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(54) **Heat-sensitive recording material.**

(57) A transparent support (e.g. of a polyester film) of thickness 20-200 μm , is coated on one side in amount of 0.01-5 g/m^2 with a matting layer containing an ester resin which is solubilized in an organic solvent (e.g. a polyester resin), and particles of size 0.01-5 μm of organic and/or organic particles (e.g. silica or polyacrylonitrile).

The other side can be activated and is coated in order with (a) an underlayer (e.g. gelatin), (b) a heat-sensitive recording layer containing a diazo compound and a coupling component, preferably one of these being microencapsulated, and optionally additives to improve color formation, and/or a heat-fusible substance, and (c) an overcoating layer which is preferably hardened and may contain white pigment or a dye.

The resultant heat-sensitive material is subjected to recording through layer (c) from a thermal head and the image is viewed in reverse through the support. With a pencil writing can be performed on the matt surface.

Description

HEAT-SENSITIVE RECORDING MATERIAL

The present invention relates to a heat-sensitive recording material, and more particularly it relates to a heat-sensitive recording material for heat-recording of images having a mirror image relation with a manuscript, which is provided with writing properties, images of high quality, and fast adhesion on a support with a matting layer, without the occurrence of blocking during the storage of such recording material in a rolled up state.

The use of a heat-sensitive recording method has been rapidly increasing recently in the fields of facsimile and printer equipments. The heat-recording method comprises recording electric signals corresponding to a manuscript on a support such as a pulp-based paper or a synthetic paper provided with a coupler and a developer by a thermal heat utilizing heat treatment, and this method is widely used.

Heat-sensitive recording papers have widely been used in various fields. When a heat-sensitive recording paper is to be used like a poster, it must be able to stand harsh conditions. When it is to be used as a hard copy like a photo, recording storage stability and gloss are needed. Various approaches have been made to satisfy these needs. It is disclosed in Japanese Patent Publication No. 15140/1975 that a transparent regenerated cellulose is adhered to a recording paper as a protective layer. It is disclosed in Japanese Patent Application (OPI) No. 19840/1978 (the term "OPI" as used herein refers to a published unexamined Japanese patent application) that a resin soluble with an organic solvent which does not dissolve a color forming layer is provided as a protective layer. Various other protective layers are disclosed. However, with those protective layers, the gloss and recording storage stability are not satisfactory. Accordingly, a heat-sensitive recording method which comprises providing a heat-sensitive recording layer containing a coupler and a developer on one surface of a substantially transparent support and heat-recording images having a mirror image relation with a manuscript has been proposed in order to provide sufficient gloss and excellent recording storage stability, as disclosed in Japanese Patent Application (OPI) No. 227086/1986.

In accordance with the above invention, a heat-sensitive recording material which is characterized by seeing images thermally recorded on a heat-sensitive recording layer provided on a transparent support through a transparent support is provided. Such recording material has an extremely smooth surface of a coated layer, because a heat sensitive layer is provided on a smooth surface which is free from roughness due to fibers in the paper support. Therefore, a heated thermal head faithfully transmits heat, with the result that unevenness of density is more reduced than with other ordinary heat-sensitive papers, and that such a recording material is suitable for forming gradation images having intermediate densities.

Further, powders crystallized with passage of time out of the melted substance in the conventional heat-sensitive layer, and the resulting decrease of densities can be neglected by viewing the recorded image from the back surface of a support in accordance with the conventional recording materials, and thus images with high quality appearance can be provided. Still further, such high quality feeling can be reinforced by ample gloss of recorded images, since the recorded images are appreciated through a support.

An object of the present invention is to provide a heat-sensitive recording material having the following characteristics of a type of appreciating recorded images from the back surface of a support, wherein a matting layer is provided on a transparent support.

(1) Writing properties.

(2) Provision of images of high quality feeling without decreasing gloss and image densities.

(3) No occurrence of blocking during storage of a rolled heat-sensitive recording material.

(4) Fast adhesion to a support with a matting layer and non-peeling off of the matting layer even after rubbing the layer with an eraser.

The present invention provides a heat-sensitive recording material comprising a transparent support having provided thereon a matting layer containing an ester resin capable of being solubilized with an organic solvent and a matting agent in an amount of from 0.5 to 20 wt% based on the weight of said ester resin, and on the opposite side of the support an underlayer, a heat-sensitive recording layer and an overcoating layer in this order.

The heat-sensitive recording material of the present invention provides good writing properties, images of high quality feeling, no occurrence of blocking and peeling off of the matting layer, and good adhesion between the support and the heat-sensitive layer, thereby providing with excellent water-resistance and scratch resistance. Therefore, the heat-sensitive recording material of the present invention has very high commercial value.

A heat-sensitive recording material of the present invention comprises a transparent support having provided thereon said matting layer, and on the opposite surface thereof an underlayer, a heat-sensitive layer, and an overcoating layer as a fundamental structure in this order.

The transparent supports used in the present invention include a polyester film such as a polyethylene terephthalate film or a polybutylene terephthalate film, a cellulose derivative film such as a triacetate cellulose film and a polyolefin film such as a polystyrene film, a polypropylene film or a polyethylene film. These films can be used alone or in combination by adhering these films.

The transparent support generally has a thickness of about 20 to 200 μm , and preferably from 50 μm to 100 μm .

Matting agents in the matting layer which provide useful writing properties in the transparent support include inorganic particles such as CaCO_3 , MgCO_3 , MgO , ZnO , BaSO_4 , TiO_2 , crystalline silica, amorphous silica or alumina, and organic particles such as polyethylene, polypropylene, polyethylene terephthalate, polystyrol, polycarbonate, an acrylic acid ester resin, a methacrylic acid resin, polyacrylonitrile and a copolymer of acrylonitrile, and may be used alone or in combination. Inorganic particles such as crystalline silica and amorphous silica, organic particles such as polyacrylonitrile and a mixture of silica and polyacrylonitrile are preferred among the above in view of writing properties, gloss, and image densities. A blend of crystalline silica with polyacrylonitrile is the most preferred. The matting agents have a particle size (average diameter) of from 0.01 to 5 μm , and preferably from 0.05 to 3 μm . When the average particle size is 0.01 μm or less, writing properties, particularly with a pencil, become poor. When the average particle size is 5 μm or more, gloss and image densities unfavorably decrease. The additive amount of matting agents is from 0.5 to 20 wt%, and preferably from 1 to 5 wt%, based on the weight of resin. When the additive amount of the matting agents is 0.5 wt% or less, writing properties with a pencil become impaired, and when the additive amount is 20 wt% or more, the gloss and image density decrease.

The ester resins which are capable of being solubilized (made soluble) with organic solvents include a polyester resin such as polyethylene terephthalate, polybutylene terephthalate, or a copolymer of ethylene terephthalate and butylene terephthalate, an acrylic ester resin, a methacrylic ester resin, a copolymer of styrene and acrylic ester and a copolymer of styrene and methacrylic ester, which can be used alone or in combination. Among those, a polyester resin is more preferred in view of blocking of a material stored in a rolled state, adhesiveness of a support with a heat-sensitive layer, gloss and image densities, and copolymer of ethylene terephthalate and butylene terephthalate is the most preferred. Solvents which solubilize resins include alcohols such as methanol and ethanol, ketones such as acetone and methyl ethyl ketone, and chlorinated hydrocarbons such as methylene chloride, ethylene chloride and tetrachloroethane, and such solvents are used alone or in mixture. Additives such as a hardening agent, a dispersing agent, an antistatic agent, an etching agent or a surface active agent can be included, if desired, in the composition of a matting layer. The coating amount (solid content) of a matting layer is preferably from 0.01 to 5.0 g/m², and more preferably from 0.05 to 1.0 g/m². If the coating amount is less than 0.01 g/m², it is impossible to coat uniformly, thereby deteriorating writing properties with a pencil. If the coating amount is 5.0 g/m² or more, image densities decrease. The degree of haze (measured by Sphere Method H.T.R. Meter manufactured by Nippon Seimitsu Kagaku KK) of a support having the above described matting layer is generally from 1 to 15%, and preferably from 2 to 5%. When it is less than 1%, it is impossible to have substantially writing properties, and when it is more than 15%, sufficient image densities can not be obtained.

