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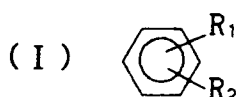
Applicant : **KANZAKI PAPER
MANUFACTURING CO., LTD
9-8 Yonchome Ginza Chuo-ku
Tokyo 104 (JP)**

Inventor : **Yoda, Syuji
4-9-18, Takamaru, Tarumi-ku
Kobe-shi, Hyogo (JP)**
 Inventor : **Shimizu, Yoshihiro
8-2-12, Minami Tsukaguchi-cho
Amagasaki-shi, Hyogo (JP)**
 Inventor : **Yoshizawa, Katsuaki
2-7-21, Kema
Amagasaki-shi, Hyogo (JP)**
 Inventor : **Mito, Hisayoshi
4-2-1, Jyokoji
Amagasaki-shi, Hyogo (JP)**

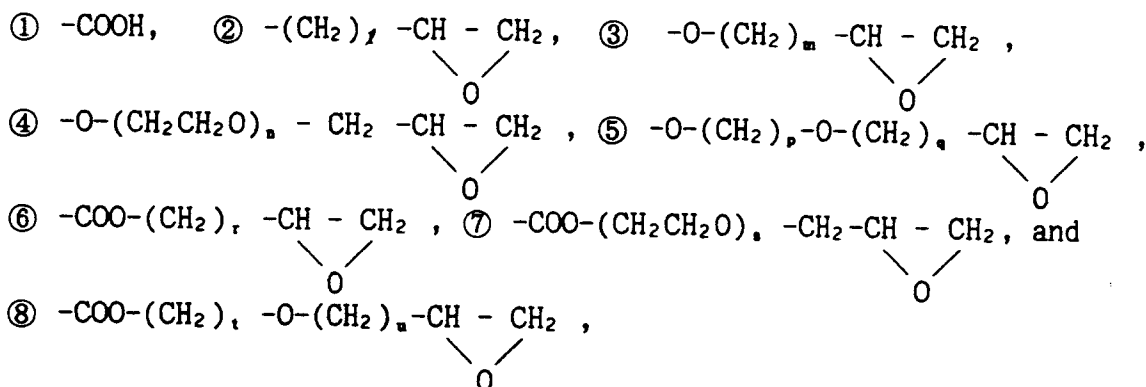
Representative : **Seaborn, George Stephen et
al
c/o Edward Evans & Co. Chancery House
53-64 Chancery Lane
London WC2A 1SD (GB)**

Heat-sensitive recording material.

A heat-sensitive recording material has on a base sheet a coating layer comprising a colorless or pale colored basic chromogenic material and a color developer which develops a color by contacting with the chromogenic material. The coating layer comprises 2,4'-dihydroxydiphenyl sulfone as the color developer, and further comprises at least one epoxy resin represented by the following formula (I) or (II) :



where each of R₁ and R₂ is one of the groups represented by the following formulae ① to ⑧ ,



l is 0 or an integer of 1 to 5 and m, n, p, q, r, s, t and u are respectively an integer of 1 to 5, but at least one of R₁ and R₂ is not -COOH, and R₃ is one of the groups represented by the above formulae ② to ⑧.

Background of the Invention

The present invention relates to a heat-sensitive, recording material and particularly to a heat-sensitive recording material superior in retainability of the recorded images.

There have been well-known heat-sensitive recording materials utilizing the colorforming reaction between a colorless or pale colored basic chromogenic material and an organic or inorganic color developer, in which the two colorforming materials are thermally contacted each other to produce recorded images. These heat-sensitive recording materials are relatively low in price and the recording equipments are compact and can be easily maintained. Therefore, they have been used not only as the recording medium of facsimiles, various computers and like, but also in the other various fields.

For example, as one of the fields of application, the application as a label has been increased with the enlargement of the POS (point of sales) systematization in retail stores and the like.

When the POS system is introduced in a super market and the like, however, the label contacts with water, lapping films and oils in many cases and as the result the recorded image (printed letters) on the heat-sensitive label is discolored disadvantageously. Hence, it is required for the heat-sensitive recording material to have good retainability of the recorded images, such as water-resistance, plasticizer-resistance and oil-resistance and the like.

