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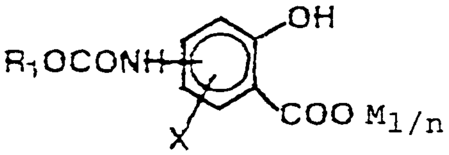
# (54) Heat-sensitive recording material.

(57) A heat-sensitive recording material comprises a support having provided thereon a heat-sensitive color forming layer containing an electron donating colorless dye and an electron accepting compound. The color forming layer contains a salicylic acid of formula (1) (or a metal salt thereof) :



(1)

wherein R$_1$ represents an alkyl group or an aryl group ; X represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, or a halogen atom ; M represents a hydrogen atom or an n-valent metal atom ; and n represents an integer, provided that n is 1 when M represents a hydrogen atom ; and a metal compound.

The material exhibits improved color-forming properties, storage stability and, after printing, a stable colored image.

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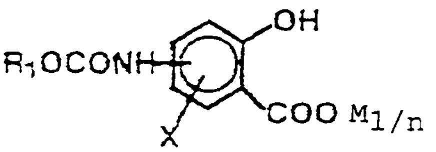
The present invention relates to a heat-sensitive recording material and, more particularly, to a heat-sensitive recording material comprising a support having provided thereon a color forming layer containing an electron donating colorless dye and an electron accepting compound, the material exhibiting improved color forming properties, storage stability before printing and colored image stability after printing.

A recording material using an electron donating colorless dye and an electron accepting compound is well known as a pressure-sensitive paper, a heat-sensitive paper, a light- and pressure-sensitive paper, an electroheat-sensitive recording paper, a heat-sensitive transfer paper and the like. These recording materials are disclosed, for example, in British Patent 2,140,449, U.S. Patents 4,480,052 and 4,436,920, JP-B-60-23992 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-57-179836, JP-A-60-123556 and JP-A-60-123557 (the term "JP-A" as used herein means a "published unexamined Japanese patent application"). Particularly, heat-sensitive recording materials are disclosed in JP-B-43-4160 and JP-B-45-14039. These heat-sensitive recording systems have been widely utilised in various fields such as facsimiles, printers and labels, and the demand therefor has increased. However, heat-sensitive recording materials have drawbacks such as fog generated by solvents and the like, and discoloration due to the action of oils and chemicals on the color formers. Consequently, their commercial value in the fields of, in particular, labels, slips, papers for word processors and plotters has been greatly impaired.

The present inventors have extensively studied the oil solubility, water solubility, distribution coefficient, pKa, substituent polarity, and substituent position of electron donating colorless dyes and electron accepting compounds with a view to developing excellent recording materials. However, they encountered a further problem in that by imparting sufficient resistance to minimise the above-mentioned drawbacks, the sensitivity of the material was greatly reduced.

Accordingly, an object of the present invention is to provide a heat-sensitive recording material which is highly sensitive, has excellent storage stability before printing and provides a stable colored image on printing.

The above and other objects of the present invention have been attained by a heat-sensitive recording material comprising a support having provided thereon a heat-sensitive color forming layer containing an electron donating colorless day and an electron accepting compound, wherein the heat-sensitive color forming layer contains a salicylic acid derivative represented by formula (1) or a metal salt thereof and a metal compound:



(1)

wherein $R_1$ represents an alkyl group or an aryl group; X represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group or a halogen atom; M represents a hydrogen atom or an n-valent metal atom; and n represents an integer, provided that n is 1 when M represents a hydrogen atom.

In formula (1), $R_1$ preferably represents an alkyl group having from 1 to 20 carbon atoms or an aryl group having from 6 to 15 carbon atoms. The alkyl group may be substituted with an alkoxy group having from 1 to 10 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or a halogen atom. The aryl group may be substituted with an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 1 to 10 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or a halogen atom. Specific examples of preferred $R_1$ include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, an n-amyl group, an n-hexyl group, an n-octyl group, a 2-ethylhexyl group, an n-decyl group, an n-dodecyl group, an n-pentadecyl group, a methoxyethyl group, a benzyl group, a 4-methylbenzyl group, a phenyl group, a tolyl group and a methoxyphenyl group.

In formula (1), X preferably represents a hydrogen atom, a chlorine atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or an alkoxy group having from 1 to 8 carbon atoms. The alkyl group, the aryl group and the alkoxy group may be substituted. Specific examples of preferred X include a hydrogen atom, a chlorine atom, a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a t-octyl group, a benzyl group, an $\alpha$-methylbenzyl group, an $\alpha,\alpha$-dimethylbenzyl group, and a phenyl group.

In formula (1), of the metal atoms represented by M, divalent or trivalent metals are preferred. n preferably represents 2 or 3. Specific examples of preferred M include metals such as zinc, magnesium, barium, calcium, aluminum, tin, titanium, nickel, cobalt, manganese and iron, and particularly zinc, aluminum, magnesium and calcium are preferred.

The substitution position of an $R_1$OCONH- group in formula (1) is preferably the 4- or 5-position of the salicylic acid.

Specific examples of salicylic acid derivatives which are used in the present invention are described below, but the present invention is not limited thereto.

Specific examples include 4-methoxycarbonylaminosalicylic acid, 4-ethoxycarbonylaminosalicylic acid, 4-n-propyloxycarbonylaminosalicylic acid, 4-isopropyloxycarbonylaminosalicylic acid, 4-n-butoxycarbonylaminosalicylic acid, 4-isobutyloxycarbonylaminosalicylic acid, 4-n-hexyloxycarbonylaminosalicylic acid, 4-n-octyloxycarbonylaminosalicylic acid, 4-(2-ethylhexyloxycarbonylamino)salicylic acid, 4-n-decyloxycarbonylaminosalicylic acid, 4-n-dodecyloxycarbonylaminosalicylic acid, 4-(2-methoxyethoxycarbonylamino)salicylic acid, 4-benzyloxycarbonylaminosalicylic acid, 4-phenoxycarbonylaminosalicylic acid, 4-p-tolyloxycarbonylaminosalicylic acid, 5-methyl-4-n-octyloxycarbonylaminosalicylic acid, 5-phenyl-4-n-octyloxycarbonylaminosalicylic acid, 5-methoxycarbonylaminosalicylic acid, 5-ethoxycarbonylaminosalicylic acid, 5-n-propyloxycarbonylaminosalicylic acid, 5-isopropyloxycarbonylaminosalicylic acid, 5-n-butoxycarbonylaminosalicylic acid, 5-isobutyloxycarbonylaminosalicylic acid, 5-n-hexyloxycarbonylaminosalicylic acid, 5-n-octyloxycarbonylaminosalicylic acid, 5-(2-ethylhexyloxycarbonylamino)salicylic acid, 5-n-decyloxycarbonylaminosalicylic acid, 5-n-dodecyloxycarbonylaminosalicylic acid, 5-(2-methoxyethoxycarbonylamino)salicylic acid, 5-benzyloxycarbonylaminosalicylic acid, 5-phenoxycarbonylaminosalicylic acid, 5-p-tolyloxycarbonylaminosalicylic acid, 3-t-butyl-5-n-octyloxycarbonylaminosalicylic acid, 3-n-octyloxycarbonylaminosalicylic acid, and 6-n-octyloxycarbonylaminosalicylic acid 4-n-Octylcarbonylaminosalicylic acid is particularly preferred.