An underlayer is provided between a transparent support and a heat-sensitive layer of a heat-sensitive recording material of the present invention to improve adhesiveness therebetween. The materials for the underlayer include gelatin, synthesized high molecular weight latex and nitrocellulose. The coating amount of the underlayer is preferably from 0.01 g/m² to 5.0 g/m², and more preferably from 0.05 g/m² to 1.0 g/m².

When the coating amount is less than 0.01 g/m², adhesiveness between a support and a heat-sensitive layer is insufficient, on the other hand, when it exceeds 5.0 g/m², adhesiveness therebetween has reached a saturation point, and such an excess amount is undesirably costly.

Additives such as hardening agents, dispersing agents, antistatic agents, etching agents and surface active agents can be added into the underlayer if desired, similarly to the matting layer.

It is desirable that a surface of a support is subjected to activation treatment by a known method prior to providing a matting layer and an underlayer. Activation treatment can be etching treatment by acid, flame treatment using a gas burner, corona treatment, glow discharge treatment and ultraviolet irradiation treatment, with corona discharge treatment is the most preferred in view of low cost and simple operation, as disclosed in U.S. Patents 2,715,075, 2,846,727, 3,549,406 and 3,590,107.

The materials for a heat-sensitive layer of the present invention are not limited, so long as materials contain components which react to form color by the contact of substances under heating, and are generally leuco color-forming type materials.

However such heat-sensitive recording materials have defects such that after recording is formed thereon, color readily forms at unexpected and undesired areas by rough handling, heating, or attachment of solvents, thereby contaminating the recorded images. Extensive research has recently been conducted to develop heat-sensitive recording materials of diazo color forming type which avoid the above described defect. For example, Japanese Patent Application (OPI) No. 123086/1982, and the Bulletin of The Electric Image Society, Vol. 11. p. 290 (1982) disclose the heat-recording method which comprises conducting heat-recording on a recording material containing diazo compounds, coupling components and basic components (including components which become basic by heating) and decomposing the unreacted diazo compounds by light exposure to stop color forming. In fact, in accordance with the above method, color forming can be stopped (hereinafter, referred to as "fixing") at areas which are unnecessary to be recorded.

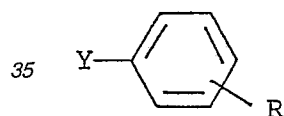
However, in the recording material of this type, pre-coupling gradually occurs during storage before use, and therefore unfavorable color formation (fog) occurs in many cases. In this case, the pre-coupling can be prevented by making one of the color forming components exist in the form of discontinuous particles (solid dispersion) so as to prevent it from contact with other components. However, the storage stability of the recording materials (hereinafter called shelf life stability) is not sufficient, and there is a defect in that the color forming property upon heating decreases. Further, it is disclosed, for example, in Japanese Patent Application

(OPI) No. 123086/82 that diazo compounds and a coupling component are incorporated into each layer separately in order to minimize the contact between the color forming components. The shelf life stability can be improved by the above method, but the color forming property by heating largely decreases and the recording material of this type can not respond to high speed recording requirements having a short pulse width, and thus is not suitable for practical use. Still further, in order to realize the satisfactory shelf life stability and satisfactory color forming property upon heating, it is known that any one of a coupling component and a basic substance can be encapsulated by a non-polar wax-like substance (as disclosed in Japanese Patent Application (OPI) Nos. 44141/82 and 142636/82) or by a hydrophobic high molecular weight substance (as disclosed in Japanese Patent Application (OPI) No. 192944/82) in order to separate the coupling component and/or basic substance from other components. These encapsulation methods comprise dissolving a wax or a high molecular weight substance in suitable solvents, and dissolving or dispersing a color forming component into the thus obtained solution to form capsules, whose function is different from that of conventional capsules where a core is covered with a shell. For the above reason, when a color forming component is dissolved to form capsules, the color forming component does not become a core substance for a capsule, but does disperse with the encapsulated substance homogeneously. Therefore, pre-coupling occurs at the wall surface of the capsule during storage, resulting in poor shelf life stability. When a color forming component is dispersed to form a capsule, it is necessary to heat and melt the wall of the capsule in order to cause the color forming reaction. Thus results in poor color forming properties upon heating. Further, the above-described method has a manufacturing problem in that the solvents used for dissolving the wax or the high molecular weight substance should be removed after the capsule is formed. Therefore the above method is not sufficiently satisfactory.

In order to solve the above problems, another encapsulation method has been studied, and it was found that the problem could be solved by an excellent heat-sensitive recording material prepared by incorporating at least one of the color forming components into a core substance and forming a wall around the core substance by polymerization to obtain microcapsules, as described in Japanese Patent Application (OPI) No. 190886/84. This method is particularly preferable.

The diazo compounds used in the present invention are diazonium salts represented by the formula ArN_2^+X^- , wherein Ar represents an aromatic part, N_2^+ represents a diazonium group, and X^- represents an acidic anion. Further, the diazo compounds are those that can form a color by the reaction with a coupling component.

Aromatic moieties are preferably those having the following formula



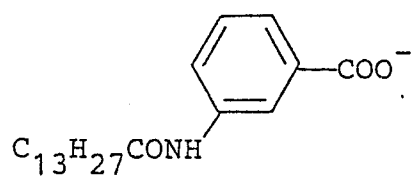
In the formula, Y represents a hydrogen atom, a substituted amino group, an alkoxy group, an alkylaryloxy group, an arylthio group, an alkylthio group or an acylamino group, and R represents a hydrogen atom, an alkyl group, an alkoxy group, an aryloxy group, an arylamino group, or a halogen atom (I, Br, Cl, F).

Substituted amino groups of Y are preferably a monoalkylamino group, a dialkylamino group, an arylamino group, a morpholino group, a piperidino group, or a pyrrolidino group.

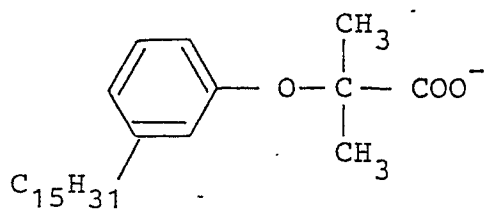
The diazonium salt in the present invention can be used in combinations of two or more.

