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**Heat sensitive recording material.**

A heat sensitive recording material having a heat sensitive recording layer formed on the front surface of a substrate and containing a colorless or light-colored basic dye and a color acceptor capable of forming a color on contact with the dye, and an adhesive layer formed on the rear surface of the substrate, the heat sensitive recording material being characterized in that a barrier layer comprising a polyvinyl alcohol having a saponification degree of 80 to 90 mole %, and a pigment is provided between the substrate and the adhesive layer.

The present invention relates to a heat sensitive recording material having excellent preservability for use as labels.

Heat sensitive recording materials are well known which are adapted to produce record images by thermally contacting a colorless or light-colored basic dye with an organic or inorganic color acceptor for a color forming reaction. These heat sensitive recording materials are relatively inexpensive and usable with recording devices which are easy to maintain, so that they are used as recording media for facsimile systems, calculators, etc. and also for a wide variety of other applications.

As one of such applications, for example, these recording materials are in increasing use as labels at retail stores with the development of POS (point of sales) systems.

The stability of recorded images is generally required of heat sensitive recording materials. Accordingly, it has been proposed to coat the heat sensitive recording layer with an emulsion of resin having film forming ability and chemical resistance (JP-A-128347/1979) or with a water-soluble high polymer compound such as polyvinyl alcohol (JP-U-125354/1981 and USP 4370370).

However, heat sensitive recording materials for use as labels are often used as affixed to wrapping films and the like which contain a plasticizer and must therefore fulfill the imperative requirement that the recorded images thereon be prevented from discoloration due to the migration of the plasticizer from the rear surface thereof.

Heat sensitive recording materials for labels generally have an adhesive layer formed on the rear surface of a substrate, and a release sheet provided over the adhesive layer. A rubber or acrylic adhesive is usually used for the adhesive layer. When the recording material for labels which has the rubber adhesive incorporated therein is used, for example, as affixed to a wrapping film containing a plasticizer, the plasticizer in the film is liable to migrate into the adhesive layer. Especially in the case where paper is used as the substrate, the plasticizer penetrates through the paper into the heat sensitive recording layer, consequently entailing the problem of seriously impairing the preservability of the recording material.

Although a heat sensitive recording material has been proposed which includes a back coat layer consisting primarily of a water-soluble high polymer to obviate this problem (JP-U-140461/1981 and USP 4370370), the material is low in the preservability of recorded images owing to insufficient barrier properties which appear attributable to the penetration of the water-soluble high polymer into the substrate.

An object of the present invention is to provide a heat sensitive recording material for labels which is excellent in preservability, especially in resistance to plasticizers.

The above and other objects of the invention will become apparent from the following description.

The present invention provides a heat sensitive recording material having a heat sensitive recording layer formed on the front surface of a substrate and containing a colorless or light-colored basic dye and a color acceptor capable of forming a color on contact with the dye, and an adhesive layer formed on the rear surface of the substrate, the heat sensitive recording material being characterized in that a barrier layer comprising a polyvinyl alcohol having a saponification degree of 80 to 90 mole %, and a pigment is provided between the substrate and the adhesive layer.

The present invention also provides a heat sensitive recording material which is characterized in that at least one of water-soluble magnesium salt, calcium salt and aluminum salt is incorporated in the barrier layer.

As already described, the present invention is characterized in that a barrier layer consisting primarily of a binder, and an inorganic pigment and/or an organic pigment is provided on the rear surface of a substrate, the binder of the barrier layer being a polyvinyl alcohol having a saponification degree of 80 to 90 mole %.

A heat sensitive recording material having a barrier layer containing a water-soluble high polymer on the rear surface of the substrate is likely to blocking between a recording layer and the barrier layer in a winding state. In order to prevent the blocking, when a pigment is added to a barrier forming coating composition and in case of a completely saponified polyvinyl alcohol is used as the water-soluble high polymer, it was necessary to add a surfactant, such as sodium dialkylsulfosuccinate, to the barrier forming coating composition in order to prevent repelling of the composition applied, with the result that the coating layer formed was invariably low in barrier properties. However, the present invention obviates the need to use such a surfactant since the above-specified partially saponified polyvinyl alcohol has the function of protective colloid. The invention therefore inhibits the repelling of the coating composition and affords a barrier layer retaining satisfactory barrier properties.