When the salicylic acid derivative represented by formula (1) is used in combination with at least one metal compound selected from an oxide, a hydroxide, a carbonate and a carboxylate of zinc, aluminum, titanium, silicon, boron, magnesium or calcium, etc., the storage stability of images is further improved. Of the metal compounds used in combination, zinc oxide, aluminum hydroxide, calcium carbonate, silicon dioxide, and aluminum silicate are preferred, and zinc oxide is particularly preferred.

The particle size of the dispersion of the salicylic acid derivative represented by formula (1) of the present invention or the metal salt thereof after being pulverized by means of a sand mill, etc., is 3 μm or less, preferably 2 μm or less, for obtaining color generation sensitivity. When the salicylic acid derivative of the present invention is used, it is preferred to use the solid dispersion solution obtained by mixing the derivative with a metal compound and dispersing using water as a dispersion medium. In this case, of the metal compounds which are used in combination, the above described zinc oxide, aluminum hydroxide, calcium carbonate, silicon dioxide, and aluminum silicate are preferred, and zinc oxide is particularly preferred.

Other electron accepting compounds such as conventionally well known salicylic acid derivatives other than the salicylic acid derivatives of the present invention, metal salts of aromatic carboxylic acids, phenol derivatives, phenol resins, novolak resins, metal treated novolak resins, metal complexes, acid clay, bentonite, etc., may be used in combination in the present invention. Examples of these electron accepting compounds are disclosed in JP-B-40-9309, JP-B-45-14039, JP-A-52-140483, JP-A-48-51510, JP-A-57-210886, JP-A-58-87089, JP-A-59-11286, JP-A-60-176795 and JP-A-61-95988.

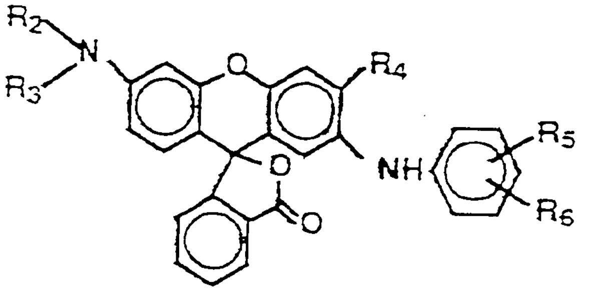
Specific examples of some of them include 4-tert-butylphenol, 4-phenylphenol, 2,2'-dihydroxybiphenyl, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 4,4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxyphenyl-3',4'-dimethylphenylsulfone, 4-(4-isopropoxyphenylsulfonyl)phenol, 4,4'-dihydroxydiphenylsulfide, 1,4-bis(4'-hydroxycumyl)benzene, 1,3-bis(4'-hydroxycumyl)benzene, 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-dihydroxydiphenylsulfone, 4-hydroxybenzoic acid benzyl ester, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-(α,α-dimethylbenzyl)salicylic acid, 3-cumyl-5-t-octylsalicylic acid, 3,5-di-t-butylsalicylic acid, 3-phenyl-5-t-octylsalicylic acid, 3-methyl-5-α-methylbenzylsalicylic acid, 3-methyl-5-cumylsalicylic acid, 3,5-di-t-octylsalicylic acid, 3,5-bis(α-methylbenzyl)salicylic acid, 3-cumyl-5-phenylsalicylic acid, 5-n-octadecylsalicylic acid, 4-pentadecylsalicylic acid, 3,5-bis(α,α-dimethylbenzyl)salicylic acid, 3,5-bis-t-octylsalicylic acid, 4-β-dodecyloxyethoxysalicylic acid, 4-methoxy-6-dodecyloxysalicylic acid, 4-β-phenoxyethoxysalicylic acid, 4-β-p-ethylphenoxyethoxysalicylic acid, 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid, N-(phenoxyacetyl)anthranyl acid, etc., and metal salts of them, etc. Above all, it is particularly preferred to use in combination with 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid and metal salt thereof.

The above described electron accepting compounds are used in an amount of preferably from 10 to 200% by weight, more preferably from 10 to 100% by weight, based on the amount of the salicylic acid derivative of the present invention.

It is further preferred to use two or more of the above described electron accepting compounds in combination. In particular, the combined use of 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid (metal salt thereof) with at least one of 2,2-bis(4-hydroxyphenyl)propane, 4-(4-isopropoxyphenylsulfonyl)phenol and 1,4-bis(4'-hydroxycumyl)benzene is preferred. In the case of using two or more kinds of electron accepting compounds in combination in addition to the salicylic acid derivative represented by formula (1), it is preferred, from the viewpoint of high sensitization, to carry out dispersion processing after each electron accepting compound is mixed.

The electron accepting compound including the salicylic acid derivative represented by formula (1) is used in an amount of preferably from 50 to 800% by weight, and more preferably from 100 to 500% by weight, based on the amount of the electron donating colorless dye.

Various compounds are available as electron donating colorless dyes, such as triphenylmethanephthalide based compounds, fluoran based compounds, phenothiazine based compounds, indolylphthalide based compounds, leucoauramine based compounds, rhodaminelactam based compounds, triphenylmethane based compounds, triazene based compounds, spiropyran based compounds and fluorene based compounds. Specific examples of phthalides are disclosed in U.S. Reissued Patent 23,024, U.S. Patents 3,491,111, 3,491,112, 3,491,116 and 3,509,174, those of fluorans are disclosed in U.S. Patents 3,624,107, 3,627,787, 3,641,011, 3,462,828, 3,681,390, 3,920,510 and 3,959,571, those of spirodipyrans are disclosed in U.S. Patent 3,971,808, those of pyridine based and pyrazine based compounds are disclosed in U.S. Patents 3,775,424, 3,853,869 and 4,246,318, and those of fluorene based compounds and disclosed in JP-A-63-94878. Preferred electron donating colorless dyes which are preferably used in the present invention are fluoran compounds represented by formula (2):



(2)

wherein $R_2$ and $R_3$ represent an alkyl group or an aryl group; and $R_4$, $R_5$ and $R_6$ represent a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group.

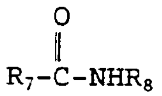
Black coloring 2-arylamino-3-H, halogen- or alkyl-6-substituted aminofluoran are particularly useful among those represented by formula (2). Specific examples include 2-anilino-3-methyl-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-cyclohexyl-N-methylaminofluoran, 2-p-chloroanilino-3-methyl-6-dibutylaminofluoran, 2-anilino-3-chloro-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-isoamylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-dodecylaminofluoran, 2-o-chloroanilino-6-dibutylaminofluoran, 2-anilino-3-pentadecyl-6-diethylaminofluoran, 2-anilino-3-methyl-6-dibutylaminofluoran, 2-o-toluidino-3-methyl-6-diisopropylaminofluoran, 2-anilino-3-methyl-6-N-isobutyl-N-ethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-tetrahydrofurfurylaminofluoran, 2-anilino-3-chloro-6-N-ethyl-N-isoamylaminofluoran, 2-anilino-3-methyl-6-N-methyl-N-y-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-y-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-y-propoxypropylaminofluoran, and 2-anilino-3-methyl-6-N-methyl-N-propylaminofluoran. 2-Anilino-3-methyl-6-dibutylaminofluoran is preferred and 2-anilino-3-methyl-6-N-methyl-N-n-propylaminofluoran is particularly preferred.