Specific examples of diazonium to form the diazonium salts are 4-diazo-1-dimethylaminobenzene, 4-diazo-1-diethylaminobenzene, 4-diazo-1-dipropylaminobenzene, 4-diazo-1-methylbenzylaminobenzene, 4-diazo-1-dibenzylaminobenzene, 4-diazo-1-ethylhydroxyethylaminobenzene, 4-diazo-1-diethylamino-3-methoxybenzene, 4-diazo-1-dimethylamino-2-methylzene, 4-diazo-1-benzoylamino-2,5-diethoxybenzene, 4-diazo-1-morpholinobenzene, 4-diazo-1-morpholino-2,5-diethoxybenzene, 4-diazo-1-morpholino-2,5-dibutoxybenzene, 4-diazo-1-anilinobenzene, 4-diazo-1-toluymercapto-2,5-diethoxybenzene, 4-diazo-1,4-methoxybenzoylamino-2,5-diethoxybenzene, 1-diazo-4-(N,N-diethylcarbamoyl)benzene, 1-diazo-2-octadecyloxybenzene, 1-diazo-4-(4-tert-octylphenoxy)benzene, 1-diazo-4-(2,4-di-tert-amylphenoxy)benzene, 1-diazo-2-(4-tert-octylphenoxy)benzene, 1-diazo-5-chloro-2-(4-tert-octylphenoxy)benzene, 1-diazo-2,5-bis-octadecyloxybenzene, 1-diazo-2,4-bis-octadecyloxybenzene, and 1-diazo-4-(N-octylstearoylamino)benzene.

Specific examples of an acidic anion are
 $\text{C}_n\text{F}_{2n+1}\text{COO}^-$ (n is an integer of from 3 to 9),
 $\text{C}_m\text{F}_{2m+1}\text{SO}_3^-$ (m is an integer of from 2 to 8),
 $\text{C}_\ell\text{F}_{2\ell+1}\text{SO}_2)_2\text{CH}^-$ (ℓ is an integer of from 1 to 18).



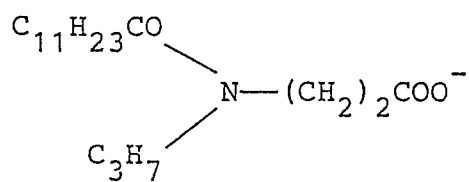
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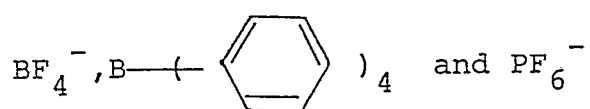
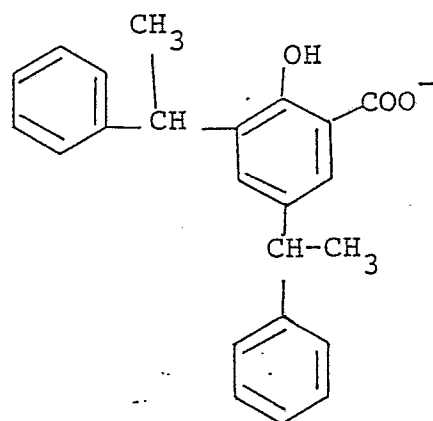
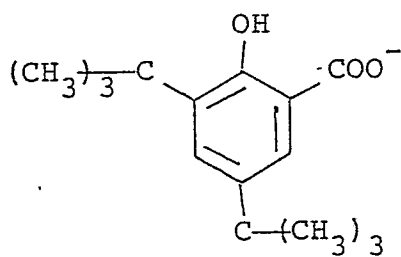
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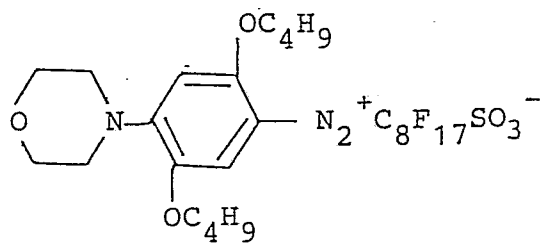
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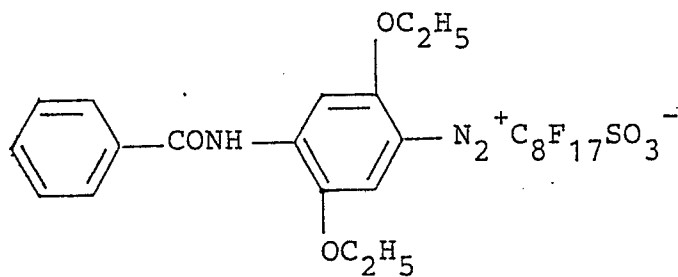
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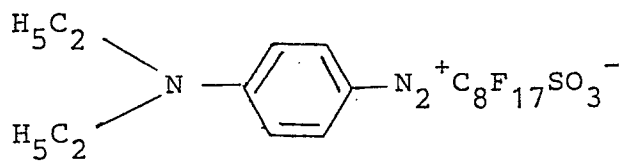
35 Specific examples of diazo compounds (diazonium salts) are illustrated below.





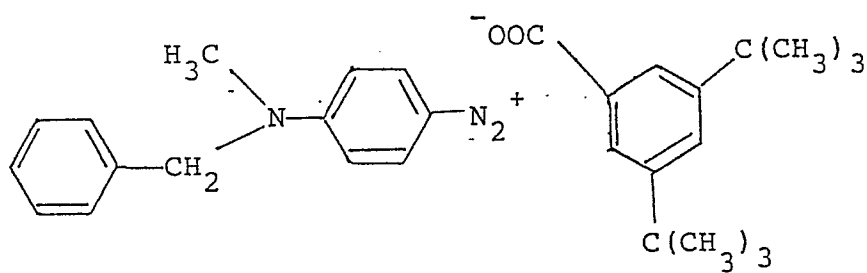
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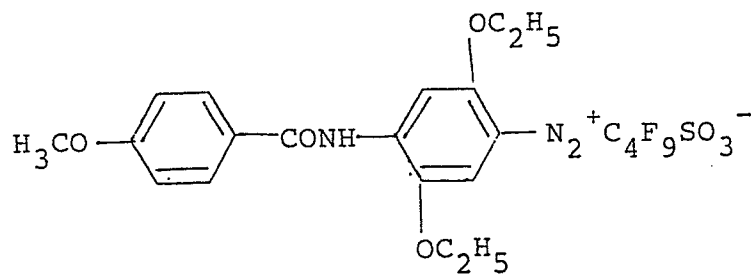


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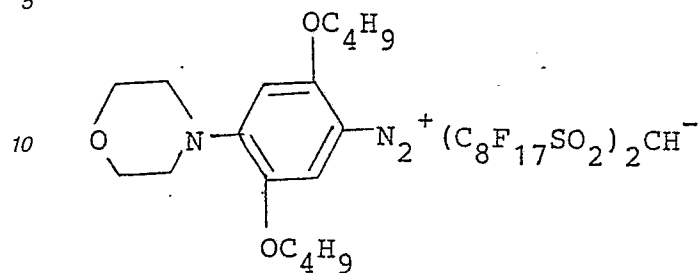
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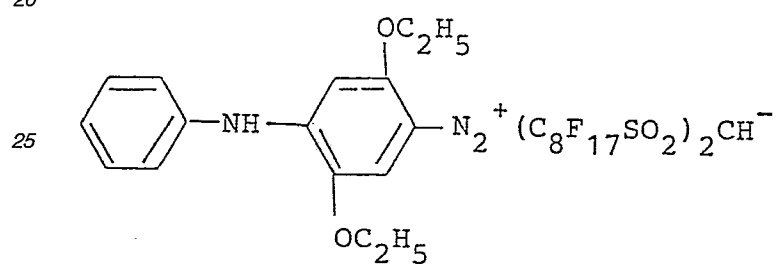
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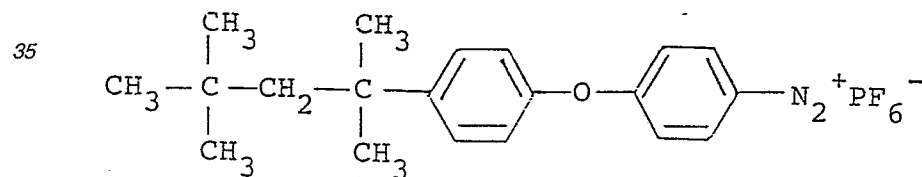
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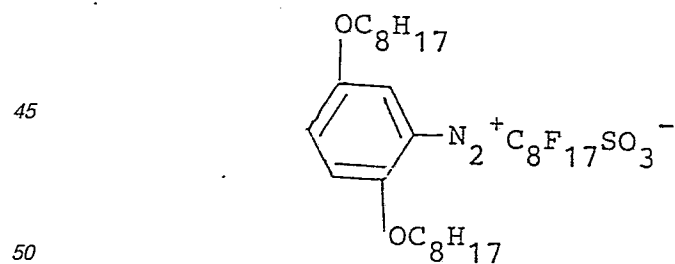
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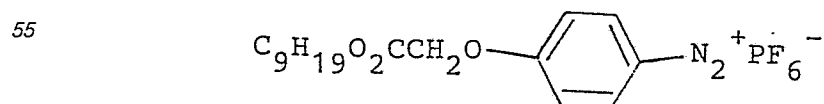
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65 The coupling component used in the present invention is a compound which can form color by a coupling reaction with diazo compounds (diazonium salts). Specific examples thereof include resorcin, phloroglucin,