If the polyvinyl alcohol has an excessively high saponification degree, the barrier coating composition is liable to penetrate into the substrate, failing to produce the desired effect, while the polyvinyl alcohol is unable to serve remarkably as a protective colloid. Conversely, when having too low a saponification degree, the polyvinyl alcohol fails to form a solution of high concentration, giving a low concentration also to the barrier coating composition, which in turn is liable to penetrate into the substrate. Accordingly, the

polyvinyl alcohol having a saponification degree of 80 to 90 mole %, preferably 85 to 90 mole % is selectively used in the present invention.

The higher the concentration of the barrier coating composition, the less is the likelihood of the coating composition penetrating into the substrate, so that the polyvinyl alcohol for use in the barrier layer is preferably about 200 to about 2000, more preferably about 200 to about 1000, most preferably about 200 to about 500, in average polymerization degree. High-concentration solutions of the polyvinyl alcohol are then easy to handle.

The polyvinyl alcohol content of the barrier layer is preferably 50 to 90 wt.%. If the content is too low, the desired barrier properties will not be available, whereas presence of an excess of the polyvinyl alcohol is likely to permit blocking while the material is in the form of a wound-up roll.

Specific examples of polyvinyl alcohols for use in the barrier layer of the present invention are products of Kuraray Co., Ltd. with the brand names of PVA-203 (saponification degree : 88 mole %, average polymerization degree : 300), -204 (88 mole %, 400), -205 (88 mole %, 500), -210 (88 mole %, 1000), -217 (88 mole %, 1700), -217E (88 mole %, 1700, a block copolymer of vinyl alcohol and vinyl acetate), -217EE (88 mole %, 1700, a block copolymer of vinyl alcohol and vinyl acetate), -220 (88 mole %, 2000), -220E (88 mole %, 2000, a block copolymer of vinyl alcohol and vinyl acetate), etc. Useful polyvinyl alcohols are not limited to these examples. When required, at least two of such polyvinyl alcohols are usable in combination. Further the polyvinyl alcohol is usable in combination with other binders, which include, for example, starches such as cationic starch, phosphatized starch and oxidized starch, cellulose derivatives such as hydroxyethyl cellulose and carboxymethyl cellulose, gelatin, casein, gum arabic, completely saponified polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, diisobutylene-maleic anhydride copolymer salt, styrene-maleic anhydride copolymer salt, urea resin, melamine resin and amide resin.

Examples of pigments for use in the barrier layer of the present invention are inorganic pigments such as kaolin, clay, calcium carbonate, aluminum hydroxide, titanium dioxide, silicon dioxide and calcined clay, and organic pigments such as styrene microballs, nylon powder, polyethylene powder, urea-formalin resin filler and particles of raw starch. These examples are not limitative.

When required, at least two of these pigments can be used in combination.

According to the present invention, water-soluble magnesium salts, calcium salts and aluminum salts for use in the barrier layer are preferably sulfates, formates, acetates or halides, more preferably sulfates, formates or acetates. More specific examples of such salts are magnesium sulfate, magnesium formate, magnesium acetate, magnesium chloride, calcium formate, calcium acetate, calcium chloride, aluminum sulfate, aluminum formate, aluminum acetate, aluminum chloride, potash alum, etc., which however, are not limitative. When required, at least two of such salts are usable in combination.

The water-soluble salt is incorporated into the barrier layer in an amount of 0.01 to 10 wt.%, preferably about 0.05 to about 3 wt.%, more preferably about 0.05 to about 1 wt.%, most preferably about 0.05 to about 0.5 wt.%, based on the total solids content of the barrier layer. If the amount is less than 0.01 wt.%, a sufficient effect will not be available, whereas amounts exceeding 10 wt.% not only lower the stability of the coating composition but also entail the likelihood that the salt will react with the adhesive to impair the adhesion of the adhesive.

The presence of the specified water-soluble salt effectively inhibits the barrier forming coating composition from penetrating into the substrate and controls flowability of the coating composition in an appropriate range, consequently making it possible to form a coating layer free from coating irregularities and uniform in barrier properties.

When required, various auxiliary agents can be incorporated into the barrier coating composition which comprises components such as those mentioned above insofar as the contemplated effect of the invention will not be impaired. Examples of useful agents are dispersants such as sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl alcohol sulfuric acid ester and metal salts of fatty acids, zinc stearate, calcium stearate, waxes such as polyethylene wax, carnauba wax, paraffin wax and ester wax, ultraviolet absorbers such as benzophenone compounds, defoaming agents, fluorescent dyes, coloring dyes, etc.

