor coat, etc. is formed. On the other hand, the fiber method yields, for example, synthetic pulp paper and spunbonded paper. Any of these may be employed in the present invention. Particularly preferably employed of the above supports are plastic films and synthetic paper made by the film method because such supports provide excellent recording properties.

The method that can be employed to form the recording layer is not particularly limited, and conventionally known techniques may be used. For instance, the coating composition may be applied on a support by such methods as bar coating, air-knife coating, rod blade coating, pure blade coating, reverse-roll coating, and short-dwell coating and subsequently dried. In the case where a plastic film is used as the support, the surface of the film may be subjected beforehand to corona discharge treatment, electron beam irradiation treatment, or the like to heighten the application efficiency. The amount of the coating composition applied is not particularly limited, but the coating amount is generally regulated in the range of from about 2 to 12 g/m^2, preferably from about 3 to 10 g/m^2, on a dry basis.

In accordance with the present invention, the heat-sensitive recording layer thus formed is then coated with an overcoat layer which contains a water-soluble resin. Especially preferred as the water-soluble resin is polyvinyl alcohol, specific examples of which are listed below.

Completely or partially saponified polyvinyl alcohol; acetoacetylated polyvinyl alcohol in which an acetoacetyl group has been introduced by reaction between polyvinyl alcohol and diketene, etc.; carboxy-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and an ethylenically unsaturated carboxylic acid such as maleic acid, fumaric acid, itaconic acid, crotonic acid, acrylic acid, or methacrylic acid; sulfonic acid-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and an olefin sulfonic acid such as ethylenesulfonic acid or allylsulfonic acid, or a salt thereof; olefin-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and an olefin such as ethylene, propylene, isobutylene, α-octene, α-dodecene, or α-octadodecene; nitrile-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and a nitrile such as acrylonitrile or methacrylonitrile; amide-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and an amide such as acrylamide or methacrylamide; pyrrolidone-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of vinyl acetate and N-vinylpyrrolidone; and silicone-modified polyvinyl alcohol obtained as a product of saponification of a copolymer of a vinyl ester and an olefinically unsaturated monomer containing a silyl group in the molecule.

Of these various types of polyvinyl alcohol, silicone-modified polyvinyl alcohol is particularly preferred because the overcoat layer employing such polyvinyl alcohol was found to show excellent barrier properties and enable the final heat-sensitive recording material to have excellent running properties, such a recording material being the most preferred embodiment of this invention. Especially preferred silicone-modified polyvinyl alcohol is one in which the content of the monomer containing a silyl group in the molecule is from 0.1 to 5 mol%. Examples of such silicone-modified polyvinyl alcohol include R-polymers (trade name: R-1130, R-2105, R-2130) manufactured by Kuraray Co., Ltd., Japan.

As the modified silicone oil to be contained in the overcoat layer according to the present invention, an epoxy- or amino-modified silicone oil is preferably employed which can be obtained by incorporating an epoxy or amino group in dimethylpolysiloxane, hydrogen polysiloxane, or the like at a side chain or terminal thereof. Such silicone oils, which are hydrophobic, may be used in the form of an emulsion or after being modified into a water-soluble form by incorporating a hydrophilic group, such as a polyether group, other than epoxy and amino groups. Specific examples of the modified silicone oil include: epoxy-modified silicone oil emulsions such as SM8715 produced by Toray Silicone Co., Ltd., Japan and Polon MF-11b and Polon MF-18 produced by Shin-Etsu Chemical Co., Ltd., Japan; epoxy-polyether-modified silicone oils such as SF-8421, BY16-845, BX16-863, BX16-864 and BX16-865 produced by Toray Silicone Co., Ltd.; and amino-modified silicone oil emulsions such as SM-8702 and SM-8709 produced by Toray Silicone Co., Ltd. and Polon MF-14, Polon MF-14D, and Polon MF-14E produced by Shin-Etsu Chemical Co., Ltd. In order that the modified silicone oil can fully perform its function, the amount thereof incorporated in the overcoat layer may be from 1 to 10 wt% based on the total amount of all the solid components.