sodium 2,3-dihydroxynaphthalene-6-sulfonate, 1-hydroxy-2-naphthoic acid-morpholinopropylamide, 1,5-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,3-dihydroxy-6-sulfanylnaphthalene, 2-hydroxy-3-naphthoic acid-morpholinopropylamide, 2-hydroxy-3-naphthoic acid-2'-methylamide, 2-hydroxy-3-naphthoic acid ethanolamide, 2-hydroxy-3-naphthoic acid-octylamide, 2-hydroxy-3-naphthoic acid tetradecylamide, acetanilide, acetoacetanilide, benzoylacetanilide, 1-phenyl-3-methyl-5-pyrazolone, 2,4-bis(benzoylacetamino)toluene, 1,3-bis-(pivaloylacetaminomethyl)benzene, 1-(2',4',6'-trichlorophenyl)-3-benzamide-5-pyrazolone, 1-(2',4',6'-trichlorophenyl)-3-anilino-5-pyrazolone and 1-phenyl-3-phenylacetamide-5-pyrazolone and the like. Images having a desired color tone can be obtained by variable combinations of these coupling components.

It is preferable to add basic substances to the recording layer of the heat-sensitive recording material of the present invention in order to accelerate the coupling reaction in a basic environment

Such basic substances are those that are hardly soluble or are insoluble in water, or those capable of producing alkali by heating.

The basic substances include organic and inorganic ammonium salts, organic amines, amides, ureas, thiourea and the derivatives thereof, thiazoles, pyrroles, pyrimidines, piperadines, guanidines, indoles, imidazoles, imidazolines, triazoles, morpholines, piperidines, amidines, formamidines and pyridines and like nitrogen-containing compounds. Specific examples thereof include ammonium acetate, tricyclohexylamine, tribenzylamine, octadecylbenzylamine, stearylamine, allylurea, thiourea, methylthiourea, allylthiourea, ethylenethiourea, 2-benzylimidazole, 4-phenylimidazole, 2-phenyl-4-methyl-imidazole, 2-undecyl-imidazoline, 2,4,5-trifuryl-2-imidazoline, 1,2-diphenyl-4,4-dimethyl-2-imidazoline, 2-phenyl-2-imidazoline, 1,2,3-triphenylguanidine, 1,2-ditolylguanidine, 1,2-dicyclohexylguanidine, 1,2,3-tricyclohexylguanidine, guanidine trichloroacetate, N,N'-dibenzylpiperazine, 4,4'-dithiomorpholine, morpholinium trichloroacetate, 2-amino-benzothiazole, and 2-benzoylhydrazino-benzothiazole. These basic substances can be used in combinations of two or more thereof.

The heat-sensitive recording material of the present invention may contain a hydroxy compound, a carbamate compound, an aromatic alkoxy compound or an organic sulfonamide compound, in order to improve the color forming property by heating. These compounds have the property of lowering the melting point of the coupling component or the basic substance, or improving the heat permeability of a microcapsule wall, and can increase the practical concentration as a result.

Specific examples of such hydroxy compounds include phenol compounds such as p-t-butylphenol, p-t-octylphenol, p- α -cumylphenol, p-t-pentylphenol, m-xenol, 2,5-dimethylphenol, 2,4,5-trimethylphenol, 3-methyl-4-isopropylphenol, p-benzylphenol, o-cyclohexylphenol, p-(diphenylmethyl)phenol, p-(α,α -diphenylethyl)phenol, o-phenylphenol, ethyl p-hydroxybenzoate, chlorophyl p-hydroxybenzoate, butyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, p-methoxyphenol, p-butoxyphenol, p-heptyloxyphenol, p-benzoyloxyphenol, dimethylvanillin 3-hydroxyphthalate, 1,1-bis(4-hydroxyphenyl)dodecane, 1,1-bis(4-hydroxyphenyl)-2-ethylhexane, 1,1-bis(4-hydroxyphenyl)-2-methylpentane, 2,2-bis(4-hydroxyphenyl)-heptanevanillin, 2-t-butyl-4-methoxyphenol, 2,6-dimethoxyphenol, 2,2'-dihydroxy-4-methoxybenzophenone, or the like, and alcohol compounds such as 2,5-dimethyl-2,5-hexandiol, resorcinol di(2-hydroxyethyl)ether, resorcinol mono(2-hydroxyethyl)ether, salicyl alcohol, 1,4-di(hydroxyethoxy)benzene, p-xylylenediol, 1-phenyl-1,2-ethanediol, diphenylmethanol, 1,1-diphenylethanol, 2-methyl-2-phenyl-1,3-propanediol, 2,6-dihydroxymethyl-p-cresolbenzyl ether, 2,6-dihydroxymethyl-p-cresolbenzyl ether, 3-(o-methoxyphenoxy)-1,2-propanediol, etc.

Specific examples of such carbamate compounds include ethyl N-phenylcarbamate, benzyl N-phenylcarbamate, phenetyl N-phenylcarbamate, benzyl carbamate, butyl carbamate, isopropyl carbamate, etc.

Specific examples of such aromatic alkoxy compounds include 2-methoxybenzoic acid, 3,5-dimethoxyphenylacetic acid, 2-methoxynaphthalene, 1,3,5-trimethoxybenzene, p-dimethoxybenzene, p-benzoyloxymethoxybenzene, etc.

Specific examples of such organic sulfonamides include p-toluenesulfonamide, o-toluenesulfonamide, benzenesulfonamide, p-toluenesulfonanilide, N-(p-methoxyphenyl)-p-toluenesulfonamide, N-(o-methoxyphenyl)-p-toluenesulfonamide, N-(p-chlorophenyl)-p-toluenesulfonamide, N-(o-chlorophenyl)-p-toluenesulfonamide, N-(p-tolyl)-p-toluenesulfonamide, N-(o-tolyl)-p-toluenesulfonamide, N-(o-hydroxyphenyl)-p-toluenesulfonamide, N-benzyl-p-toluenesulfonamide, N-(2-phenetyl)-p-toluenesulfonamide, N-(2-hydroxyethyl)-p-toluenesulfonamide, N-(3-methoxypropyl)-p-toluenesulfonamide, methanesulfonanilide, N-(p-tolyl)sulfonamide, N-(o-tolyl)-sulfonamide, N-(p-methoxyphenyl)sulfonamide, N-(o-methoxy)sulfonamide, N-(p-chlorophenyl)sulfonamide, N-(o-chlorophenyl)sulfonamide, N-(2,4-xylyl)sulfonamide, N-(p-ethoxyphenyl)sulfonamide, N-benzylmethanesulfonamide, N-(2-phenoxyethyl)methanesulfonamide, 1,3-bis(methanesulfonylamino)benzene, 1,3-bis(p-toluenesulfonylamino)propane, etc.