The barrier layer can be formed by conventional techniques already known, for example, by applying the coating composition to the substrate by suitable means, such as an air knife coater, blade coater, bar coater, roll coater, gravure coater or curtain coater, and drying the coating.

The coating composition is applied to the substrate in an amount which, although not limited specifically, is adjusted preferably to the range of 0.5 to 30 g/m<sup>2</sup>, more preferably about 1 to about 10 g/m<sup>2</sup>, calculated as dry weight.

The substrate to be used is not limited specifically and is paper, synthetic paper or the like.

In the present invention, it is essential to form the above barrier layer on the rear surface of the substrate but as required it is possible to form a similar barrier layer on the front surface of the substrate. Further, the barrier layer on the rear surface can be formed prior to or after forming the heat sensitive recording layer.

As a basic dye contained in the heat sensitive recording layer in the present invention are used various known colorless or light-colored basic dyes. Examples thereof are :

Triarylmethane-based dyes, e.g., 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)phthalide, 3,3-bis(1,2-dimethylindole-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindole-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazole-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindole-3-yl)-6-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrole-3-yl)-6-dimethylaminophthalide, etc.

Diphenylmethane-based dyes, e.g., 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halophenyl-leucoauramine, N-2,4,5-trichlorophenyl-leucoauramine, etc.

Thiazine-based dyes, e.g., benzoyl-leucomethyleneblue, p-nitrobenzoyl-leucomethyleneblue, etc.

Spiro-based dyes, e.g., 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methylnaphtho-(6'-methoxybenzo)spiropyran, 3-propyl-spiro-dibenzopyran, etc.

Lactam-based dyes, e.g., rhodamine-B-anilinolactam, rhodamine-(p-nitroanilino)lactam, rhodamine-(o-chloroanilino)lactam, etc.

Fluoran-based dyes, e.g., 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-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-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-phenylaminofluoran, 3-piperidino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-di-n-butylamino-7-(o-chlorophenylamino)fluoran, 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, 3-diethylamino-7-(o-fluorophenylamino)fluoran, 3-dibutylamino-7-(o-fluorophenylamino)fluoran, 3-di-n-butylamino-6-methyl-7-phenylaminofluoran, 3-di-n-pentylamino-6-methyl-7-phenylaminofluoran, 3-(N-methyl-N-n-amy)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-n-amy)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-isoamy)amino-6-methyl-7-phenylaminofluoran, 3-(N-methyl-N-n-hexyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-n-hexyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N- $\beta$ -ethylhexyl)amino-6-methyl-7-phenylaminofluoran, etc. These basic dyes can be used, as required, in a mixture of at least two of them.

As a color acceptor are used various known inorganic and organic acidic materials which form color in contact with the basic dyes. Examples of useful inorganic acidic materials are activated clay, attapulgite, colloidal silica and aluminum silicate. Examples of organic acidic materials include 4-tert-butylphenol, 4-hydroxydiphenoxide,  $\alpha$ -naphthol,  $\beta$ -naphthol, 4-hydroxyacetophenone, 4-tert-octylcatechol, 2,2'-dihydroxydiphenyl, 4,4'-isopropylidenebis(2-tert-butylphenol), 4,4'-sec-butylidenediphenol, 4-phenylphenol, 4,4'-isopropylidenediphenol, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 2,2'-methylenebis(4-chlorophenol), hydroquinone, 4,4'-cyclohexylidenediphenol, hydroquinone monobenzyl ether, 4-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2,4,4'-trihydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, dimethyl 4-hydroxyphthalate, methyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, sec-butyl 4-hydroxybenzoate, pentyl 4-hydroxybenzoate, phenyl 4-hydroxybenzoate, benzyl 4-hydroxybenzoate, tolyl 4-hydroxybenzoate, chlorophenyl 4-hydroxybenzoate, phenylpropyl 4-hydroxybenzoate, phenethyl 4-hydroxybenzoate, p-chlorobenzyl 4-hydroxybenzoate, p-methoxybenzyl 4-hydroxybenzoate, novolak phenol resin, phenolic polymer and like phenolic compounds; 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, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-( $\alpha$ -methylbenzyl)salicylic acid, 3-chloro-5-( $\alpha$ -methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-( $\alpha$ ,  $\alpha$ -dimethylbenzyl)salicylic acid, 3,5-di- $\alpha$ -methylbenzylsalicylic acid, 4-(3-p-tolylsulfonylpropyloxy)salicylic acid and like aromatic carboxylic acids, 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxy-4'-methyldiphenylsulfone, 3,4-dihydroxydiphenylsulfone, 3,4-dihydroxy-4'-methyldiphenylsulfone and like 4-hydroxydiphenylsulfone derivatives, 4,4'-dihydrox-