The coating composition for forming an overcoat layer further contains a hardener in order to still more improve the preservability under various conditions, plasticizer resistance, and other properties of the heat-sensitive recording material. In the case where the coating composition contains polyvinyl alcohol and an epoxy- or amino-modified silicone oil, examples of the hardener for crosslinking both materials include glyoxal, methylolmelamine, potassium persulfate, ammonium persulfate, sodium persulfate, ferric chloride, magnesium chloride, boric acid, alum, and ammonium chloride. Boric acid is particularly suited for the combination of polyvinyl alcohol and an epoxy-modified silicone oil, while glyoxal is particularly suited for the combination of polyvinyl alcohol and an amino-modified silicone oil. The above two systems can be cured at low temperatures and, hence, are especially advantageous as the overcoat layer to be formed on the heat-sensitive recording layer. The crosslinkable modified silicone oil described above does not adversely affect the preservability because it is fixed in the overcoat layer by the action of the hardener, whereas non-crosslinkable silicone oils, if used, are not fixed in the overcoat layer to cause discoloration of the recording layer or decrease the sensitivity of the recording layer.

The amount of the hardener incorporated in the overcoat layer may be in the range from 0.1 to 5 wt% based on the total amount of all the solid components. The coating composition for forming the overcoat layer is generally provided in the form of a water-based coating fluid. After this coating composition is optionally mixed by means of a suitable mixer/stirrer such as a mixer, an attritor, a ball mill, or a roll mill into a sufficiently mixed and dispersed state, the coating composition is applied on the heat-sensitive recording layer by a coating apparatus selected from various known coating apparatus. Examples of the coating method which can be employed include bar coating, air knife coating, rod blade coating, pure blade coating, reverse roll coating, short dwell coating, curtain coating, etc. Among these coating methods, the curtain coating is preferred because when applied for the formation of the overcoat layer, a uniform coat layer can be formed without causing selective absorption of the overcoat coating composition, resulting in obtaining a heat-sensitive recording material with higher quality. After the application, the coating is dried. The coating applied may be irradiated with ultraviolet rays or electron beams to accelerate crosslinking reactions.

If desired and necessary, various additives may suitably be incorporated in the coating composition for forming the overcoat layer. Examples of such additives include: lubricants such as zinc stearate, calcium stearate, stearic acid amide, polyethylene wax, carnauba wax, paraffin wax, and ester waxes; surfactants such as sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salts of lauryl alcohol sulfuric acid esters, alginic acid salts, and metal salts of fatty acids; ultraviolet light absorbers such as benzo phenone- and triazole-based compounds; defoaming agents; fluorescent dyes; and coloring dyes.

For the purpose of improving suitability for writing, an inorganic or organic pigment may be incorporated such as, for example, heavy calcium carbonate, light calcium carbonate, talc, clay, natural silicates, synthetic silicates, titanium oxide, aluminum hydroxide, zinc oxide, or urea-formaldehyde resin powder. However, since too large proportions of such additives and pigments incorporated result in decreases in the gloss and color density of recorded images, the amount of the additives and pigments used is preferably not more than 50% by weight based on the total weight of the overcoat layer.

The amount of the coating composition applied for forming the overcoat layer is not particularly limited. However, if the coating composition is applied in an amount less than 0.1 g/m^2, the intended effects of the present invention are not fully attained, while if the coating composition is applied in an amount exceeding 20 g/m^2, the recording sensitivity of the resulting heat-sensitive recording material may be reduced markedly. Therefore, the coating amount for the coating composition is generally regulated in the range from about 0.1 to 20 g/m^2, preferably from about 0.5 to 10 g/m^2, on a dry basis.

Supercalendering may be performed, if desired and necessary, after the heat-sensitive recording layer is formed and/or after the overcoat layer is formed, in order to improve the quality and color density of recorded images.

In the case where paper is employed as the support, it is preferred to form on the base paper an undercoat layer comprising a binder and a pigment as major components and then form a heat-sensitive recording layer and the specific overcoat layer on this undercoat layer, because not only the color density of recorded images can be heightened, but the adverse effect of oils and plasticizers in contact with the back side of the support can be lessened and, hence, a heat-sensitive recording material that is excellent in the preservability of recorded images can be obtained. For the purpose of even more diminishing the effect of oils and plasticizers in contact with the back side of the support to thereby further improve the preservability, a back barrier layer comprising a binder and a pigment as major components may be formed on the back side of the recording material. As the binder and pigment for use in the undercoat layer and back barrier layer, ones which can be employed in the heat-sensitive recording layer described hereinbefore may be used.