However, the present invention is not limited to the above compounds.

The above compounds are used together with a core substance of a microcapsule to prepare a microcapsule, or can be added to the coating solution of a heat-sensitive recording material so as to be present outside of a microcapsule. It is preferred that the above compounds are used as a dispersion in water with microcapsules. In all cases, the additive amount thereof is generally from 0.01 to 10 parts by weight, and preferably from 0.1 to 5 parts by weight per part by weight of a coupling component. The additive amount can be selected as desired in order to adjust the desired color forming density.

In the preferred microcapsule to be in the present invention, reactive substances contained in the core substance of a microcapsule are dissolved or dispersed in a water-soluble organic solvent to form an emulsion, if desired, and then a wall of a microcapsule is formed therearound by polymerization. Organic

solvents having a boiling point of 180°C or higher are preferred. Specific examples thereof are phosphates, phthalic acid esters, other carboxylic acid esters, fatty acid amides, alkylated biphenyls, alkylated phenols, chlorinated paraffins, alkylated naphthalenes, and diaryl ethanes. More specific examples are tricresyl phosphate, dioctyl phosphate, octyldiphenyl phosphate, tricyclohexyl phosphate, dibutyl phthalate, dioctyl phthalate, dilauryl phthalate, dicyclohexyl phthalate, butyl oleate, diethylene glycol dibenzoate, dioctyl sebacate, dibutyl sebacate, dioctyl adipate, trioctyl trimellitate, acetyltriethyl citrate, octyl maleate, dibutyl maleate, isopropyl biphenyl, isoamyl biphenyl, chlorinated paraffin, diisopropyl naphthalene, 1,1'-ditolylethane, 2,4-di-tretaminophenol, N,N-dibutyl-2-butoxy-5-tert-octylaniline, N,N-diphenylformamidine, N,N',N'-triphenylbenzamidine, and N,N'-diphenylbenzamidine.

Among these solvents, ester solvents such as dibutyl phthalate, tricresyl phosphate, diethyl phthalate, and dibutyl maleate are particularly preferred.

The microcapsule in the present invention is prepared by emulsifying the core substance containing reactive substances, and thereafter forming a wall made of a high molecular weight substance around the oil drop. A reactant which forms a high molecular weight substance is added inside and/or outside of the oil drop.

Specific examples of the high molecular weight substances are polyurethane, polyurea, polyamide, polyester, polycarbonate, urea-formaldehyde resin, a melamine resin, polystyrene, styrene-methacrylate copolymer, styrene-acrylate copolymer, gelatin, polyvinyl pyrrolidone and polyvinyl alcohol.

The high molecular weight substances can be used in combination. Preferred high molecular weight substances are polyurethane, polyurea, polyamide, polyester and polycarbonate, and the most preferred substances are polyurethane and polyurea.

For preparing the wall of a microcapsule of the present invention, the method of microencapsulation by polymerizing reactants from the inside of an oil drop is the most effective. That is, in accordance with the above method, a capsule which is preferably used for a recording material having a good shelf life stability before recording and having a uniform average particle size can be prepared in a short time.

The above method and the specific examples of such compounds are disclosed in U.S. Patents 3,726,804 and 3,796,669.

When polyurethane is used as a material for the wall, the microcapsule wall is prepared by mixing polyhydric isocyanate, and if desired, a second substance, for example, a polyol, which, forms a capsule wall by the reaction with polyhydric isocyanate in the oily liquid to be encapsulated, emulsifying and dispersing the mixture in water, and causing a reaction to form a high molecular weight wall on the surface of oil droplets by increasing the temperature. In this case, an auxiliary solvent having a low boiling point and having high dissolving power can be used in oily liquid, and examples thereof include ethylacetate, propylacetate, butyl acetate and methylene chloride.

In this instance, polyisocyanate and the second substance to be reacted, for example, polyol or polyamine, are disclosed in U.S. Patents, 3,281,383, 3,773,695, 3,793,268, Japanese Patent Publication Nos. 40347/73 and 24159/74 and Japanese Patent Applications (OPI) Nos. 80191/73 and 84086/73. These can be used in the present invention.

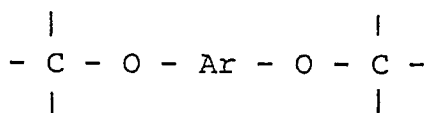
Tin salt can be used in combination to accelerate the urethanation reaction.

It is preferred that polyhydric isocyanate be used as a first wall forming substance, and polyol or water be used as a second wall forming substance in order to increase shelf life stability. Heat permeability of the reacted substance can be optionally varied by varying the combination of the first and the second substances.

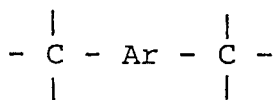
The polyhydric isocyanate to be used as a first wall forming substance includes diisocyanate such as m-phenylene diisocyanate, p-phenylene diisocyanate, 2,6-tolylene diisocyanate, 2,4-tolylene diisocyanate, naphthalene-1,4-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, oxylylene-1,4-diisocyanate, 4,4'-diphenylpropane diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate, propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, or cyclohexylene 1,4-diisocyanate; triisocyanate such as 4,4',4''-triphenylmethane triisocyanate or toluene-2,4,6-triisocyanate; tetraisocyanate such as 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate; and isocyanate prepolymer such as an adduct product of hexamethylene diisocyanate and trimethylol propane, an adduct product of 2,4-tolylene diisocyanate and trimethylol propane, an adduct product of xylylene diisocyanate and trimethylol propane, and an adduct product of tolylene diisocyanate and hexane triol.

The polyol used as a second wall forming substance can be an aliphatic or aromatic polyhydric alcohol, hydroxypolyester or hydroxy polyalkylene ether. The preferred polyol is a polyhydroxy compound having a molecular weight of 5,000 or less and having the following groups (A), (B), (C) or (D) between two hydroxy groups in the molecule.

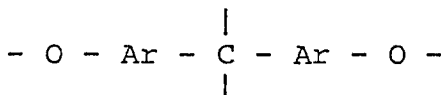
(A) Aliphatic hydrocarbon group having from 2 to 8 carbon atoms



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In the above groups, Ar in (B), (C) and (D) is a substituted or unsubstituted aromatic moiety. The aliphatic hydrocarbon group in (A) has the fundamental structure of $-C_nH_{2n}-$.

Specific examples of (A) are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, propylene glycol, 2,3-dihydroxybutane, 1,2-dihydroxybutane, 1,3-dihydroxybutane, 2,2-dimethyl-1,3-propanediol, 2,4-pentanediol, 2,5-hexanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, dihydroxycyclohexane, diethylene glycol, 1,2,6-trihydroxyhexane, phenylethylene glycol, 1,1,1-trimethylol propane, hexanetriol, pentaerythritol, and glycerine.

20

Specific examples of (B) are a condensed product of aromatic polyhydric alcohol and alkylene oxide such as 1,4-di(2-hydroxyethoxy)benzene or resorcinol dihydroxyethyl ether.

25

Specific examples of (C) are p-xylylene glycol, m-xylylene glycol and α,α' -dihydroxy-p-diisopropyl benzene.