ydiphenylsulfide, bis(3-tert-butyl-4-hydroxy-6-methylphenyl)sulfide, bis(2-methyl-4-hydroxy-6-tert-butylphenyl)sulfide, di(4-hydroxyphenylthioethoxy)methane, 1,5-di(4-hydroxyphenylthio)-3-oxapentane and like sulfide derivatives; also, salts of such phenolic compounds or aromatic carboxylic acids with zinc, magnesium, aluminum, calcium, titanium, manganese, tin, nickel and like polyvalent metals; complex of antipyrine and zinc thiocyanate, etc.

With the heat sensitive recording materials of the invention, the proportions of basic dye and color acceptor are not particularly limited but can be determined suitably according to the kinds of basic dye and color acceptor. For example, usually 1 to 50 parts by weight, preferably 2 to 10 parts by weight, of the color acceptor is used per part by weight of the basic dye.

For preparing the coating composition for the heat sensitive recording layer, the dye and the color acceptor are dispersed, together or individually, into water serving as a dispersion medium, using stirring and pulverizing means such as a ball mill, attritor or sand mill.

In the coating composition, a binder can be conjointly used. Examples of useful binders are starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, gum arabic, polyvinyl alcohol, carboxy-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, diisobutylene-maleic anhydride copolymer salt, styrene-maleic anhydride copolymer salt, ethylene-acrylic acid copolymer salt, styrene-acrylic acid copolymer salt, styrene-butadiene copolymer emulsion, urea resin, melamine resin, amide resin, etc.

Various other auxiliary agents can be further added to the coating composition. Examples of useful agents are dispersants such as sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl alcohol sulfuric acid ester, fatty acid metal salts, etc., waxes such as zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax and ester wax, etc, ultraviolet absorbers such as benzophenone compounds, defoaming agents, fluorescent dyes, coloring dyes, etc.

Further, to the coating composition may be added a pigment. Examples of useful pigments are kaolin, clay, calcium carbonate, calcined clay, calcined kaolin, titanium dioxide, kieselguhr, finely divided anhydrous silica, activated clay or like inorganic pigment, styrene microballs, nylon powder, polyethylene powder, urea-formalin resin filler, particles of raw starch or like organic pigment.

Further, a sensitizer can be used as required. Examples of useful sensitizers are caproic acid amide, capric acid amide, palmitic acid amide, stearic acid amide, oleic acid amide, erucic acid amide, linoleic acid amide, linolenic acid amide, N-methylstearic acid amide, stearic acid anilide, N-methyloleic acid amide, benzanilide, linoleic acid anilide, N-ethylcapric acid amide, N-butyllauric acid amide, N-octadecylacetamide, N-oleylacetamide, N-oleylbenzamide, N-stearylcylohexylamide, polyethylene glycol, 1-benzoyloxynaphthalene, 2-benzoyloxynaphthalene, 1-hydroxynaphthoic acid phenyl ester, 1,2-diphenoxyethane, 1,4-diphenoxybutane, 1,2-bis(3-methylphenoxy)ethane, 1,2-bis(4-methoxyphenoxy)ethane, 1-phenoxy-2-(4-chlorophenoxy)ethane, 1-phenoxy-2-(4-methoxyphenoxy)ethane, 1-(2-methylphenoxy)-2-(4-methoxyphenoxy)ethane, dibenzyl terephthalate, dibenzyl oxalate, di(4-methylbenzyl)oxalate, benzyl p-benzoyloxybenzoate, p-benzylbiphenyl, 1,5-bis(p-methoxy-phenoxy)-3-oxapentane, 1,4-bis(2-vinyloxyethoxy)benzene, p-biphenyl p-tolyl ether and benzyl p-methylthiophenyl ether.