The coated amount of the electron donating colorless dye is generally from 0.1 to 2.0 g/m$^2$, and preferably from 0.2 to 1.0 g/m$^2$.

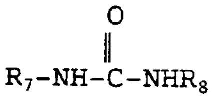
Sensitizers may be used in addition to electron donating colorless dyes and electron accepting compounds in the present invention. Compounds which are described in JP-A-58-57989, JP-A-58-87094 and JP-A-63-39375 are examples of such sensitizers. Representative examples include aromatic ethers (particularly, benzyl ethers, di(substituted-phenoxy)alkanes, diphenyl ethers, particularly preferably 2-benzyloxynaphthalene, 1,2-di(3-methylphenoxy)ethane, and 4-biphenyl-p-tolyl ethers), aromatic esters (particularly, oxalic acid dibenzyl ester derivatives, particularly preferably di(p-methylbenzyl)oxalate, and biphenyl derivatives (particularly, p-benzylbiphenyl, m-terphenyl), or aliphatic amide and aliphatic urea, or aromatic amide and aromatic urea.

A sensitizer is used in an amount of preferably from 50 to 800% by weight, and more preferably from 100 to 500% by weight, based on the amount of the electron donating colorless dye.

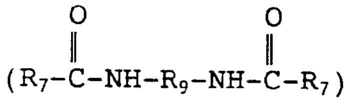
The use of sensitizers such as aromatic ether, aromatic ester and biphenyl derivative in combination with aliphatic amide and aliphatic urea is particularly preferred. Aliphatic amide and aliphatic urea which are preferably used are represented by formulae (3) to (5):



$$R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8 \qquad (3)$$



$$R_7-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8 \qquad (4)$$



$$(R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R_9-NH-\overset{\overset{\displaystyle O}{\|}}{C}-R_7) \qquad (5)$$

wherein $R_7$ represents an alkyl group having from 12 to 24 carbon atoms or an alkenyl group; $R_8$ represents a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms or a methylol group; and $R_9$ represents an alkylene group having from 1 to 8 carbon atoms.

Specific examples thereof include stearic acid amide, palmitic acid amide, oleic acid amide, stearylurea, and palmitylurea. In addition, N-substituted amide compounds of methylolstearic acid amide and ethylenebis-stearic acid amide are also included. These amide compounds or urea compounds are used in an amount of preferably from 1 to 100% by weight, and more preferably from 2 to 50% by weight, based on the amount of the sensitizers such as aromatic ethers, aromatic esters and bisphenyl derivatives.

The typical process of producing the heat-sensitive color forming layer of the present invention is described below. An electron donating colorless dye, an electron accepting compound and a sensitizer are dispersed in an aqueous solution of a water-soluble high molecular weight compound, such as polyvinyl alcohol, by means of a ball mill, a sand mill, etc., to a particle size of several microns or less. A sensitizer may be added to either or both of an electron donating colorless dye or/and an electron accepting compound and dispersed simultaneously, or a solution soluble with an electron donating colorless dye or an electron accepting compound is previously prepared and may be dispersed in the solution. These dispersions are mixed after dispersing and, if necessary, a surfactant, a binder, a metal soap, a wax, an antioxidant, an ultraviolet absorber, etc., are added to produce a heat-sensitive coating solution. The thus-obtained heat-sensitive coating solution is coated on a high quality paper, a high quality paper having a subbing layer, a synthetic paper, a plastic film, etc., dried and imparted with smoothness by subjecting to calendering to produce an objective heat-sensitive recording material.

A support for use in the present invention is preferably a support having smoothness regulated by JIS-8119 of 500 sec or more, preferably 800 sec or more, from the viewpoint of dot reproduction. There are various means to obtain a support having smoothness of 500 sec or more, for example,

(1) using a high smoothness paper such as a synthetic paper or a plastic film,
(2) providing a subbing layer comprising a pigment as a major component on a support,
(3) raising the smoothness of a support by subjecting to supercalendering, etc.

The present inventors have found that, by providing a subbing layer comprising a pigment as a major component, not only good dot reproduction can be achieved, but it also becomes difficult to generate fog at the white portions when the material is stored under high temperature conditions. Examples of pigments for use in the present invention for the subbing layer include calcined kaolin, aluminum hydroxide, calcium carbonate, barium sulfate, zinc oxide, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Two or more of these pigments may be used in combination. Calcined kaolin is particularly preferred. The coated amount of the pigment in the subbing layer is generally from 1 to 20 g/m$^2$, and preferably from 3.0 to 15.0 g/m$^2$.

A coating solution for a subbing layer can be prepared by mixing a binder with a solution of pigment dispersion. Further, a mold releasing agent, a waterproofing agent, a surfactant, a sizing agent, a wax, etc., may be added, if necessary. The preservability of the white portions can be further improved by the addition of, in particular, a sizing agent such as alkenyl succinate, an alkyl ketene dimer, a rosin compound, etc., and a water repellant such as a wax, e.g., paraffin wax, microcrystalline wax, carnauba wax, montan wax, polyethylene wax, etc. A sizing agent and a water repellant are used in amounts of generally from 0.2 to 20% by weight, preferably from 0.5 to 5% by weight, based on the amount of the pigment contained in the subbing layer.

The obtained coating solution for a subbing layer is coated on a support using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a subbing layer of the present invention. A heat-sensitive recording material can be obtained by coating a heat-sensitive color forming layer on the thus obtained subbing layer. A subbing layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a subbing layer is coated, dried, and then a heat-sensitive color forming layer may be coated. The dry coating weight of the subbing layer is preferably from 3.0 to 20.0 g/m$^2$, more preferably from 5.0 to 12.0 g/m$^2$. When the coating amount is too small, heat sensitivity is extremely reduced: on the contrary, when it is too great, sufficient coated film strength and paper strength cannot be obtained. A calendering treatment may be carried out after coating of the subbing layer and after coating of the heat-sensitive color forming layer, as required.

A protective layer may be provided in the present invention, if necessary. Examples of pigments for a protective layer include aluminum hydroxide, calcium carbonate, barium sulfate, zinc oxide, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Two or more of these pigments may be used in combination. Particularly, when aluminum hydroxide is used, surface slipperiness is good when the surface of the heat-sensitive paper is written with a pencil and also sensitivity is difficult to reduce. The coated amount of the pigment in the protective layer is generally from 0 to 5 g/m$^2$, and preferably from 0.1 to 2.0 g/m$^2$.