Specific examples of (D) are 4,4'-dihydroxydiphenylmethane, 2-(p,p'-dihydroxydiphenylmethyl)-benzylalcohol, an adduct product of bisphenol A with ethylene oxide and an adduct product of bisphenol A with propylene oxide. Polyol is preferably used in an amount such that the hydroxyl group is used in an amount of from 0.02 to 2 moles per mole of isocyanate group. When polyurea is used as a material for the wall, the above-described procedure can be conducted without using polyol.

30

A water-soluble high molecular weight substance can be used to prepare a microcapsule and can be any one of water-soluble anionic high molecular weight substances, nonionic high molecular weight substances, and amphoteric high molecular weight substances. An anionic high molecular weight substance can be a natural or synthetic substance and those having $-COO-$, $-SO_3-$ and the like can be used. Natural anionic high molecular weight substances include gum arabic and alginic acid and semi-synthetic substances include carboxymethyl cellulose, phthalated gelatin, sulfated starch, sulfated cellulose and lignin sulfonic acid.

35

Synthetic anionic high molecular weight substances include maleic anhydride copolymers (including hydrolysis compounds) polymers and copolymers of acrylate (including methacrylate), polyvinyl alcohol, and carboxy modified polyvinyl alcohol.

40

The nonionic high molecular weight substance include polyvinyl alcohol, hydroxyethyl cellulose, and methyl cellulose.

The amphoteric compound includes gelatin and the like.

These water-soluble high molecular weight substances are used as a 0.01 to 10 wt% aqueous solution. The average particle size of the microcapsules is adjusted to be 20 μm or less. Generally, when the average particle size thereof exceeds 20 μm , the quality of printed images becomes inferior in many cases.

45

Particularly when heating by a thermal head is conducted from the side of a coated layer, the average particle size is preferably 8 μm or less in order to prevent fog caused by pressure from the thermal head.

In the present invention, it is preferable to use at least one compound selected from diazo compounds and a coupling component as a core substance of a microcapsule. When two of the substances are included in a core substance of a microcapsule, they may be included in each microcapsule respectively or they may be included in one microcapsule. The other components which are not incorporated as a core material of a microcapsule are incorporated into a heat-sensitive recording layer outside of the microcapsule. The basic substance of the present invention can not be incorporated in microcapsules containing a diazo compound and a coupling component.

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A microcapsule can be prepared from an emulsion containing 0.2 wt% or more of components to be encapsulated.

Whenever diazo compounds, a coupling component and a basic substance, are included inside of a microcapsule or are included in a heat-sensitive layer outside of a microcapsule, it is preferred that the diazo compound is included inside of a microcapsule and the coupling component and the basic substance are present outside of a microcapsule.

60

The coupling component is used in an amount of 0.1 to 30 parts by weight, and the basic substance is used in an amount of 0.1 to 30 parts by weight, per part by weight of diazo compound(s). It is also preferred that the diazo compound(s) is (are) coated in an amount of from 0.05 to 5.0 g/m².

65

When diazo compounds, a coupling component, an agent for improving heat color forming property and a

basic substance are not microencapsulated, they are preferably used as a solid dispersion together with a water-soluble high molecular weight substance, and are dispersed with a sand mill or the like. The preferable water-soluble high molecular weight substance used therein is that used for preparing a microcapsule. The concentration of the water-soluble high molecular weight substance is from 2 to 30 wt%, and diazo compounds, a coupling component and a basic substance are introduced into the solution of the water-soluble high molecular weight substance in an amount of from 5 to 40 wt%, respectively.

The average particle size of the dispersion is preferably 10 μm or less.

In the heat-sensitive recording material of the present invention, pigments such as silica, barium sulfate, titanium oxide, aluminum hydroxide, zinc oxide or calcium carbonate and fine particles such as styrene beads or urea-melamine resin can be used in order to prevent sticking to a thermal head or to improve the writing property.

Metal soaps can also be used to prevent sticking, and are generally used in an amount of 0.2 to 7 g/m².

In the heat-sensitive recording material of the present invention, a heat-fusible substance can be used to increase heat recording density. The heat-fusible substance is a substance which is solid at normal room temperature (about 20°C), can be fused by heating with a thermal head as they have a melting point of from 50 to 150°C and can dissolve diazo compounds, coupling components or basic substances. The heat-fusible substance is used as a dispersion having an average particle size of from 0.1 to 10 μm and in an amount of from 0.2 to 7 g/m² (solid content). Specific examples of the heat-fusible substance include fatty acid amines, N-substituted fatty acid amides, ketone compounds, urea compounds and esters.

A recording layer can be coated by using suitable binders to prepare a heat-sensitive recording material of the present invention.

Binders include various emulsions of polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, gum arabic, gelatin, polyvinyl pyrrolidone, casein, styrene-butadiene latex, acrylonitrile-butadiene latex, polyvinyl acetate, polyacrylates and a copolymer of ethylene-vinyl acetate. The additive amount is from 0.5 to 20 g/m², and preferably from 0.5 to 5 g/m², by solid content.

In addition to the materials described above, citric acid, tartaric acid, oxalic acid, boric acid, phosphoric acid and pyrophosphoric acid can be added as acid stabilizing agents.

If necessary, additives such as wax surface active agents, antistatic agents, defoaming agents, anti-foaming agents, fluorescent whitening agents, dispersing agents, hardening agents or coloring agents can be incorporated into the heat-sensitive layer.

The coating amount of the heat-sensitive layer is generally from 3 g/m² to 20 g/m², and preferably from 5 g/m² to 15 g/m². When the coating amount is 3 g/m² or less, sufficient sensitivities can not be obtained. When the coating amount exceeds 20 g/m², it is economically unfavorable, because the quality is not further improved.

An overcoating layer is provided on the heat-sensitive layer of the heat-sensitive recording material of the present invention to provide water resistance and scratch resistance. The materials for the overcoating layer include polyvinyl alcohol, silica modified polyvinyl alcohol, gelatin, copolymer of styrene and maleic anhydride and starch which are used alone or in combination as a binder, and hardening agents similar to those as used for hardening the underlayer, borax, boric acid and colloidal silica for hardening the above binders.

The white areas are further whitened and a head can be prevented from undesirable contact during printing by incorporating white pigments such as kaolin, calcium carbonate, titanium dioxide, barium sulfate, zinc oxide, magnesium oxide or clay into the overcoating layer.

An overcoating layer of a heat-sensitive recording material can be further whitened by adding fluorescent dyes and coloring dyes in a small amount, and can be uniformly dyed by adding suitable dyes such that the color hue of the background becomes the desired colors other than white. If desired, additives such as wax surface active agents, antistatic agents, defoaming agents, anti-foaming agents, dispersing agents, and the like can be incorporated into the overcoating layer.

The coating amount of the overcoating layer is generally from 0.3 g/m² to 5 g/m², and more preferably from 0.5 g/m² to 4 g/m².

When the coating amount is less than 0.3 g/m², water substance and scratch resistance are not sufficient, and when it is more than 4 g/m², excess energy is necessary for printing.

The coating solutions in the present invention can be coated by a generally known method, such as a dip coating method, an air knife coating method, a curtain coating method, a roller coating method, a doctor coating method, a wire bar coating method, a slide coating method, a gravure coating method or an extrusion coating method using a hopper as described in U.S. Patent 2,681,294. If desired, a simultaneous multi-layer coating method as described in U.S. Patents, 2,761,791, 3,508,947, 2,941,898, and 3,526,528 and in Yuji Harasaki "Coating Engineering", p 253, published by Asakura Shoten, Japan (1973) can be used. The particular method can optionally be selected depending upon coating amounts and coating speed rates.

The present invention is illustrated in more detail by the following Example, but is not limited thereto. In the Example, all parts are by weight.