Since recorded images on the heat-sensitive recording material of the present invention show excellent preservability, a heat-sensitive recording material for use as a high-quality adhesive label that meets high-level preservability requirements can be obtained by providing the recording material with a pressure-sensitive adhesive layer on the back side thereof to give an adhesive label.

The present invention will be explained below in more detail by reference to the following examples, which should not, of course, be construed to be limiting the scope of the invention. In the examples, all parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

(1) Preparation of Dispersion A:	
3-(N-Cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran	10 parts
5% Aqueous solution of methyl cellulose	5 parts
Water	30 parts

A mixture of these components was pulverized by a sand mill until the average particle diameter became 3 µm.

(2) Preparation of Dispersion B:	
4,4′-Isopropylidenediphenol	20 parts
5% Aqueous solution of methyl cellulose	5 parts
Water	55 parts

A mixture of these components was pulverized by a sand mill until the average particle diameter became 3 µm.

(3) Formation of Recording Layer:

45 parts of Dispersion A, 80 parts of Dispersion B, 50 parts of a 20% aqueous solution of oxidized starch, and 10 parts of water were mixed by stirring to give a coating composition. This coating composition was coated on a 80 g/m^2 synthetic paper (trade name, FPG-80; manufactured by Oji-Yuka Co., Ltd., Japan) in a coating amount of 6 g/m^2 on a dry basis and then dried, thereby obtaining a heat-sensitive recording material.

(4) Formation of Overcoat Layer:

A coating fluid having the composition specified below was coated on the above-obtained heat-sensitive recording material on its heat-sensitive layer side in a coating amount of 2 g/m^2 on a dry basis by an air knife coater and then dried. The resulting heat-sensitive recording material was subjected to surface-smoothing treatment with a supercalender. Thus, a heat-sensitive recording material with an overcoat layer was obtained.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufacture by Kuraray Co., Ltd., Japan)	100 parts
Epoxy-modified silicone oil emulsion (trade name, Polon MF-11B; manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 30%)	3 parts
5% Aqueous solution of boric acid	2 parts
50% Dispersion of light calcium carbonate	1 part

EXAMPLE 2

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying a coating fluid having the composition as specified below in a coating amount of 2 g/m^2 on a dry basis.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufactured by Kuraray Co., Ltd., Japan)	100 parts
Amino-modified silicone oil emulsion (trade name, Polon MF-14D; manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 30%)	3 parts
5% Aqueous solution of glyoxal	1 part
50% Dispersion of light calcium carbonate	1 part

EXAMPLE 3

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

8% Aqueous solution of acetoacetylated polyvinyl alcohol (trade name, Gohsefimer Z-200; manufactured by Nippon Synthetic Chemical Industry Co., Ltd., Japan)	100 parts
Amino-modified silicone oil emulsion (trade name, Polon MF-14D; manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 30%)	3 parts
5% Aqueous solution of glyoxal	1 part
5% Aqueous solution of alum	1 part
Silicon oxide pigment	0.5 part

EXAMPLE 4

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

10% Aqueous solution of silicone-modified polyvinyl alcohol (trade name, R-2105; manufactured by Kuraray Co., Ltd., Japan)	100 parts
Epoxy-modified silicone oil emulsion (trade name, Polon MF-11B; manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 30%)	1.5 parts
5% Aqueous solution of boric acid	2 parts
50% Dispersion of light calcium carbonate	1 part

EXAMPLE 5

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

10% Aqueous solution of silicone-modified polyvinyl alcohol (trade name, R-2105; manufactured by Kuraray Co., Ltd., Japan)	100 parts
Amino-modified silicone oil emulsion (trade name, Polon MF-11B; manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 30%)	1.5 parts
5% Aqueous solution of glyoxal	2 parts
50% dispersion of light calcium carbonate	1 part

EXAMPLE 6

A heat-sensitive recording material was obtained in the same manner as in Example 4 except that a corona-treated polypropylene film (trade name, Pylen Film; thickness, 60 µm; manufacture by Toyobo Co., Ltd., Japan) was used as a support.

EXAMPLE 7

A heat-sensitive recording material was obtained in the same manner as in Example 4 except that a corona-treated polyester film (trade name, Ester Film; thickness, 60 µm; manufactured by Toyobo Co., Ltd., Japan) was used as a support.