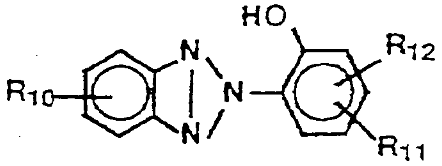
A coating solution for a protective layer of the present invention can be prepared by mixing a binder with a solution of pigment dispersion. Further, a mold releasing agent, a waterproofing agent, a surfactant, a wax, etc., may be added, if necessary. The obtained coating solution for a protective layer is coated on a heat-sensitive color forming layer using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a protective layer of the present invention. A protective layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a heat-sensitive color forming layer is coated, dried, and then a protective layer may be coated. The dry coating weight of the protective layer is preferably from 0.5 to 5.0 g/m$^2$, more preferably from 0.8 to 3.0 g/m$^2$. When the coating amount is too great, heat sensitivity is extremely reduced: on the contrary, when it is too small, a sufficiently protective effect cannot be obtained. A calendering treatment may be carried out after coating of the protective layer, as required.

A binder which can be used in the present invention is preferably a compound having a water solubility of 5% by weight or more in water at 25°C, and specific examples thereof include polyvinyl alcohols (including modified polyvinyl alcohols such as carboxy-modified, acetoacetyl-modified, itaconic acid-modified, maleic acid-modified and silica-modified), methyl cellulose, carboxymethyl cellulose, starches (including modified starch), gelatin, gum arabic, casein, a hydrolyzed product of a styrene-maleic anhydride copolymer, polyacrylamide, and a saponification product of a vinyl acetate-polyacrylic acid copolymer. These binders are used not only for the dispersing process, but also for the purpose of improving the coated film strength; and for this purpose a synthetic high molecular weight latex series binder can be used in combination, such as a styrene-butadiene copolymer, a vinyl acetate copolymer, an acrylonitrile-butadiene copolymer, a methyl acrylate-butadiene copolymer, and a polyvinylidene chloride. Further, an appropriate crosslinking agent for a binder may be added according to the kind of a binder, if necessary.

Examples of pigments for use in the present invention include calcium carbonate, barium sulfate, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Metal salts of higher fatty acids are used as a metal soap, such as zinc stearate, calcium stearate, and aluminum stearate. Further, a surfactant, an antistatic agent, an ultraviolet absorber, a defoaming agent, an electroconductive agent, a fluorescent dye, a coloring dye, etc., may be added, if necessary.

When the salicylic acid derivatives and metal salts thereof of the present invention are used, white portions and images portions show excellent resistance to chemicals, and by the addition of an ultraviolet absorber for the purpose of improving discoloration of white portions due to light, light fastness of white portions can be improved. An ultraviolet absorber may be added to any of a heat-sensitive color forming layer, a subbing layer, a backing layer, or a protective layer, but the addition to a color forming layer or a protective layer is preferred. When an ultraviolet absorber is included in a protective layer, a protective layer not containing an ultraviolet absorber may further be provided on the first protective layer.

Examples of the ultraviolet absorber include benzophenone based ultraviolet absorbers, benzotriazole based ultraviolet absorbers, cyanoacrylate based ultraviolet absorbers, and hindered amine based ultraviolet absorbers, and benzotriazole based ultraviolet absorbers are preferred of these. Particularly, benzotriazole based ultraviolet absorbers represented by formula (6) are preferred:



(6)

wherein $R_{10}$, $R_{11}$ and $R_{12}$ represent a hydrogen atom, an alkyl group having from 1 to 15 carbon atoms, an alkoxy group, an aralkyl group, an aryl group or a halogen atom, which group may be further substituted.

Specific examples include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-sec-butyl-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-(α,α-dimethylbenzyl)phenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, 2-(2'-hydroxy-3'-dodecyl-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-4'-(2"-ethylhexyl)oxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-octylphenyl)benzotriazole, and a polyethylene glycol (molecular weight: 300) solution of methyl-3-(3-tert-butyl-5-(2H-benzotriazol-2-yl)-4-hydroxyphenyl)propionate

The amount used of an ultraviolet absorber is preferably from 10 to 500% by weight, more preferably from 50 to 400% by weight, based on the amount of the electron donating colorless dye in the heat-sensitive color forming layer.

Ultraviolet absorbers may be used in the form of a solid dispersion, or those having low melting points or those which are liquid at normal temperature may be used by being microencapsulated. Microcapsules for use in the present invention can be prepared according to various conventionally known methods. In general, microcapsules are prepared by a method in which a core material (oily liquid) obtained by dissolving an ultraviolet absorber in an organic solvent as appropriate is emulsified and dispersed in an aqueous medium, and a thin shell comprising a high molecular weight material is formed around each oily droplet. Specific examples of high molecular weight materials useful for forming microcapsule shells include a polyurethane resin, a polyurea resin, a polyester resin, a polycarbonate resin, an aminoaldehyde resin, a melamine resin, a polystyrene resin, a styrene-acrylate copolymer resin, a styrene-methacrylate copolymer resin, gelatin and polyvinyl alcohol. Organic solvents which are used for core materials include low boiling point solvents such as ethyl acetate, butyl acetate, and oils used for pressure-sensitive recording materials.

When an ultraviolet absorber is added to a protective layer in the present invention, a pigment dispersion solution and a binder are mixed with an ultraviolet absorber dispersion solution or ultraviolet absorber-containing microcapsules to obtain a coating solution for a protective layer. Further, a mold releasing agent, a waterproofing agent, a surfactant, a wax, etc., may be added, if necessary. The obtained coating solution for a protectuve layer is coated on a heat-sensitive color forming layer using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a protective layer of the present invention. A protective layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a heat-sensitive color forming layer is coated, dried, and then a protective layer may be coated. Moreover, a protective layer not containing an ultraviolet absorber may further be provided on the protective layer containing an ultraviolet absorber, if necessary. The dry coating weight of the protective layer is preferably from 0.5 to 5.0 g/m$^2$, more preferably from 0.8 to 3.0 g/m$^2$. When the coating amount is too great, heat sensitivity is extremely reduced: on the contrary, when it is too small, a sufficiently protective effect cannot be obtained. A calendering treatment may be carried out after coating of the protective layer, if required.

A back coating layer may be provided on the opposite side of the heat-sensitive color forming layer of the support, if necessary. Any back coating layers conventionally known as back coating layers for heat-sensitive recording materials can be used.

The present invention is described in detail with reference to the Examples; however, it should not be construed as being limited thereto.

## EXAMPLE 1

20 g of 2-anilino-3-methyl-6-dibutylaminofluoran as an electron donating colorless dye and 20 g of di(p-methylbenzyl)oxalate as a sensitizer were respectively dispersed with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night so that the average particle size became 1.5 μm or less to thereby obtain each dispersion solution. Further, 20 g of 4-benzyloxycarbonylaminosalicylic acid as an electron accepting compound were mixed with 5 g of zinc oxide and the mixture

was then dispersed with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night so that the average particle size became 1.5 μm or less to thereby obtain a dispersion solution of electron accepting compound. Still further, 80 g of calcium carbonate was dispersed with 160 g of a 0.5% solution of sodium hexametaphosphate in a homogenizer to thereby obtain a pigment dispersion solution. Each of the thus-obtained dispersion solutions were mixed with the ratio of the dispersion solution of the electron donating colorless dye being 5 g, the dispersion solution of the electron accepting compound being 10 g, the dispersion solution of di(p-methylbenzyl)oxalate being 10 g, and the dispersion solution of calcium carbonate being 5 g, and further 3 g of a 21% emulsion of zinc stearate was added thereto to thereby obtain a coating solution for a heat-sensitive layer. This coating solution for a heat-sensitive layer was coated on a high quality paper of weighing 50 g/m$^2$ using a wire bar coater so as to the dry weight of the coated layer became 5 g/m$^2$, and dried at 50°C for 1 min to obtain a heat-sensitive recording paper.