EXAMPLE

Preparation of a coating solution for a matting layer

The coating solution having the following formula was prepared using dispersed crystalline silica having an average particle size of 0.1 μm and dispersed polyacrylonitrile having an average particle size of 0.1 μm .

<u>Raw Materials</u>	<u>Coating Solutions for a Matting Layer</u>			
	<u>No. 1</u> (parts)	<u>No. 2</u> (parts)	<u>No. 3</u> (parts)	
Copolymer of ethylene terephthalate and butylene terephthalate	2	2	2	10
Crystalline silica	0.0005	0.02	0.17	15
Polyacrylonitrile particles	0.0015	0.05	0.43	
Methyl ethyl ketone	55	55	55	20
Acetone	43	43	43	

A coating solution having the following formula was prepared for comparison.

<u>Raw Materials</u>	<u>Coating Solutions for a Matting Layer No.4</u> (parts)	
Gelatin	2	
Crystalline silica	0.02	35
Polyacrylonitrile particles	0.05	
2,4-dichloro-6-hydroxy-S-triazine (sodium salt)	0.01	40
Water	98	

Preparation of coating solution for an underlayer

The coating solution having the following formula was prepared for an underlayer.

<u>Raw Materials</u>	<u>Amounts</u> (parts)	
Gelatin	1	50
Water	1	
Salicylic acid	0.1	
Polyamide-polyamine epichlorohydrin resin	0.3	55
Parachlorophenol	10	
Ethanol	87.6	60

Preparation of a coating solution for a heat-sensitive layer

Coating solution 1 for a heat-sensitive layer:

10 parts by weight of 2-anilino-3-methyl-6-diethyl-aminofluoran as a color former and 50 parts by weight of 50% polyvinyl alcohol (saponification degree: 98%, degree of polymerization: 500) were dispersed in a ball mill for one day and one night to obtain a color former dispersing solution (A).

20 parts by weight of 2,2-bis(4-hydroxyphenyl)-propane as a developer, 5 parts by weight of the compound (I) of the present invention as shown in Table 1, 10 parts of the compound (II) or (III) and 200 parts by weight of 50% polyvinyl alcohol were dispersed in a ball mill for one day and one night to obtain a dispersing solution (B).

40 parts by weight of calcium carbonate ("Briliant-15", trademark for product manufactured by Shiraishi Kogyo Co., Ltd.) and 40 parts by weight of 1% sodium hexametaphosphate were mixed and dispersed by a homogenizer to obtain a dispersing solution (C).

The dispersing solutions (A), (B), and (C) were mixed and each 10 parts of 20% zinc stearate dispersion and 20% paraffin wax were added thereto and stirred sufficiently to prepare a coating solution No. 1 for a heat-sensitive layer.

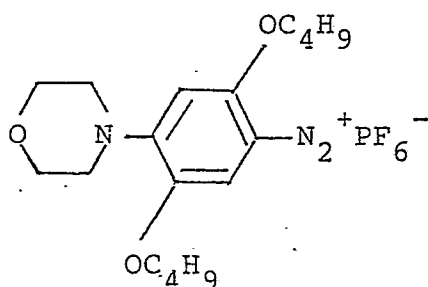
Coating solution 2 for a heat-sensitive layer:

(a) Preparation of a capsule solution:

150 parts of methylene chloride, 50 parts of tricresyl phosphate, 150 parts of trimethylol propane trimethacrylate and 200 parts of 75% ethyl acetate solution of m-xylylene diisocyanate-trimethylol-propane adduct product (3:1) (Takenate DIION", trademark for product manufactured by Takeda Chemical Industries, Ltd.) were added to 50 parts of the compound A-1 and uniformly mixed to obtain an oil solution.

600 parts of 7% polyvinyl alcohol ("PVA 217E", trademark for product manufactured by KURARAY Co., Ltd. degree of saponification: 88-89%, a degree of polymerization: 1700) were prepared as a water-soluble high molecular weight aqueous solution.

An aqueous solution of protective colloid was added in a 5 liter stainless pot equipped with a hot water bath and a dissolver and then the oil solution was added thereto while stirring the dissolver to conduct emulsification and dispersion to have an average particle size of about 1.5 μm . After dispersion was completed, stirring was made slow, a hot water at 42°C was introduced into the bath and reaction of encapsulation was conducted for 3 hours at 40°C. 25 cc of ion exchange resin ("MB-3", a trademark for product manufactured by Japan Organo Co., Ltd.) was added to the thus obtained solution, stirred, and filter to obtain a capsule solution.

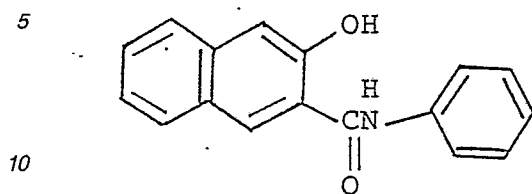


(b) Preparation of a dispersing solution A:

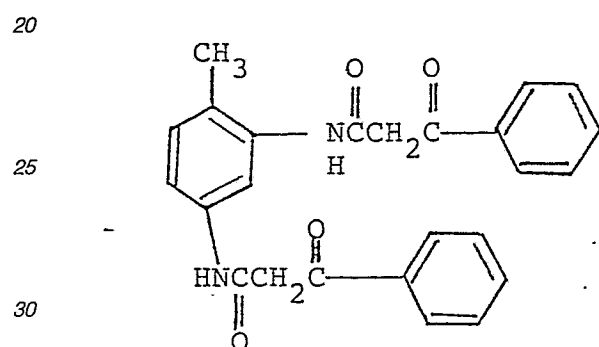
The following mixture was dispersed by a dissolver and then dispersed by a Dyno mill (manufactured by Willy.A.Bachofenag.) to prepare a dispersing solution A having an average particle size of 2 μm .

<u>Raw Materials</u>	<u>Amounts</u> <u>(parts)</u>
15% aqueous solution of PVA 205 (manufactured by Kuraray Co., Ltd.)	10
Compound B-1	1.5
" B-2	0.2
" C	2
" D	7
Water	20

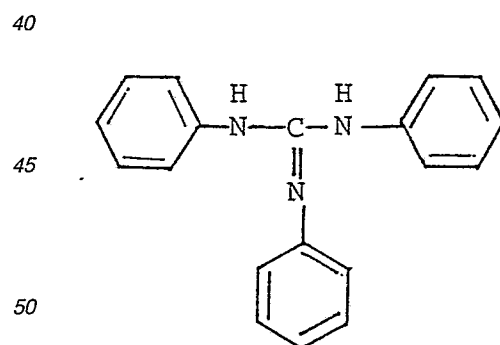
Compound B-1: Coupler



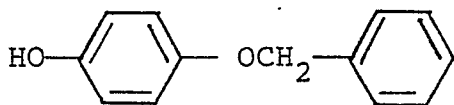
Compound B-2: Coupler



Compound C: Organic basic compound



Compound D: Color forming improving agent



(c) Preparation of a dispersing solution B:

A dispersing solution B having an average particle size of 3 μm was prepared in the same manner of preparation as the dispersing solution A.

Raw Material	Amounts (parts)
Capsule solution ("Unibur 70", manufactured by Shiraishi Kogyo Co., Ltd.)	8
Sodium hexametaphosphate	0.2
Water	12

The above described capsule solution, dispersing solutions A and B were mixed in the following mixing ratio to prepare a coating solution No. 2 for a heat-sensitive layer.