Conventionally, to improve the retainability of the recorded images, various methods have been proposed including a method of applying an aqueous emulsion of a resin having film-forming ability and chemical resistance on a heat-sensitive recording layer (Japanese Laid-Open Patent Publication No.128,347 of 1979) and a method of applying a water-soluble polymer such as polyvinylalcohol and the like (Japanese Laid-Open Utility Model Publication No.125,354 of 1981). A method of adding various agents for improving the image retainability in the heat-sensitive recording layer has been also proposed. However, in all cases, other disadvantages such as lowering the color density of the recorded images, lowering the whiteness (brightness) of the heat-sensitive recording layer and the like are accompanied with the improvement. And also no satisfactory effect has been attained yet on the wet plasticizer-resistance in which water-resistance and plasticizer-resistance are required at the same time.

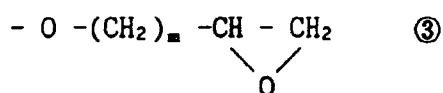
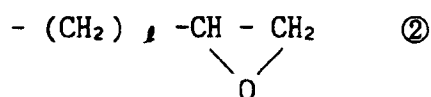
Therefore, it is an object of the present invention to provide a heat-sensitive recording material which is superior in the retainability of the recorded image, especially plasticizer-resistance, oil-resistance, water-resistance and wet plasticizer-resistance and shows no lowering of whiteness due to fogging in the white portion even when exposed to a high temperature environment.

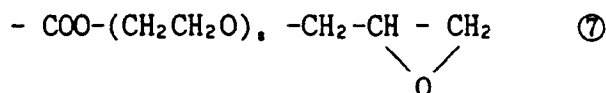
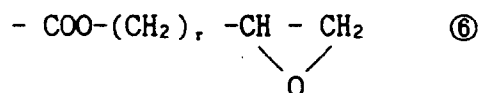
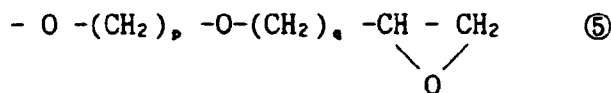
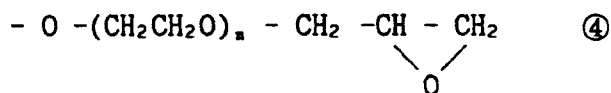
Summary of the Invention

A heat-sensitive recording material according to the present invention has on a base sheet a coating layer comprising a colorless or pale colored basic chromogenic material and a color developer which develops a color by contacting with the chromogenic material. The coating layer comprises 2,4'-dihydroxydiphenyl sulfone as the color developer, and further comprises at least one epoxy resin represented by the following formula (I) or (II):

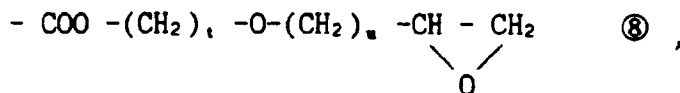


where each of R_1 and R_2 is one of the groups represented by the following formulae ① to ⑧,





and



l is 0 or an integer of 1 to 5 and m, n, p, q, r, s, t and u are respectively an integer of 1 to 5, but at least one of R_1 and R_2 is not $-COOH$, and R_3 is one of the groups represented by the above formulae (2) to (8).

The coating layer may be either a single layer of a heat-sensitive recording layer comprising the chromogenic material and the color developer, or multiple layers comprising the heat-sensitive recording layer and a protective layer. The epoxy resin may be comprised either in the heat-sensitive recording layer or the protective layer.

Detailed Description of the Invention

The heat-sensitive recording material according to the present invention uses selectively 2,4'-dihydroxydiphenyl sulfone as a color developer to constitute the recording layer as mentioned above and also uses an epoxy resin represented by the above formula (I) or (II) in combination with the specific color developer to attain the expected purpose.

Although the epoxy resin used in the present invention can be contained in the protective layer of the heat-sensitive recording material, satisfactory effect cannot necessarily be attained. Hence, it is preferred to be contained in the recording layer. When the epoxy resin is contained in the recording layer, the retainability of the recorded image is remarkably improved with no lowering of whiteness of the recording layer. Further, an additional effect of improvement in recording sensitivity can be also attained.