## EXAMPLE 2

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 4-n-octyloxycarbonylaminosalicylic acid.

## EXAMPLE 3

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 4-n-hexyloxycarbonylaminosalicylic acid.

## EXAMPLE 4

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 4-n-decyloxycarbonylaminosalicylic acid.

## EXAMPLE 5

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 4-p-tolyloxycarbonylaminosalicylic acid.

## EXAMPLE 6

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 5-benzyloxycarbonylaminosalicylic acid.

## EXAMPLE 7

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 5-n-octyloxycarbonylaminosalicylic acid.

## EXAMPLE 8

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by changing the amount of zinc oxide used to 2 g in the preparation of the dispersion solution of an electron accepting compound.

## EXAMPLE 9

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by changing the amount of zinc oxide used to 10 g in the preparation of the dispersion solution of an electron accepting compound.

EXAMPLE 10

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with 2-benzyloxynaphthalene.

EXAMPLE 11

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with p-benzylbiphenyl.

EXAMPLE 12

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with m-terphenyl.

EXAMPLE 13

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with 4-biphenyl-p-tolyl ether.

EXAMPLE 14

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with 1,2-di(3-methylphenoxy)ethane.

EXAMPLE 15

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by further adding 2 g of a 21% dispersion of stearic acid amide (Hymicron G270, a product of Chukyo Yushi K.K.).

EXAMPLE 16

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing di(p-methylbenzyl)oxalate with 2-benzyloxynaphthalene, and further adding 2 g of a 22% dispersion of methylolstearoamide (Hidrin D-130, a product of Chukyo Yushi K.K.).

EXAMPLE 17

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 2-anilino-3-methyl-6-dibutylaminofluoran with 2-anilino-3-methyl-6-N-ethyl-N-isoamylaminofluoran.

EXAMPLE 18

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 2-anilino-3-methyl-6-dibutylaminofluoran with 2-anilino-3-methyl-6-N-methyl-N-n-propylaminofluoran.

EXAMPLE 19

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a coating solution for a heat-sensitive layer was prepared by replacing 2-anilino-3-methyl-6-dibutylaminofluoran with 2-o-chloroanilino-6-dibutylaminofluoran.

## EXAMPLE 20

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except for using the undercoat paper prepared as described below instead of using a high quality paper of weighing 50 g/m$^2$.

### Preparation of Undercoat Paper 1

80 g of calcined kaolin (Ansilex 90, Engelhardt) was dispersed in a homogenizer with 160 g of a 0.5% solution of sodium hexametaphosphate, and 100 g of a 10% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) was added to the above dispersion solution to thereby obtain a coating solution for a subbing layer. This coating solution for a subbing layer was coated on a high quality paper of weighing 50 g/m$^2$ using a wire bar coater so that the dry weight of the subbing layer became 7.0 g/m$^2$, and dried at 50°C for 1 min to obtain an undercoat paper. The thus-obtained undercoat paper was subjected to a surface treatment by calendering so as to adjust the smoothness to be 300 ± 100 sec as Bekk smoothness.

## EXAMPLE 21

A heat-sensitive recording material was prepared in the same manner as in Example 20 except that a subbing layer coating solution was prepared by the addition of 15 g of a 15.5% alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.).

## EXAMPLE 22

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 12 g of an alkyl ketene dimer compound (Sizepine K287, a product of Arakawa Chemical Co., Ltd.).

## EXAMPLE 23

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Sizepine W116H, a product of Arakawa Chemical Co., Ltd.).

## EXAMPLE 24

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Hidrin D-337, a product of Chukyo Yushi K.K.).

## EXAMPLE 25

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Hidrin P-7, a product of Chukyo Yushi K.K.).

## EXAMPLE 26

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% reinforced rosin sizing agent (Sizepine E, a product of Arakawa Chemical Co., Ltd.).

## EXAMPLE 27

A heat-sensitive recording material was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 6 g of a potassium salt (40%) of a compound which is an alkenyl group having 12 carbon atoms.

## EXAMPLE 28

A heat-sensitive recording paper was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing calcined kaolin with calcium carbonate (Cal-light KT, manufactured by Shiraishi Chuo Kenkyusho).

## EXAMPLE 29

A heat-sensitive recording paper was prepared in the same manner as in Example 21 except that a subbing layer coating solution was prepared by replacing calcined kaolin with noncrystal silica (Mizukasil P-832, a product of Mizusawa Chemical Co.,Ltd.).

## EXAMPLE 30

A heat-sensitive recording paper was prepared in the same manner as in Example 21 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of the calcined kaolin with 70 g of calcined kaolin and 10 g of calcium carbonate.

## EXAMPLE 31

A heat-sensitive recording paper was prepared in the same manner as in Example 21 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of the calcined kaolin with 60 g of calcined kaolin and 20 g of calcium carbonate.

## EXAMPLE 32

A protective layer coating solution 1 obtained as described below was coated on the heat-sensitive recording paper obtained in Example 1 using a wire bar coater so that the dry weight of the protective layer became 2.0 g/m$^2$, and dried at 50°C for 1 min to thereby obtain a heat-sensitive recording paper.

### Preparation of Protective Layer Coating Solution 1

80 g of aluminum hydroxide (Higilite H42, a product of Showa Denko Co., Ltd.) was dispersed in a homogenizer with 160 g of a 0.5% solution of sodium hexametaphosphate, and 800 g of a 10% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) and 100 g of a 21% emulsion of zinc stearate were added to this dispersion solution to thereby obtain a protective layer coating solution.

## EXAMPLE 33

A heat-sensitive recording paper was prepared in the same manner as in Example 32 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of aluminum hydroxide with 60 g of aluminum hydroxide and 20 g of kaolin (Kaobright, a product of Shiraishi Kogyo Co., Ltd.).

## EXAMPLE 34

A heat-sensitive recording paper was prepared in the same manner as in Example 32 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of aluminum hydroxide with 40 g of aluminum hydroxide and 40 g of kaolin.

EXAMPLE 35

A heat-sensitive recording paper was prepared in the same manner as in Example 32 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of aluminum hydroxide with 60 g of aluminum hydroxide and 20 g of calcium carbonate (Unibur 70, a product of Shiraishi Kogyo Co., Ltd.).

EXAMPLE 36

A heat-sensitive recording paper was prepared in the same manner as in Example 32 except that a heat-sensitive layer coating solution was prepared by adding 10 g of a dispersion solution obtained by dispersing 20 g of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole as an ultraviolet absorber in a ball mill with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) over a whole day and night so that an average particle size became 1.5 μm or less.