It is desired that the amount of sensitizer to be used be adjusted generally within the range of up to about 4 parts by weight per part by weight of the color acceptor although not limited specifically.

The recording layer can be formed by a method which is not limited specifically, for example, by applying a coating composition for the layer to the substrate by a suitable method such as air knife coating, varibar blade coating, rod blade coating, pure blade coating, short-dwell coating or bar coating, and drying the resulting coating. The amount of coating composition to be applied is not limited specifically either and is adjusted usually to the range of 2 to 12 g/m<sup>2</sup>, preferably about 3 to about 10 g/m<sup>2</sup>, in dry weight.

It is desirable to form a protective layer over the heat sensitive recording layer since the recorded images on the layer can then be preserved more effectively. Water-soluble or water-dispersible high polymers are used for forming the protective layer. Examples of useful high polymers are polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, silicon-modified polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, starch and derivatives thereof, casein, sodium alginate, polyvinylpyrrolidone, polyacrylamide, styrene-maleic acid copolymer salt, polyurethane resin, urea resin, melamine resin, polyamide resin, epichlorohydrin-modified polyamide resin and synthetic high polymer emulsions such as styrene-butadiene emulsion, styrene-acrylic acid ester emulsion and acrylic acid ester emulsion.

At least two of such high polymer compounds may of course be used in admixture.

Among these high polymer compounds, acetoacetyl-modified polyvinyl alcohol and silicon-modified polyvinyl alcohol form tough resin films and are therefore preferable to use.

Pigments can be incorporated into the protective layers. Examples of useful pigments are inorganic

pigments such as calcium carbonate, zinc oxide, aluminum oxide, titanium dioxide, silicon dioxide, aluminum hydroxide, barium sulfate, zinc sulfate, talc, kaolin, clay, calcined kaolin, calcined clay and colloidal silica, and organic pigments such as styrene microballs, nylon powder, polyethylene powder, urea-formalin resin filler and raw starch particles. Generally, such a pigment is used preferably in an adjusted amount of about 20 to about 500 parts by weight per 100 parts by weight of the high polymer compound.

Further when required, various auxiliary agents can be incorporated into the coating composition for forming the protective layer. Examples of suitable agents are lubricants such as zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax and ester wax, surfactants such as sodium dioctylsulfosuccinate, defoaming agents, etc.

Also usable are curing agents, such as glyoxal, boric acid, dialdehyde starch and epoxy compounds, for giving improved water resistance to the layer.

The coating composition thus prepared is applied to the heat sensitive recording layer with a suitable coating device. If the amount applied is less than 1 g/m<sup>2</sup> by dry weight, recorded images will not be preserved with sufficiently improved stability, and the coating is liable to stick to the thermal head, whereas amounts exceeding 20 g/m<sup>2</sup> are likely to seriously reduce the recording sensitivity of the heat sensitive recording layer. It is therefore generally desirable to adjust the amount to the range of 1 to 20 g/m<sup>2</sup>, preferably about 2 to about 10 g/m<sup>2</sup>.

Incidentally, various techniques already known in the art of preparing heat sensitive recording materials can be additionally resorted to. For example, an undercoat layer can be interposed between the heat sensitive recording layer and the substrate.

The heat sensitive recording material thus obtained is further provided over the rear side thereof with an adhesive layer and usually with a release sheet, and is thereby rendered adhesive.

Although not limited specifically, the release sheet to be used is, for example, one comprising a base which is glassine paper or like high-density base paper, clay-coated paper, or a laminated base paper prepared by laminating polyethylene to kraft paper or wood-free paper, and which is coated with a silicone compound, fluorine compound or like releasing agent. Examples of useful adhesives are rubber, acrylic, vinyl ether or like adhesives of the emulsion, solvent or solvent-free type.

The present invention will be described in greater detail with reference to the following examples, to which the invention is of course not limited.

The parts and percentages in these examples are all by weight unless otherwise specified.

#### Example 1

##### (1) Composition (A)

Kaolin

(brand name: UW-90, product of Engelhard

Minerals & Chemicals Corp.)

50 parts

20 % Aqueous solution of polyvinyl alcohol

(brand name: PVA-205, product of Kuraray

Co., Ltd., saponification degree; 88 mole % ,

polymerization degree; 500)

500 parts

Water

50 parts

These ingredients were mixed together by stirring and made into a coating composition.