Typical examples of the epoxy resins represented by the above formula (I) include, for example, 1,4-di(1,2-epoxyethyl)benzene, 1,4-diglycidyl benzene, 1,4-di(2-glycidyloxy)benzene, 1,4-di(2-glycidyloxyethoxy)benzene, 1,4-di(4-glycidyloxybutoxy) benzene, 1,3-di(glycidyloxy)benzene, 1,2-di(glycidyloxy)benzene, 1,4-diglycidyl phthalate, 1,4-di(2-glycidyloxyethyl) phthalate, monoglycidyl phthalate and the like. Particularly, the epoxy resins represented by the formula (I) in which R_1 is identical with R_2 are preferred.

Typical examples of the epoxy resins represented by the formula (II) include, for example, glycidyloxybenzene, 1-phenoxy-14-glycidyloxy-3,6,9,12-tetraoxatetradecane and the like.

Among these various epoxy resins, especially 1,4-di(glycidyloxy)benzene and 1,4-diglycidyl phthalate are used most preferably as they are excellent in plasticizer-resistance and shows low formation of fogging.

The amount of the epoxy resin used is not especially restricted but it is generally used in the range of 0.1 to 500 parts by weight, preferably 1 to 200 parts by weight based on 100 parts by weight of the color developer.

According to the invention, 2,4'-dihydroxydiphenyl sulfone is essentially used as the color developer, but

the other color developers may be used together with it in such an amount as the advantages of the present invention is not inhibited.

Among the color developers which may be used together with 2,4'-dihydroxydiphenyl sulfone, there are included inorganic acidic compounds such as activated clay, attapulgite, colloidal silica, aluminum silicate and the like; organic acidic compounds such as phenolic compounds, e.g., 4-tert-butylphenol, 4-hydroxydiphenoxide, α -naphthol, β -naphthol, 4-hydroxyacetophenol, 4-tert-octylcatechol, 2,2'-dihydroxydiphenol, 4,4'-iso-propylidenebis(2-tert-butylphenol), 4,4'-sec-butylidenediphenol, 4-phenylphenol, 4,4'-isopropylidene-diphenol, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 2,2'-methylenebis(4-chlorophenol), hydroquinone, 4,4'-cyclohexylidenediphenol, 4,4'-dihydroxydiphenylsulfide, hydroquinone monobenzyl ether, 4-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2,4,4'-tri-hydroxybenzophenone, 2,2',4,4'-tetrahydroxy-benzophenone, dimethyl 4-hydroxyphthalate, methyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, sec-butyl 4-hydroxybenzoate, pentyl 4-hydroxybenzoate, phenyl 4-hydroxybenzoate, benzyl 4-hydroxybenzoate, tolyl 4-hydroxybenzoate, chlorophenyl 4-hydroxybenzoate, phenylpropyl 4-hydroxybenzoate, phenethyl 4-hydroxybenzoate, p-chlorobenzyl 4-hydroxybenzoate, p-methoxybenzyl 4-hydroxybenzoate, novolak phenol resin, phenol polymers and the like; aromatic carboxylic acids, e.g., benzoic acid, p-tert-butylbenzoic acid, trichlorobenzoic acid, terephthalic acid, 3-sec-butyl-4-hydroxybenzoic acid, 3-cyclohexyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-(α -methylbenzyl)salicylic acid, 3-chloro-5-(α -methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-(α , α -dimethylbenzyl)salicylic acid, 3,5-di- α -methylbenzylsalicylic acid and the like; diphenylsulfone derivatives, e.g., 3,4-dihydroxydiphenylsulfone, 3,4-dihydroxy-4'-methylidiphenylsulfone, bis-(4-hydroxyphenyl)sulfone, bis(3-allyl-4-hydroxyphenyl)sulfone, 2-hydroxy-5-tert-butylphenyl-4'-hydroxyphenylsulfone, 2-hydroxy-5-tert-butylphenyl-4'-hydroxyphenylsulfone, 2-hydroxy-5-isopropylphenyl-4'-hydroxyphenylsulfone, 2-hydroxy-5-tert-butylphenyl-3'-methyl-4'-hydroxyphenylsulfone, 2-hydroxy-5-tert-butylphenyl-3'-isopropyl-4'-hydroxyphenylsulfone, 2-hydroxy-5-tert-butylphenyl-2'-methyl-4'-hydroxyphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, 4-hydroxy-4'-methoxydiphenylsulfone, 4-hydroxy-4'-methylidiphenylsulfone and the like; sulfide derivatives, e.g., bis(3-tert-butyl-4-hydroxy-6-methylphenyl)sulfide, bis(2-methyl-4-hydroxy-6-tert-butylphenyl)sulfide and the like; and salts of the above phenolic compounds or aromatic carboxylic acids with polyvalent metals, e.g., zinc, magnesium, aluminum, calcium, titanium, manganese, tin and nickel; and organic acidic compounds such as antipyrine complex of zinc thiocyanate and the like.