EXAMPLE 37

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 5 g.

EXAMPLE 38

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 15 g.

EXAMPLE 39

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 50 g.

EXAMPLE 40

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole.

EXAMPLE 41

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole.

EXAMPLE 42

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except that a heat-sensitive layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole.

EXAMPLE 43

A heat-sensitive recording paper was prepared in the same manner as in Example 36 except for not providing a protective layer.

EXAMPLE 44

A heat-sensitive recording paper was prepared in the same manner as in Example 42 except for not providing a protective layer.

## EXAMPLE 45

A protective layer coating solution 2 obtained as described below was coated on the heat-sensitive recording paper obtained in Example 1 using a wire bar coater so that the dry weight of the protective layer became 3.0 g/m$^2$, and dried at 50°C for 1 min to thereby obtain a heat-sensitive recording paper.

### Preparation of Protective Layer Coating Solution 2

20 g of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole as an ultraviolet absorber was dispersed in a ball mill with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) over a whole day and night so that the average particle size became 1.5 μm or less to thereby obtain a dispersion solution of an ultraviolet absorber. To 100 g of this dispersion solution were added 50 g of the dispersion solution obtained by dispersing 80 g of aluminum hydroxide (Higilite H42, a product of Showa Denko Co., Ltd.) with 160 g of a 0.5% solution of sodium hexametaphosphate in a homogenizer, 200 g of a 10% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) and 20 g of a 21% emulsion of zinc stearate to thereby obtain a protective layer coating solution 2.

## EXAMPLE 46

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 30 g.

## EXAMPLE 47

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 50 g.

## EXAMPLE 48

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by changing the amount added of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole to 150 g.

## EXAMPLE 49

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole.

## EXAMPLE 50

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole.

## EXAMPLE 51

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by replacing 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole.

## EXAMPLE 52

A heat-sensitive recording paper was prepared in the same manner as in Example 45 except that a protective layer coating solution was prepared by replacing 100 g of a dispersion solution of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole with 200 g of a capsule solution of 2-(2'-hydroxy-3'-dodecyl-5'-methylphenyl)benzotriazole (a dispersion solution of microcapsules of a particle size of 3 μm having a shell of a film comprising a polyurethane-polyurea resin which was obtained by emulsifying the mixed solution of 100 g of 10% polyvinyl alcohol (PVA-217E), 8 g of ethyl acetate, 30 g of 2-(2'-hydroxy-3'-dodecyl-5'-methylphenyl)benzotriazole, and 40 g of a solution of xylidenediisocyanate-trimethylolpropane addition product (Takenate D-110N) using a homogenizer, then the resulting emulsion was reacted at 60°C for 2 hours).

## EXAMPLE 53

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a heat-sensitive layer coating solution was prepared by replacing 20 g of 4-benzyloxycarbonylaminosalicylic acid as an electron accepting compound with 10 g of 4-octylcarbonylaminosalicylic acid, and using 10 g of 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid and further adding 2 g of a 21% dispersion of stearic acid amide (Hymicron G270, a product of Chukyo Yushi K.K.).

## EXAMPLE 54

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a heat-sensitive layer coating solution was prepared by replacing 2-anilino-3-methyl-6-dibutylaminofluoran as an electron donating colorless dye with 2-anilino-3-methyl-6-N-methyl-N-propylaminofluoran, replacing di(p-methylbenzyl)oxalate as a sensitizer with 2-benzyloxynaphthalene, further replacing a dispersion solution of electron accepting compound, which was obtained by mixing 20 g of 4-benzyloxycarbonylaminosalicylic acid as an electron accepting compound with 5 g of zinc oxide and then dispersing with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night, with a dispersion solution of electron accepting compound, which was obtained by mixing 8 g of zinc 4-octylcarbonylaminosalicylate, 8 g of 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid, 2 g of zinc oxide, and 4 g of 2,2-bis-(4-hydroxyphenyl)propane and then dispersing with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night, and by further adding 2 g of a 21% dispersion of stearic acid amide (Hymicron G270, a product of Chukyo Yushi K.K.).

## EXAMPLE 55

A heat-sensitive recording paper was prepared in the same manner as in Example 54 except that a heat-sensitive layer coating solution was prepared by replacing 2,2-bis(4-hydroxyphenyl)propane as a dispersion solution of electron accepting compound with 1,4-bis(4'-hydroxycumyl)benzene.

## EXAMPLR 56

A heat-sensitive recording paper was prepared in the same manner as in Example 54 except that a heat-sensitive layer coating solution was prepared by replacing 2,2-bis(4-hydroxyphenyl)propane as a dispersion solution of electron accepting compound with 4-(4-isopropoxyphenylsulfonyl)phenol.

## COMPARATIVE EXAMPLE 1

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a heat-sensitive layer coating solution was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with bisphenol A.

## COMPARATIVE EXAMPLE 2

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a heat-sensitive layer coating solution was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with benzyl 4-hydroxybenzoate.

## COMPARATIVE EXAMPLE 3

A heat-sensitive recording paper was prepared in the same manner as in Example 1 except that a heat-sensitive layer coating solution was prepared by replacing 4-benzyloxycarbonylaminosalicylic acid with 4-(4-isopropoxyphenylsulfonyl)phenol.

The thus-obtained heat-sensitive recording papers were subjected to a surface treatment by calendering so as to adjust the smoothness to be 300 ± 50 sec as Bekk smoothness. The evaluation of heat-sensitive recording papers was conducted as follows. (1) Printing was conducted using Kyocera printing tester at a printing energy of 30 mJ/mm$^2$ and color density was measured using a Macbeth densitometer. The higher value means the higher sensiitivity of the heat-sensitive recording paper. (2) Chemical resistance was evaluated by the degree of fog at white portions and discoloration (fading) of colored portions by writing down on the coloring face of the above obtained recording paper with a fluorescent pen (Spotliter, pink, a product of PILOT Co., Ltd.). (3) Light fastness was evaluated by the density of white portions (yellow density) and image density after the above-obtained recording paper was directly exposed to the sun for 1 week (Fujinomiya, Japan on January). (4) Heat fastness was evaluated by measuring the white portion density after a recording paper was stored in a constant temperature constant humidity bath of 60°C 30% RH for 24 hours. (5) Plasticizer resistance test was evaluated by the degree of discoloration of colored portions after a recording paper was contacted with a polyvinyl chloride film (a product of Sinetsu Seien) for 120 hours. The results obtained are shown in Tables 1 and 2 below.