EXAMPLE 8

A heat-sensitive recording material was obtained in the same manner as in Example 4 except that a 50 g/m^2 base paper was used as a support.

EXAMPLE 9

A heat-sensitive recording material was obtained in the same manner as in Example 8 except that a coating fluid having the composition as specified below was coated on the same base paper as that used in Example 8 in a coating amount of 6 g/m^2 on a dry basis and then dried, thereby forming an undercoat layer.

Calcined clay (trade name, Ansilex; manufactured by Engelhard Minerals & Chemicals Corporation)	100 parts
Styrene-butadiene copolymer latex (trade name, L-1571; manufactured by Asahi Chemical Industry Co., Ltd., Japan; concentration, 48%)	25 parts
10% Aqueous solution of polyvinyl alcohol (trade name, PVA-110; manufactured by Kuraray Co., Ltd., Japan)	15 parts
Water	100 parts

EXAMPLE 10

A coating fluid having the composition as specified below was coating on the heat-sensitive recording material obtained in Example 8 on the back side thereof in a coating amount of 6 g/m^2 on a dry basis and then dried, thereby forming a back barrier layer.

50% Aqueous dispersion of kaolin	100 parts
Styrene-butadiene copolymer latex (trade name, L-1571; manufacture by Asahi Chemical Industry Co., Ltd., Japan; concentration, 48%)	20 parts
10% Aqueous solution of polyvinyl alcohol (trade name, PVA-110; manufactured by Kuraray Co., Ltd., Japan)	10 parts
Water	70 parts

EXAMPLE 11

The same coating fluid for forming a back barrier layer as that used in Example 10 was coated on the back side of the heat-sensitive recording material obtained in Example 9 in a coating amount of 6 g/m^2 on a dry basis and then dried, thereby forming a back barrier layer.

EXAMPLE 12

A pressure-sensitive adhesive layer was formed on the back side of the heat-sensitive recording material as obtained in Example 11, thereby obtaining a heat-sensitive recording material in the form of an adhesive label.

EXAMPLE 13

A heat-sensitive recording material was obtained in the same manner as in Example 4 except that the coating fluid for overcoat layer was applied by a curtain coater and then dried.

COMPARATIVE EXAMPLE 1

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was not formed.

COMPARATIVE EXAMPLE 2

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufactured by Kuraray Co., Ltd., Japan)	100 parts
50% Dispersion of light calcium carbonate	1 part

COMPARATIVE EXAMPLE 3

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufactured by Kuraray Co., Ltd., Japan)	100 parts
50% Dispersion of light calcium carbonate	20 parts
30% Aqueous solution of zinc stearate (trade name, Hidorin Z-7; manufactured by Chukyo Yushi Co., Ltd., Japan)	5 parts

COMPARATIVE EXAMPLE 4

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufactured by Kuraray Co., Ltd., Japan)	100 parts
Dimethylpolysiloxane emulsion (trade name, SH-7036; non-crosslinkable silicone emulsion manufactured by Shin-Etsu Chemical Co., Ltd., Japan; concentration, 38%)	2.5 parts
50% Dispersion of light calcium carbonate	1 part

COMPARATIVE EXAMPLE 5

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

8% Aqueous solution of polyvinyl alcohol (trade name, PVA-117; manufactured by Kuraray Co., Ltd., Japan)	100 parts
Dimethylpolysiloxane emulsion (trade name, SH-7036; non-crosslinkable silicone emulsion manufactured by Shin-Etsu Chemical Co., Ltd.; concentration, 38%)	2.5 parts
5% Aqueous solution of boric acid	2 parts
50% Dispersion of light calcium carbonate	1 part

COMPARATIVE EXAMPLE 6

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that an overcoat layer was formed by applying and drying a coating fluid having the following composition.

10% Aqueous solution of silicone-modified polyvinyl alcohol (trade name, R-2105; manufactured by Kuraray Co., Ltd., Japan)	100 parts
5% Aqueous solution of boric acid	2 parts
50% Dispersion of light calcium carbonate	1 part

The thus-obtained 18 kinds of heat-sensitive recording materials were subjected to image recording using a heat-sensitive recording simulator having a 6-dot/mm thermal head (manufactured by Matsushita Electronic Components Co., Ltd., Japan; heating resistor 300 Ω/dot). Recording condition was that the input energy to head was 0.9 W/dot. Evaluations were made with respect to the following items and the results obtained are summarized in Table.