As the basic chromogenic materials used in the present invention, various known colorless or pale colored basic chromogenic materials can be exemplified. They include triallyl methane chromogenic materials such as 3,3-bis(p-di methylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(2,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindol-3-yl)-6-dimethylaminophthalide and 3-p-dimethylaminophenyl-3-(1-methylpyrrol-3-yl)-6-dimethylaminophthalide; diphenylmethane chromogenic materials such as 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halophenyl-leucoauramine and N-2,4,5-trichlorophenyl-leucoauramine; thiazine chromogenic materials such as benzoyl-leucomethylene blue and p-nitrobenzoyl-leucomethylene blue; spiro chromogenic materials such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(6'-methoxybenzo)spiropyran and 3-propyl-spiro-dibenzopyran; lactam chromogenic materials such as Rhodamine-B-anilinolactam, Rhodamine(p-nitroanilino)lactam and Rhodamine(o-chloroanilino)lactam; fluoram chromogenic materials such as 3-dimethylamino-7-methoxyfluoran, 3-diethylamino-6-methoxyfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-diethylamino-7-N-acetyl-N-methylaminofluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-N-methyl-N-benzylaminofluoran, 3-diethylamino-7-N-chloroethyl-N-methylaminofluoran, 3-diethylamino-7-N-diethylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran, 3-dimethylamino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-phenylaminofluoran, 3-diethylamino-7-(2-carbomethoxy-phenylamino)fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-phenylaminofluoran, 3-piperidino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-dibutylamino-7-(o-chlorophenylamino)fluoran, 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, 3-diethylamino-7-(o-fluorophenylamino)fluoran, 3-dibutylamino-7-(o-fluorophenylamino)fluoran, 3-di(n-butyl)amino-6-methyl-7-phenylaminofluoran, 3-di(n-pentyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-methyl-N-n-amy)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-n-amy)amino-6-methyl-7-phenylaminofluoran, 3-(N-methyl-N-n-hexyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-n-hexyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N- β -ethyl-

hexyl)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-cyclopentyl)amino-6-methyl-7-phenylaminofluoran and 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-phenylaminofluoran. These basic chromogenic materials may be used either solely or in combination.

The ratio of the basic chromogenic material to the above specific color developer may be adjusted appropriately in accordance with the type of the basic chromogenic material. Generally, the color developer is used in an amount of 0.1 to 50 parts by weight, preferably 1 to 10 parts by weight, based on 1 part by weight of the basic chromogenic material.

The coating composition for heat-sensitive recording layer containing these substances is prepared in general by dispersing them in water as the dispersion medium by using a stirring pulverizer such as a ball mill and a sand mill.

5 to 40 weight %, preferably 10 to 30 weight % of the binder based on the total solid is incorporated in the coating composition for heat-sensitive recording layer. Typical binders include, for example, starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, gum arabic, polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, silicon-modified polyvinyl alcohol, diisobutylene-maleic anhydride copolymer salt, styrene-maleic anhydride copolymer salt, ethylene-acrylic acid copolymer salt, styrene-acrylic acid copolymer salt, styrene-butadiene copolymer emulsion, urea resin, melamine resin and amide resin.