##### (2) Composition (B)

|                                                           |          |
|-----------------------------------------------------------|----------|
| 3'-(N-Ethyl-N-isoamyl)amino-6-methyl-7-phenylaminofluoran | 10 parts |
| 5 % Aqueous solution of methyl cellulose                  | 5 parts  |
| Water                                                     | 40 parts |

These ingredients were pulverized to a mean particle size of 3  $\mu$  m by a sand mill.

(3) Composition (C)

|                                          |          |
|------------------------------------------|----------|
| 4-Hydroxy-4'-isopropoxydiphenylsulfone   | 30 parts |
| 5 % Aqueous solution of methyl cellulose | 5 parts  |
| Water                                    | 80 parts |

These ingredients were pulverized to a mean particle size of 3  $\mu$  m by a sand mill.

(4) Composition (D)

|                                          |          |
|------------------------------------------|----------|
| 1,2-Di(3-methylphenoxy)ethane            | 20 parts |
| 5 % Aqueous solution of methyl cellulose | 5 parts  |
| Water                                    | 55 parts |

These ingredients were pulverized to a mean particle size of 3  $\mu$  m by a sand mill.

(5) Formation of recording layer

The composition A was applied to one surface of base paper weighing 60 g/m<sup>2</sup> in an amount of 3 g/m<sup>2</sup> when dried, followed by drying to form a barrier layer. A coating composition prepared by mixing together 55 parts of the composition B, 115 parts of the composition C, 80 parts of the composition D, 80 parts of 10 % aqueous solution of polyvinyl alcohol and 35 parts of calcium carbonate with stirring was applied to the other surface of the base paper opposite to the barrier layer in an amount of 6 g/m<sup>2</sup> when dried, followed by drying to obtain a heat sensitive recording material.

(6) Composition (E)

|                                                                             |           |
|-----------------------------------------------------------------------------|-----------|
| 10 % Aqueous solution of acetoacetyl-modified polyvinyl alcohol             | 200 parts |
| Kaolin (brand name: UW-90, product of Engelhard Minerals & Chemicals Corp.) | 100 parts |
| 30 % Dispersion of zinc stearate                                            | 30 parts  |
| Water                                                                       | 100 parts |

These four ingredients were mixed together with stirring to obtain a protective layer coating composi-

tion, which was then applied to the recording layer in an amount of 5 g/m<sup>2</sup> when dried, followed by drying. The sheet thus prepared was calendered to obtain a heat sensitive recording material.

#### Example 2

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A heat sensitive recording material was prepared in the same manner as in Example 1 with the exception of applying the composition A to both surfaces of the base paper in an amount of 3 g/m<sup>2</sup> when dried, drying the coating, and forming the recording layer over one side of the resulting substrate.

#### 10 Example 3

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-203, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 300) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

#### Example 4

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A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-204, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 400) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

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#### Example 5

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-210, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 1000) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

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#### Example 6

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 667 parts of 15 % aqueous solution of polyvinyl alcohol (brand name: PVA-217, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 1700) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

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#### Example 7

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 667 parts of 15 % aqueous solution of polyvinyl alcohol (brand name: PVA-217E, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 1700) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

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#### 50 Example 8

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 667 parts of 15 % aqueous solution of polyvinyl alcohol (brand name: PVA-217EE, product of Kuraray Co., Ltd., saponification degree; 88 mole %, polymerization degree; 1700) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

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#### Example 9



A heat sensitive recording material was obtained in the same manner as in Example 1 except that 10 parts of 3 % aqueous solution of potash alum was further added to the composition A.

#### Examples 10 to 12

Three kinds of heat sensitive recording materials were obtained in the same manner as in Example 9 except that, in the composition A, each of 10 parts of 3 % aqueous solution of calcium formate (Example 10), 10 parts of 3 % aqueous solution of aluminum acetate (Example 11) and 10 parts of 3 % aqueous solution of magnesium acetate (Example 12) was respectively used instead of 10 parts of 3 % aqueous solution of potash alum.

#### Example 13

##### (1) Composition (F)

|                                               |           |
|-----------------------------------------------|-----------|
| Calcined clay (brand name: Ansilex, product   |           |
| of Engelhard Minerals & Chemicals Corp., oil  |           |
| absorption; 110 ml/100 g)                     | 100 parts |
| 10 % Aqueous solution of polyvinyl alcohol    |           |
| (brand name: PVA-210, product of Kuraray      |           |
| Co., Ltd., saponification degree; 88 mole % , |           |
| polymerization degree; 1000)                  | 100 parts |
| Water                                         | 200 parts |

These ingredients were mixed together by stirring to obtain a dispersion.