Color density of recorded image:

The maximum color density of the recorded image was measured with a Macbeth densitometer (type RD-100R; manufactured by Macbeth Company).

Gloss:

Measured with a varied-angle photometer at an incident light angle of 75°.

Running properties (Sticking properties):

Running properties were examined along with recording noise when the heat-sensitive recording material was evaluated on a printer.

Heat-resistant preservability:

The recorded image was allowed to stand for a day in an atmosphere of 60°C and fading caused thereby was visually examined.

Moisture-resistant preservability:

The recorded image was allowed to stand for a day in an atmosphere of 40° C, 90% RH and fading caused thereby was visually examined.

Resistance to plasticizer:

The recording material was sandwiched between wrapping films of vinylidene chloride polymer containing a plasticizer and allowed to stand at 40° C for 15 hours, and fading caused thereby was visually examined.

Criteria for evaluation:

Criteria for evaluating the running properties, heat-resistant preservability, moisture-resistant preservability, and plasticizer resistance were as follows.

◎.......... ○.......... △.......... ×
extremely good .... extremely poor

The heat-sensitive recording materials of Comparative Examples 2 and 6 showed so poor running properties that no recorded image was obtained therefrom.

TABLE

		Color density	Gloss	Running property	Heat-resistant Preservability	Moisture-resistant Preservability	Resistant to plasticizer
Example	1	1.80	90	○	○	○	○
"	2	1.82	91	○	○	○	○
"	3	1.79	91	○	○	○	○
"	4	1.80	90	○	○	○	◎
"	5	1.81	90	○	○	○	◎
"	6	1.77	89	○	○	○	◎
"	7	1.78	90	○	○	○	◎
"	8	1.60	70	○	○	○	△
"	9	1.75	85	○	○	○	○
"	10	1.60	70	○	○	○	◎
"	11	1.76	87	○	○	○	◎
"	12	1.77	88	○	○	○	○
"	13	1.85	93	○	○	○	◎

TABLE (cont'd)

	Color density	Gloss	Running property	Heat-resistant Preservability	Moisture-resistant Preservability	Resistant to plasticizer
Comparative Example 1	1.33	45	△	○	○	×
" 2	-	90	×	-	-	-
" 3	1.33	60	○	○	○	△
" 4	1.80	89	○	×	×	×
" 5	1.79	88	○	×	×	×
" 6	-	89	×	-	-	-

The results in the table show that the heat-sensitive recording materials of the present invention were excellent not only in running properties in recording, color density of recorded images, and gloss but also in preservability.

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 heat-sensitive recording material comprising a support having thereon a recording layer containing a color former and a color developer which makes said color former produce a color upon heating and an overcoat layer in that order, said overcoat layer containing a water-soluble resin, a modified silicone oil, and a hardener which reacts with both of said water-soluble resin and modified silicone oil.

2. A heat-sensitive recording material as claimed in claim 1, wherein said water-soluble resin is polyvinyl alcohol.

3. A heat-sensitive recording material as claimed in claim 1, wherein said modified silicone oil is an epoxy-modified silicone oil or an amino-modified silicone oil.

4. A heat-sensitive recording material as claimed in claim 1, wherein said hardener is boric acid or a dialdehyde compound.

5. A heat-sensitive recording material as claimed in claim 2, wherein said polyvinyl alcohol is silicone-modified polyvinyl alcohol.

6. A heat-sensitive recording material as claimed in claim 1, wherein said support is a paper having an undercoat layer comprising a binder and a pigment as major components, said recording layer being formed on said undercoat layer.

7. A heat-sensitive recording material as claimed in claim 1, wherein said support is a paper having on the back side thereof a back barrier layer comprising a binder and a pigment as major components.

8. A heat-sensitive recording material as claimed in claim 1, wherein said support is a plastic film or a synthetic paper.

9. A heat-sensitive recording material as claimed in claim 1, provided with a pressure-sensitive adhesive layer on the back side thereof, thereby being an adhesive label.

10. A heat-sensitive recording material as claimed in claim 1, wherein said overcoat layer is provided by curtain coating.