Further, if necessary, there may be added to the coating composition various additives such as dispersing agents, e.g., sodium dioctylsulfosuccinate, sodium dodecylbenzene sulfonate, sodium lauryl sulfate, a metal salt of a fatty acid and the like, ultraviolet absorbers; e.g., benzophenone compounds and the like; defoaming agents; fluorescent dyes; coloring dyes; waxes e.g., zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and the like; inorganic pigments, e.g., kaolin, clay, talc, calcium carbonate, calcined kaolin, titanium oxide, diatomaceous earth, fine particle anhydrous silica, activated clay and the like. A sensitizer may be used simultaneously.

Typical examples of the sensitizers include such as fatty amides, e.g., stearic amide, stearic methylenebisamide, oleic amide, palmitic amide and coconut fatty amide; hindered phenols, e.g., 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,4-di-tert-butyl-3-methylphenol, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane, 1,1,3-tris(5-cyclohexyl-4-hydroxy-2-methylphenyl)butane and 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate; ultraviolet ray absorbers, e.g., 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and 2-hydroxy-4-benzoyloxybenzophenone; 1,2-di(3-methylphenoxy)ethane, 1,2-diphenoxyethane, 1-phenoxy-2-(4-methylphenoxy)ethane, 1-(2-methylphenoxy)-2-(4-methoxyphenoxy) ethane, p-benzylbiphenyl, naphthyl benzyl ether, benzyl-4-methylthiophenyl ether, phenyl 1-hydroxy-2-naphthoate, dibenzyl oxalate, di-p-methyl-benzyl oxalate, di-p-chlorobenzyl oxalate, dimethyl terephthalate, dibutyl terephthalate, dibenzyl terephthalate, dibutyl isophthalate, phenyl 1-hydroxynaphthoate and various known thermoplastic substances.

In the heat-sensitive recording material according to the present invention, especially 1,2-di(3-methylphenoxy)ethane, 1, 2-diphenoxyethane and 1-(2-ethylphenoxy)-2-(4-methoxyphenoxy) ethane are preferably used among these sensitizers. The used amount of the sensitizer is preferably in general within the range of not higher than 400 parts by weight based on 100 parts by weight of the color developer.

The method for forming the recording layer is not especially restricted. It may be formed by a method, for example, in which a coating solution for forming a heat-sensitive recording layer is applied on a base sheet by a known coating process such as air knife coating, rod blade coating, pure blade coating and short dwelltime coating and dried. The amount of the coating composition applied is not also especially restricted but usually controlled within the range of 2 to 12 g/m², preferably 3 to 10 g/m² on dry basis.

In the heat-sensitive recording material according to the present invention, the retainability of the recorded image can be further improved by providing a protective layer on the heat-sensitive recording layer.

The protective layer is generally formed by using a water-soluble or water-dispersible polymer as the main component. As the polymers, there are exemplified various binders as mentioned above. Among them, carboxyl-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol and silicon-modified polyvinyl alcohol are most preferably used because they are excellent in the effect as the protective layer.

To further improve the water resistance of the protective layer, curing agents such as glyoxal, formalin, glycine, glycidyl ether, dimethylol urea, ketene dimer, dialdehyde starch, melamine resin, polyamide resin, polyamide-epichlorohydrin resin, ketone-aldehyde resin, borax, boric acid, zirconium ammonium carbonate and epoxy compounds may be also used in combination.

Furthermore, to improve printability and to minimize sticking, inorganic pigments such as calcium carbonate, zinc oxide, aluminum oxide, titanium dioxide, silicon dioxide, aluminum hydroxide, barium sulfate, zinc sulfate, talc, kaolin, clay, calcined kaolin and colloidal silica, and organic pigments such as styrene microballs, nylon powder, polyethylene powder, urea-formaldehyde resin filler and raw starch particles may be added to

the protective layer if required. The added amount of the pigment is preferably controlled within the range of 5 to 500 parts by weight based on 100 parts by weight of the binder.