Raw Material	Amounts (parts)
Capsule solution	25
Dispersing solution A	35
" " B	14
3% aqueous solution of polyoxyethylene lauryl alcohol ether (10 mol of ethylene oxide adduct)	2.5
50% aqueous solution of fluorescent whitening agent ("Kayaphor PAS", manufactured by Nippon Kayaku Co., Ltd.)	1.0
30% aqueous dispersion of zinc stearate	2.5
22% aqueous dispersion of methylol stearoamide wax	3.5

Preparation of a coating solution for an overcoating-layer

Thus, the coating solution for an overcoating layer having the following composition was prepared.

	Raw Material	Amounts (parts)
5	10% aqueous solution of "PVA R2105" manufactured by Kuraray Co., Ltd.	6
	Water	12.5
10	40% aqueous dispersion of kaolin	5
	30% aqueous dispersion of zinc stearate	0.2
15	22% aqueous dispersion of methylol stearoamide wax	0.3
20	Colloidal silica ("Snowtex S", manufactured by Nissan Chemical Industries, Ltd.)	2

25 A biaxially stretched polyethylene terephthalate film having a thickness of 75 μm was exposed to ultraviolet ray irradiation, and the above described coating solutions were coated thereon to obtain samples and evaluation was made thereon, as shown in Table 1.

It is clear from the results in Table 1 below that the heat-sensitive recording materials of the present invention are superior to the comparative samples.

30 Evaluations

(1) Writing properties:

35 Writing was conducted with a pencil (HB) on the heat-sensitive paper opposite surface to a heat-sensitive recording layer. A stands for the case when letters were written and B stands for the case when letters could not be written.

(2) Gloss and image densities:

40 The images of ultrasonic waves were printed using "Thermal Imager FTI-100" manufactured by Fuji Photo Film Co., Ltd. and gloss was evaluated by viewing the images from the opposite side of the recorded surfaces. A stands for the case when gloss is great, B stands for the case when gloss is not so great, and C stands for the case when gloss is poor. Image densities were measured using a Macbeth densitometer from the same side of the above.

(3) Blocking:

45 Samples in a rolled state were allowed to stand at 40°C and 90% humidity for 24 hours, and then were checked as to whether blocking took place. A stands for the case that blocking did not occur, and B stands for the case that blocking did occur.

(4) Adhesiveness between support and matting layer:

50 The surface opposite to the heat-sensitive recording layer was rubbed with an eraser to check whether the matting layer was rubbed off. A stands for the case that the matting layer was not rubbed off, and B stands for the case that the matting layer was rubbed off.

Table 1

Sample No.	Matting Layer ¹⁾		Additive Amount of Matting Agent Based on Resin (wt%)	Heat-Sensitive ²⁾ Layer	Under ³⁾ Layer	Overcoating ⁴⁾ Layer
	Coating sol.	Resin				
1	Coating sol.	None		Coating soln. No. 1	presence	presence
2	"	4 gelatin	3.5	"	"	"
3	"	1 copolymer of ethylene-phthalate and butylenephthalate	0.1	"	"	"
4	"	2	3.5	"	"	"
5	"	3	30.0	"	"	"
6	"	2	3.5	"	"	absence
7	"	2	3.5	"	absence	presence
8	Coating sol.	None		Coating soln. No. 2	presence	presence
9	"	4 gelatin	3.5	"	"	"
10	"	1 copolymer of ethylene-phthalate and butylenephthalate	0.1	"	"	"
11	"	2	3.5	"	"	"
12	"	3	30.0	"	"	"
13	"	2	3.5	"	"	"
14	"	2	3.5	"	"	absence

Remarks: 1) Coating amount of matting layer (by solid content)
 2) Coating amount of heat-sensitive layer (by solid content)
 3) Coating amount of underlayer (by solid content)
 4) Coating amount of overcoating layer (by solid content)

0.1 g/m²
 12 g/m²
 0.5 g/m²
 1.5 g/m

Table 1 (cont'd)

Sample No.	Results of Evaluation					Adhesiveness between Support and Matting Layer
	Writing Properties	Gloss	Image Density	Blocking		
1	B	A	1.54	A	-	
2	A	B	1.45	B	B	
3	B	A	1.54	A	A	
4	A	A	1.55	A	A	
5	A	C	1.35	A	A	
6	A	A	1.54	A	A	
7	A	A	1.55	A	A	
8	B	A	1.51	A	-	
9	A	B	1.40	B	B	
10	B	A	1.50	A	A	
11	A	A	1.52	A	A	
12	A	C	1.30	A	A	
13	A	A	1.52	A	A	
14	A	A	1.51	A	A	

Remarks: Sample Nos. 4, 6, 7, 11, 13 and 14 are present invention.

Claims

1. A heat-sensitive recording material comprising a transparent support having provided thereon a matting layer containing an ester resin capable of being solubilized with an organic solvent and a matting agent in an amount of from 0.5 to 20 wt% based on the weight of said ester resin, and on the opposite side of the support an underlayer, a heat-sensitive recording layer and an overcoating layer in this order. 5
2. A heat-sensitive recording material as in Claim 1, wherein said matting agent comprises particles selected from the CaCO_3 , MgCO_3 , MgO , ZnO , BaSO_4 , TiO_2 , crystalline silica, amorphous silica or alumina, polyethylene, polypropylene, polyethylene terephthalate, polystyrol, polycarbonate, an acrylic acid ester resin, a methacrylic acid resin polyacrylonitrile, a copolymer of acrylonitrile, and the mixture thereof. 10
3. A heat-sensitive recording material as in 2, wherein said matting agent comprises particles selected from crystalline silica, amorphous silica, polyacrylonitrile, and a mixture of crystalline silica and polyacrylonitrile. 15
4. A heat-sensitive recording material as in Claim 3, wherein said matting agent comprises a mixture of crystalline silica and polyacrylonitrile.
5. A heat-sensitive recording material as in any preceding claim, wherein said matting agent has an average particle size of from 0.01 to 5 μm . 20
6. A heat-sensitive recording material as in Claim 5, wherein said matting agent has an average particle size of from 0.05 to 3 μm .
7. A heat-sensitive recording material as in any preceding Claim, wherein said matting agent is present in said matting layer in an amount of from 1 to 5 wt% based on the weight of said ester resin. 25
8. A heat-sensitive recording material as in any preceding claim, wherein said ester is selected from a polyester resin, an acrylic resin, a methacrylic ester resin, a copolymer of styrene and acrylic ester, a copolymer of styrene and methacrylic ester, and a mixture thereof.
9. A heat-sensitive recording material as in Claim 8, wherein the said ester resin comprises a polyester resin. 30
10. A heat-sensitive recording material as in Claim 9, wherein said polyester resin is polyethylene terephthalate, polybutylene terephthalate or a copolymer of ethylene terephthalate and butylene terephthalate.
11. A heat-sensitive recording material as in Claim 10, wherein said polyester resin is a copolymer of ethylene terephthalate and butylene terephthalate. 35
12. A heat-sensitive recording material as in any preceding claim, wherein the solids content of the coated matting layer is from 0.01 to 50 g/m^2 .
13. A heat-sensitive recording material as in Claim 12, wherein the solids content of the coating matting layer is from 0.05 to 1.0 g/m^2 .
14. A process for producing a heat-sensitive recording material as claimed in any preceding claim, which comprises dissolving an ester resin capable of being solubilized with an organic solvent in an organic solvent, dispersing a matting agent in an amount of from 0.5 to 20 wt% based on the weight of said ester resin into the resulting solution to prepare a coating solution, coating the coating solution on the one side of a transparent support to form a matting layer and then providing on the opposite side of the support an underlayer, a heat-sensitive recording layer and an overcoating layer in this order. 40 45

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