##### (2) Preparation of recording material

In a manner similar to the procedure of Example 1, the composition A was applied to one surface of base paper weighing 60 g/m<sup>2</sup> in an amount of 3 g/m<sup>2</sup> when dried, and the coating was dried to form a barrier layer. The composition F was applied to the other surface of the base paper opposite to the barrier layer in an amount of 7 g/m<sup>2</sup> when dried, and the coating was dried to form an intermediate layer. A coating composition prepared by mixing together 55 parts of the composition B, 115 parts of the composition E, 80 parts of the composition D, 80 parts of 10 % aqueous solution of polyvinyl alcohol and 35 parts of calcium carbonate with stirring was further applied to the intermediate layer in an amount of 6 g/m<sup>2</sup> when dried, and the coating was dried to form a heat sensitive recording layer. The composition E was applied to this layer in an amount of 5 g/m<sup>2</sup> when dried, followed by drying. The sheet obtained was calendered to obtain a heat sensitive recording material.

#### Comparative Example 1

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 667 parts of 15 % aqueous solution of polyvinyl alcohol (brand name: PVA-105, product of Kuraray Co., Ltd., saponification degree; 98.5 mole %, polymerization degree; 500) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 2

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 667 parts of 15 % aqueous solution of polyvinyl alcohol (brand name: PVA-110, product of Kuraray Co., Ltd., saponification degree; 98.5 mole % , polymerization degree; 1000) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 3

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 1000 parts of 10 % aqueous solution of polyvinyl alcohol (brand name: PVA-117, product of Kuraray Co., Ltd., saponification degree; 98.5 mole % , polymerization degree; 1700) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 4

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % aqueous solution of oxidized starch (brand name: Ace A, product of Oji Corn Starch Co., Ltd.,) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 5

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % etherified starch (brand name: Avelex 2530, product of Avebe Co., Ltd.,) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 6

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 500 parts of 20 % methyl cellulose (brand name: Metholose 60SH03, product of Shin-Etsu Chemical Co., Ltd.,) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 7

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 200 parts of 50 % SBR latex (brand name: CP-620NA, product of The Dow Chemical Co.) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Example 14

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 200 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Example 15

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 1400 parts of 7 % aqueous solution of polyvinyl alcohol (brand name: PVA-224, product of Kuraray Co., Ltd., saponification degree; 88 mole % , polymerization degree; 2400) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Example 16

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 1000 parts of 10 % aqueous solution of polyvinyl alcohol (saponification degree; 82 mole %, polymerization degree; 500) instead of 500 parts of the 20 % aqueous solution of; polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Comparative Example 8

A heat sensitive recording material was prepared in the same manner as in Example 1 except that the composition A was prepared by using 2000 parts of 5 % aqueous solution of polyvinyl alcohol (saponification degree; 75 mole %, polymerization degree; 2000) instead of 500 parts of the 20 % aqueous solution of polyvinyl alcohol (brand name: PVA-205) used in Example 1.

Evaluation Tests

The heat sensitive recording materials obtained in Examples 1 to 16 and Comparative Examples 1 to 8 were tested for evaluation by the following methods. The results are shown in Table 1.

Initial Color Density

The color density of recorded images produced by pressing the heat sensitive recording material to a plate heated at 120 °C for 5 seconds (4 kg/cm<sup>2</sup>) was measured by a Macbeth densitometer (Model RD-100R, product of Macbeth Corp.).

Plasticizer Resistance-I

To the rear surface of the heat sensitive recording material having the recorded images formed as above was applied a rubber adhesive (ECOMELT L-302, product of ECOMELT AG, Germany) in an amount of 20 g/m<sup>2</sup> when dried to form an adhesive layer. Next, a polyvinyl chloride wrapping film (product of Mitsui Toatsu Chemicals Inc.) was wound around a polypropylene pipe (40 mm in diameter) in three layers, the recording material formed with the adhesive layer was placed over the winding with the color bearing surface out, a plasticizer-free polyethylene film was further wound around the pipe over the recording material in three layers, and the assembly was allowed to stand at 40 °C for 24 hours. The color density of the recorded images was thereafter measured to evaluate the Plasticizer Resistance-I of the recording material.