Further, there may be added in the coating composition for forming the protective layer, if required, various known additives including lubricants such as zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax and ester wax, and surface active agents (dispersants and lubricants) such as sodium dioctyl sulfosuccinate and antifoaming agents.

The coating composition for forming the protective layer thus prepared may be coated on the heat-sensitive recording layer by a suitable coating equipment. The used amount of the coating composition is preferably controlled within the range of 0.1 to 20 g/m², more preferably 0.5 to 10 g/m², in general, as the recording sensitivity of the heat-sensitive recording material is lowered when the amount applied exceeds 20 g/m².

The retainability of the recorded image may be further improved if required by providing a protective layer also on the back of the heat-sensitive recording material. Furthermore, there may be added various known technologies in the field of producing the heat-sensitive recording material such as formation of primer layer on the base sheet and application of an adhesive on the back of the recording material to make an adhesive label.

A primer layer may be formed between the base sheet and the heat-sensitive recording layer. In the primer layer, there may be included such inorganic or organic pigments and binders as described above. Oil-absorbing pigments are preferably used.

As the base sheet, paper, plastic film and synthetic paper and the like may be used. Paper is most preferably used in terms of cost and coatability.

Preferred Embodiments of the Invention

The following examples serve to illustrate the invention in more detail although the invention is not limited to the examples. Unless otherwise indicated, parts and % signify parts by weight and % by weight, respectively.

Example 1

① Preparation of Dispersion A

The following composition was pulverized in a sand mill, and the pulverization was continued until an average particle size of 0.8 μm.

3-di(n-butyl)amino-6-methyl-7-phenylaminofluoran	10 parts
5 % aqueous solution of methyl cellulose	5 parts
Water	40 parts

② Preparation of Dispersion B

The following composition was pulverized in a sand mill, and the pulverization was continued until an average particle size of 1.2 μm.

2,4'-dihydroxydiphenylsulfone	30 parts
5 % aqueous solution of methyl cellulose	5 parts
Water	80 parts

③ Preparation of Dispersion C

The following composition was pulverized in a sand mill, and the pulverization was continued until an average particle size of 1.2 μm.

	1,2-di(3-methylphenoxy)ethane	20 parts
	5 % aqueous solution of methyl cellulose	5 parts
5	Water	55 parts

④Preparation of Dispersion D

10 The following composition was pulverized in a sand mill, and the pulverization was continued until an average particle size of 2.1 μm .

15	1,4-di(glycidyloxy)benzene (Trade name "Denacol EX-203" manufactured by Nagase Kasei Kogyo Co., Ltd., melting point: 100 °C)	20 parts
	5 % aqueous solution of methyl cellulose	5 parts
20	Water	55 parts

⑤Preparation of a recording layer

25 55 parts of Dispersion A, 115 parts of Dispersion B, 80 parts of Dispersion C, 24 parts of Dispersion D, 80 parts of 10 % aqueous solution of polyvinyl alcohol and 35 parts of calcium carbonate were mixed together under stirring and the resultant coating composition was coated in the weight of an amount of 6 g/m² on dry basis on a base paper sheet of 50 g/m² and dried to obtain a heat-sensitive recording material.

Example 2

30 A heat-sensitive recording material was prepared in the same manner as in Example 1 except that 1,4-diglycidyl phthalate (Trade name "Denacol EX-711" manufactured by Nagase Kasei Kogyo Co., Ltd., melting point: 100°C) was used instead of 1,4-di(glycidyloxy)benzene to prepare Dispersion D.

35 Example 3

40 A heat-sensitive recording material was prepared in the same manner as in Example 1 except that 1-phenoxy-14-glycidyloxy-3, 6,9,12-tetraoxatetradecane (Trade name "Denacol EX-145" manufactured by Nagase Kasei Kogyo Co., Ltd., aqueous solution) was used instead of 1,4-di(glycidyloxy)benzene to prepare Dispersion D.

Comparative Example 1

45 A heat-sensitive recording material was prepared in the same manner as in Example 1 except that Dispersion D was not added to the coating composition for forming the recording layer.

Comparative Example 2

50 A heat-sensitive recording material was prepared in the same manner as in Example 1 except that bis-(4-hydroxyphenyl) sulfone was used instead of 2,4'-dihydroxydiphenylsulfone to prepare Dispersion B.