TABLE 1

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 1 | 1.32 | 1.19 | o | o | 0.07 | 0.11 | 0.05 | 0.11 |
| Example 2 | 1.34 | 1.20 | o | o | 0.06 | 0.11 | 0.05 | 0.12 |
| Example 3 | 1.29 | 1.18 | o | o | 0.08 | 0.13 | 0.06 | 0.11 |
| Example 4 | 1.28 | 1.15 | o | o | 0.07 | 0.11 | 0.05 | 0.09 |
| Example 5 | 1.31 | 1.18 | o | o | 0.08 | 0.12 | 0.06 | 0.13 |
| Example 6 | 1.30 | 1.18 | o | o | 0.07 | 0.12 | 0.05 | 0.10 |
| Example 7 | 1.33 | 1.19 | o | o | 0.07 | 0.11 | 0.05 | 0.07 |
| Example 8 | 1.26 | 1.14 | o | o | 0.06 | 0.10 | 0.05 | 0.07 |
| Example 9 | 1.35 | 1.21 | o | ◎ | 0.07 | 0.11 | 0.05 | 0.10 |
| Example 10 | 1.34 | 1.21 | o | ◎ | 0.06 | 0.12 | 0.05 | 0.12 |
| Example 11 | 1.29 | 1.18 | o | o | 0.08 | 0.14 | 0.07 | 0.14 |

◎: Very excellent (no change)

o: Excellent (little change)

x: Impracticable (images were very difficult to read)

TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 12 | 1.29 | 1.17 | o | o | 0.07 | 0.12 | 0.05 | 0.15 |
| Example 13 | 1.30 | 1.18 | o | o | 0.08 | 0.11 | 0.06 | 0.14 |
| Example 14 | 1.35 | 1.18 | o | o | 0.07 | 0.11 | 0.06 | 0.10 |
| Example 15 | 1.36 | 1.22 | o | o | 0.08 | 0.12 | 0.06 | 0.14 |
| Example 16 | 1.37 | 1.22 | o | o | 0.07 | 0.11 | 0.05 | 0.13 |
| Example 17 | 1.35 | 1.24 | o | ◎ | 0.08 | 0.13 | 0.06 | 0.14 |
| Example 18 | 1.30 | 1.20 | ◎ | o | 0.08 | 0.10 | 0.06 | 0.12 |
| Example 19 | 1.28 | 1.15 | ◎ | o | 0.07 | 0.09 | 0.05 | 0.10 |
| Example 20 | 1.36 | 1.24 | o | o | 0.07 | 0.11 | 0.05 | 0.09 |

◎: Very excellent (no change)

o: Excellent (little change)

x: Impracticable (images were very difficult to read)

TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 21 | 1.37 | 1.25 | o | o | 0.06 | 0.10 | 0.05 | 0.08 |
| Example 22 | 1.36 | 1.23 | o | o | 0.05 | 0.09 | 0.05 | 0.08 |
| Example 23 | 1.38 | 1.25 | o | o | 0.06 | 0.10 | 0.05 | 0.08 |
| Example 24 | 1.37 | 1.24 | o | o | 0.07 | 0.11 | 0.06 | 0.08 |
| Example 25 | 1.39 | 1.24 | o | o | 0.06 | 0.10 | 0.05 | 0.08 |
| Example 26 | 1.35 | 1.21 | o | o | 0.07 | 0.11 | 0.05 | 0.08 |
| Example 27 | 1.34 | 1.17 | o | o | 0.06 | 0.09 | 0.05 | 0.07 |
| Example 28 | 1.34 | 1.22 | o | o | 0.07 | 0.11 | 0.05 | 0.09 |
| Example 29 | 1.33 | 1.21 | o | o | 0.08 | 0.11 | 0.06 | 0.10 |

◎: Very excellent (no change)

o: Excellent (little change)

x: Impracticable (images were very difficult to read)

TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 30 | 1.38 | 1.26 | o | o | 0.07 | 0.11 | 0.05 | 0.08 |
| Example 31 | 1.38 | 1.25 | o | o | 0.06 | 0.10 | 0.05 | 0.08 |
| Example 32 | 1.23 | 1.15 | ◎ | o | 0.06 | 0.10 | 0.06 | 0.11 |
| Example 33 | 1.22 | 1.14 | ◎ | o | 0.07 | 0.10 | 0.06 | 0.11 |
| Example 34 | 1.24 | 1.15 | ◎ | o | 0.06 | 0.09 | 0.05 | 0.10 |
| Example 35 | 1.22 | 1.13 | o | o | 0.07 | 0.11 | 0.05 | 0.12 |
| Example 36 | 1.24 | 1.17 | ◎ | o | 0.07 | 0.10 | 0.06 | 0.13 |
| Example 37 | 1.23 | 1.17 | ◎ | o | 0.08 | 0.11 | 0.07 | 0.13 |
| Example 38 | 1.22 | 1.18 | ◎ | o | 0.08 | 0.10 | 0.07 | 0.15 |

◎: Very excellent (no change)

o: Excellent (little change)

×: Impracticable (images were very difficult to read)

TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 39 | 1.23 | 1.19 | ◎ | o | 0.08 | 0.10 | 0.07 | 0.15 |
| Example 40 | 1.22 | 1.18 | o | o | 0.07 | 0.10 | 0.06 | 0.12 |
| Example 41 | 1.21 | 1.17 | o | o | 0.06 | 0.09 | 0.05 | 0.13 |
| Example 42 | 1.23 | 1.18 | o | o | 0.08 | 0.10 | 0.07 | 0.14 |
| Example 43 | 1.35 | 1.24 | o | o | 0.07 | 0.10 | 0.05 | 0.12 |
| Example 44 | 1.32 | 1.22 | o | o | 0.07 | 0.10 | 0.06 | 0.12 |
| Example 45 | 1.26 | 1.21 | o | o | 0.07 | 0.08 | 0.06 | 0.12 |
| Example 46 | 1.27 | 1.20 | o | o | 0.07 | 0.08 | 0.06 | 0.10 |
| Example 47 | 1.26 | 1.21 | o | o | 0.07 | 0.08 | 0.06 | 0.12 |

◎: Very excellent (no change)

o: Excellent (little change)

×: Impracticable (images were very difficult to read)

TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Example 48 | 1.25 | 1.22 | o | o | 0.08 | 0.09 | 0.07 | 0.13 |
| Example 49 | 1.24 | 1.20 | o | o | 0.08 | 0.09 | 0.07 | 0.11 |
| Example 50 | 1.22 | 1.19 | o | o | 0.07 | 0.08 | 0.06 | 0.10 |
| Example 51 | 1.24 | 1.19 | o | o | 0.07 | 0.08 | 0.06 | 0.11 |
| Example 52 | 1.21 | 1.18 | o | ◎ | 0.07 | 0.08 | 0.06 | 0.10 |
| Example 53 | 1.35 | 1.26 | o | o | 0.06 | 0.09 | 0.06 | 0.12 |
| Example 54 | 1.37 | 1.27 | o | ◎ | 0.07 | 0.11 | 0.06 | 0.13 |
| Example 55 | 1.36 | 1.30 | o | ◎ | 0.07 | 0.09 | 0.06 | 0.12 |
| Example 56 | 1.38 | 1.26 | o | ◎ | 0.07 | 0.13 | 0.06 | 0.14 |

◎: Very excellent (no change)

o: Excellent (little change)

x: Impracticable (images were very difficult to read)