Plasticizer Resistance-II

The assembly prepared in the same manner as in Plasticizer Resistance-I was allowed to stand at 40 °C for 72 hours. The color density of the recorded images was thereafter measured to evaluate the Plasticizer Resistance-II of the recording material.

Table 1

|    | Initial Color | Plasticizer  | Plasticizer   |
|----|---------------|--------------|---------------|
|    | Density       | Resistance-I | Resistance-II |
| 5  | Ex. 1         | 1.22         | 1.18          |
|    | Ex. 2         | 1.20         | 1.19          |
|    | Ex. 3         | 1.22         | 1.18          |
| 10 | Ex. 4         | 1.23         | 1.17          |
|    | Ex. 5         | 1.22         | 1.16          |
|    | Ex. 6         | 1.22         | 1.15          |
|    | Ex. 7         | 1.22         | 1.15          |
| 15 | Ex. 8         | 1.22         | 1.15          |
|    | Ex. 9         | 1.23         | 1.22          |
|    | Ex. 10        | 1.22         | 1.22          |
| 20 | Ex. 11        | 1.23         | 1.23          |
|    | Ex. 12        | 1.23         | 1.22          |
|    | Ex. 13        | 1.28         | 1.25          |
|    | Ex. 14        | 1.21         | 1.08          |
| 25 | Ex. 15        | 1.22         | 1.08          |
|    | Ex. 16        | 1.22         | 1.15          |
|    | Com. Ex. 1    | 1.22         | 0.71          |
|    | Com. Ex. 2    | 1.22         | 0.68          |
| 30 | Com. Ex. 3    | 1.22         | 0.65          |
|    | Com. Ex. 4    | 1.23         | 0.50          |
|    | Com. Ex. 5    | 1.23         | 0.45          |
| 35 | Com. Ex. 6    | 1.22         | 0.48          |
|    | Com. Ex. 7    | 1.20         | 0.32          |
|    | Com. Ex. 8    | 1.22         | 0.75          |

40 As apparent from Table 1, the heat sensitive-recording material of the present invention are all excellent in initial color density and plasticizer resistance.

### Claims

- 45 1. A heat sensitive recording material having a heat sensitive recording layer formed on the front surface of a substrate and containing a colorless or light-colored basic dye and a color acceptor capable of forming a color on contact with the dye, and an adhesive layer formed on the rear surface of the substrate,
- 50 characterized in that a barrier layer comprising a polyvinyl alcohol having a saponification degree of 80 to 90 mole %, and a pigment is provided between the substrate and the adhesive layer.
2. A heat sensitive recording material as defined in claim 1 wherein at least one of water-soluble magnesium salt, calcium salt and aluminum salt is further incorporated in the barrier layer.
- 55 3. A heat sensitive recording material as defined in claim 2 wherein the water-soluble magnesium salt, calcium salt or aluminum salt is sulfate, formate, acetate or halide thereof.
4. A heat sensitive recording material as defined in claim 2 or 3 wherein the water-soluble salt is

incorporated into the barrier layer in an amount of 0.01 to 10 wt.% based on the total solids content of the barrier layer.

5     **5.** A heat sensitive recording material as defined in claim 4 wherein the water-soluble salt is incorporated into the barrier layer in an amount of 0.05 to 3 wt.% based on the total solids content of the barrier layer.

10    **6.** A heat sensitive recording material as defined in claim 5 wherein the water-soluble salt is incorporated into the barrier layer in an amount of 0.05 to 1 wt.% based on the total solids content of the barrier layer.

**7.** A heat sensitive recording material as defined in any of claims 1-6 wherein the polyvinyl alcohol has an average polymerization degree of 200 to 2000, preferably 200 to 1000.

15    **8.** A heat sensitive recording material as defined in any of claims 1-7 wherein the polyvinyl alcohol has a saponification degree of 85 to 90 mole %.

**9.** A heat sensitive recording material as defined in any of claims 1-8 wherein the barrier layer comprises 50 to 90 wt. % of the polyvinyl alcohol.

20    **10.** A heat sensitive recording material as defined in any of claims 1-9 wherein a barrier layer comprising a polyvinyl alcohol having a saponification degree of 80 to 90 mole %, and a pigment is provided between the substrate and the heat sensitive recording layer.

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