Comparative Example 3

55 A heat-sensitive recording material was prepared in the same manner as in Example 2 except that 4,4'-isopropylidene diphenol was used instead of 2,4'-dihydroxydiphenylsulfone to prepare Dispersion B.

The properties of six heat-sensitive recording materials thus prepared were evaluated by the following methods. The results are shown in Table 1.

Whiteness (Brightness)

The whiteness of the recording layer was measured by using a Hunter reflectometer.

5 Fogging

The heat-sensitive recording material was treated at 50 °C for 15 hours and then the whiteness of the recording layer was measured by using a Hunter reflectometer.

10 Color density

The color density of the recorded image obtained by printing with a thermal printer (PC-100A manufactured by Texas Instruments Inc.) was measured by using a Macbeth densitometer (RD-914 manufactured by Macbeth Corp.).

15

Plasticizer resistance

A polyvinyl chloride film manufactured by Mitsui Toatsu Kagaku Co., Ltd. was wrapped threefold around a polypropylene pipe having a diameter of 40 mm. A heat-sensitive recording material after developing color image was put on it in a manner the color images are exposed outward and further the same polyvinyl chloride film was wrapped threefold around the heat-sensitive recording material. The resultant material was stood at 30°C for 24 hours and the color density was measured to evaluate plasticizer resistance.

Table 1

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	Whiteness (%)	Fogging (%)	Color density	Plasticizer resistance
Example 1	83.1	80.2	1.24	1.10
2	83.2	80.0	1.22	1.10
3	82.9	80.1	1.21	1.08
Comparative Example				
1	83.1	80.3	1.22	0.48
2	83.2	80.2	1.25	0.47
3	82.0	77.7	1.27	0.80

45 Example 4

①Formation of a recording layer

A heat-sensitive recording material was prepared in the same manner as in Example 1.

50

②Formation of a protective layer

80 parts of 10 % aqueous solution of acetoacetylated polyvinyl alcohol, 20 parts of 10 % aqueous solution of partly saponified polyvinyl alcohol (PVA-217 manufactured by Kuraray Co., Ltd.), 20 parts of calcium carbonate and 50 parts of water were mixed together under stirring and the resultant coating composition was applied on the recording layer of the above heat-sensitive recording material in the weight of an amount of 6 g/m² on dry basis and dried to obtain a heat-sensitive recording material having a protective layer.

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Example 5

①Formation of a recording layer

5 A recording layer was formed on the base sheet in the same manner as in Example 2.

②Formation of a protective layer

10 A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Example 6

①Formation of a recording layer

15 A recording layer was formed on the base sheet in the same manner as in Example 3.

②Formation of a protective layer

20 A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Example 7

25 ①Formation of a primer layer

100 part of calcinated clay (Trade name "Ansilex" manufactured by Engelhard Co., Ltd.), 20 parts of magnesium carbonate, 15 parts of an ethylene-butadiene copolymer latex (Trade name "L-1571" manufactured by Asahi Kasei Co., Ltd.), 25 parts of 12 % aqueous solution of polyvinyl alcohol and 200 parts of water were mixed together under stirring and the resultant coating composition was applied, on a base paper sheet of 50 g/m², in the weight of an amount of 6 g/m² on dry basis and dried to obtain a substrate for the heat-sensitive recording material.

35 ②Formation of a recording layer

A heat-sensitive recording layer was formed on the substrate in the same manner as Example 1.

③Formation of a protective layer

40 A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Comparative Example 4

45 ①Formation of a recording layer

A heat-sensitive recording layer was formed in the same manner as in Comparative Example 1.

③Formation of a protective layer

50 A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Comparative Example 5

55 ①Formation of a recording layer

A heat-sensitive recording layer was formed in the same manner as in Comparative Example 2.

③Formation of a protective layer

A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Comparative Example 6

①Formation of a recording layer

A heat-sensitive recording layer was formed in the same manner as in Comparative Example 3.

②Formation of a protective layer

A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

Comparative Example 7

①Formation of a primer layer

A substrate for a heat-sensitive recording material prepared in the same manner as in Example 7.