### TABLE 1 (cont'd)

| | Light Fastness of Image Portion | | Fluorescent Pen | | Light Fastness of White Portion (Y) | | Heat Fastness of White Portion | |
|---|---|---|---|---|---|---|---|---|
| | Initial Density | After Processing | Fog | Discoloration | Initial Density | After Processing | Initial Density | After Processing |
| Comparative Example 1 | 1.42 | 1.14 | × | × | 0.08 | 0.15 | 0.06 | 0.08 |
| Comparative Example 2 | 1.40 | 1.12 | × | × | 0.09 | 0.16 | 0.07 | 0.18 |
| Comparative Example 3 | 1.38 | 1.04 | × | × | 0.09 | 0.18 | 0.06 | 0.10 |

◎: Very excellent (no change)

o: Excellent (little change)

×: Impracticable (images were very difficult to read)

TABLE 2

| | Plasticizer Resistance of Image Portion | | |
|---|---|---|---|
| | Initial Density | Density after Processing | Sharpness of Image Portion after Processing |
| Example 1 | 1.22 | 1.17 | △ |
| Example 53 | 1.35 | 1.34 | ○ |
| Example 54 | 1.37 | 1.29 | ○ |
| Example 55 | 1.36 | 1.32 | ○ |
| Example 56 | 1.38 | 1.30 | ○ |
| Comparative Example 1 | 1.42 | 0.07 | × |
| Comparative Example 2 | 1.40 | 0.08 | × |
| Comparative Example 3 | 1.38 | 0.09 | × |

◎: Very excellent (no change)

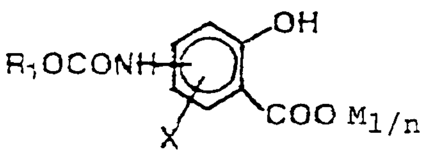
○: Excellent (little change)

×: Impracticable (images were very difficult to read)

As can be seen from Tables 1 and 2, the recording material of the present invention exhibits high sensitivity, fog coloration or discoloration of colored portions due to chemicals does not occur; discoloration of colored portions due to plasticizers does not occur; and, in particular, the sharpness of the colored portions can be maintained. Therefore, the recording material of the present invention possesses extremely excellent properties.

## Claims

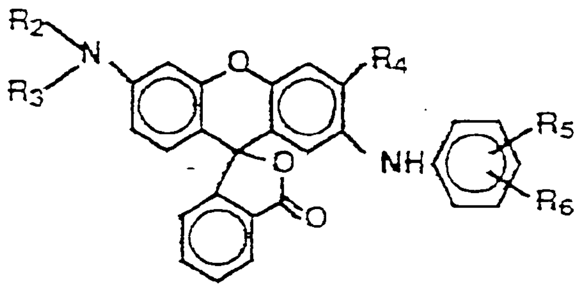
1. A heat-sensitive recording material comprising a support having provided thereon a heat-sensitive color forming layer containing an electron donating colorless dye and an electron accepting compound, wherein said heat-sensitive color forming layer contains a salicylic acid derivative represented by formula (1) or a metal salt thereof, and a metal compound:



(1)

wherein $R_1$ represents an alkyl group or an aryl group; X represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, or a halogen atom; M represents a hydrogen atom or an n-valent metal atom; and n represents an integer, provided that n is 1 when M represents a hydrogen atom.

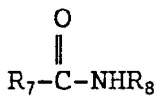
2. A recording material as claimed in claim 1, wherein said heat-sensitive color forming layer contains zinc oxide and a fluoran compound represented by formula (2):



(2)

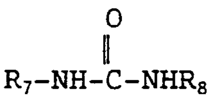
wherein $R_2$ and $R_3$ each independently represent an alkyl group or an aryl group; and $R_4$, $R_5$ and $R_6$ each independently represent a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group.

3. A recording material as claimed in claim 1 or 2, wherein said heat-sensitive color forming layer contains a sensitizer selected from di(p-methylbenzyl)oxalate, 2-benzyloxy-naphthalene, p-benzylbiphenyl, m-terphenyl, 4-biphenyl-p-tolyl ether, 1,2-di(3-methylphenoxy)ethane, aliphatic amide compounds, and aliphatic urea compounds represented by the following formulae (3) to (5):



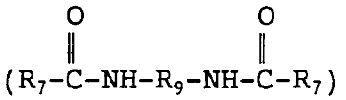
$$R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8$$

(3)



$$R_7-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8$$

(4)



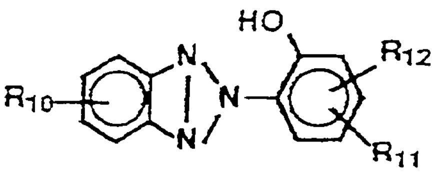
$$(R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R_9-NH-\overset{\overset{\displaystyle O}{\|}}{C}-R_7)$$

(5)

wherein $R_7$ represents an alkyl group having from 12 to 24 carbon atoms, or an alkenyl group; $R_8$ represents a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, or a methylol group; and $R_9$ represents an alkylene group having from 1 to 8 carbon atoms.

4. A recording material as claimed in any one of claims 1 to 3, wherein a protective layer is provided on said heat-sensitive color forming layer, said protective layer containing aluminum hydroxide.

5. A recording material as claimed in any one of claims 1 to 4, wherein said heat-sensitive recording material contains an ultraviolet absorber represented by formula (6):



(6)

wherein $R_{10}$, $R_{11}$ and $R_{12}$ represent a hydrogen atom, an alkyl group having from 1 to 15 carbon atoms, an alkoxy group, an aralkyl group, an aryl group, or a halogen atom.

6. A recording material as claimed in any one of claims 1 to 5, wherein a subbing layer is provided between

said support and said heat-sensitive color forming layer, said subbing layer containing at least one of calcined kaolin, a sizing agent and a wax.

**7.** A recording material as claimed in any one of claims 1 to 6, wherein said heat-sensitive recording material contains a salicylic acid derivative represented by formula (1) or a metal salt thereof and 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid or a metal salt thereof.

**8.** A recording material as claimed in claim 7, wherein said heat-sensitive recording material contains at least one of 2,2-bis(4-hydroxyphenyl)propane, 1,4-bis(4'-hydroxycumyl)benzene and 4-(4-isopropoxyphenylsulfonyl)phenol.

**9.** A recording material as claimed in claim 7 or 8, wherein said salicylic acid derivative represented by formula (1) is 4-n-octylcarbonyl-aminosalicylic acid or a metal salt thereof.

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 95 30 1790

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X | EP-A-0 534 257 (MITSUI TOATSU CHEMICALS, INC. AND MITSUBISHI PAPER MILLS, LIMITED)<br>* page 4, line 15 - page 5, line 14 *<br>* page 8, line 20 - page 19, line 20 *<br>* claims 1-5 *<br>--- | 1-9 | B41M5/30 |
| X | EP-A-0 253 666 (FUJI PHOTO FILM COMPANY LIMITED)<br>* page 2, line 34 - page 3, line 29 *<br>* page 4, line 34 - line 39 *<br>* page 6, line 8 - line 17 *<br>* page 15; claims 1,2; example 13; table 1 *<br>----- | 1-9 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | B41M |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 18 May 1995 | Bacon, A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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