②Formation of a recording layer

A heat-sensitive recording layer was formed on the substrate in the same manner as in Comparative Example 1 except that the above substrate was used.

③Formation of a protective layer

A protective layer was formed on the above recording layer in the same manner as in Example 4 to obtain a heat-sensitive recording material having a protective layer.

The properties of the eight heat-sensitive recording materials thus prepared were evaluated in the same manner as described above except that the plasticizer-resistance and the wet plasticizer-resistance were evaluated by the following methods. The results are shown in Table 2.

Plasticizer-resistance

A polyvinyl chloride film manufactured by Mitsui Toatsu Kagaku Co., Ltd. was wrapped threefold around a polypropylene pipe having a diameter of 40 mm. A heat-sensitive recording material after developing color images was put on it in the manner color images are exposed outward and further the same polyvinyl chloride film was wrapped threefold around the heat-sensitive recording material. The resultant material was stood at 40 °C for 24 hours and then the color density was measured to evaluate plasticizer resistance.

Wet plasticizer-resistance

The heat-sensitive recording material after developing color images was slightly wet with water and then evaluated in the same manner as in the above plasticizer-resistance test to give wet plasticizer-resistance.

Table 2

	Whiteness (%)	Fogging (%)	Color density	Plasticizer- resistance	Wet plast- icizer resistance
Example 4	81.5	79.9	1.16	1.14	1.00
5	81.6	80.0	1.15	1.13	1.01
6	81.5	80.0	1.14	1.12	1.00
7	83.5	82.1	1.17	1.15	1.02
Comparative Example					
4	81.5	80.2	1.14	0.50	0.20
5	81.5	80.2	1.15	0.50	0.19
6	81.0	77.5	1.17	0.85	0.50
7	83.6	82.3	1.18	0.53	0.23

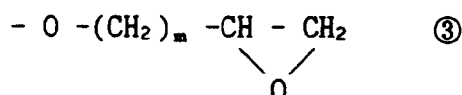
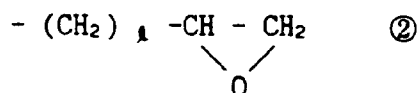
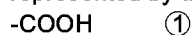
As apparent from Tables 1 and 2, the heat-sensitive recording material according to the present invention is excellent in storage stability (retainability of images) and shows no fogging.

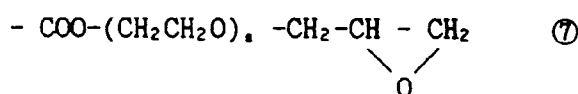
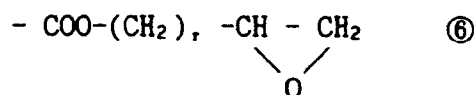
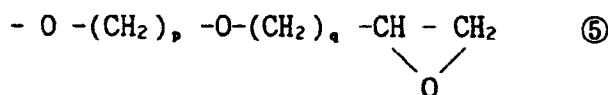
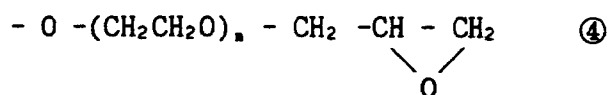
Claims

(1) A heat-sensitive recording material having on a base sheet a coating layer in which a colorless or pale colored basic chromogenic material and a color developer developing a color by contacting with the chromogenic material are comprised, characterized in that said coating layer comprises 2,4'-dihydroxydiphenyl sulfone as the color developer, and further comprises at least one epoxy resin represented by the following formula (I) or (II):

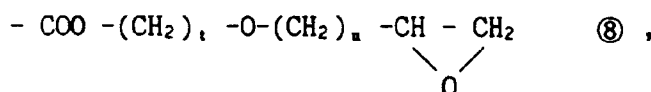


where each of R₁ and R₂ is one of the groups represented by the following formulae ① to ⑧,





and



ℓ is 0 or an integer of 1 to 5 and m, n, p, q, r, s, t and u are respectively an integer of 1 to 5, but at least one of R_1 and R_2 is not -COOH, and R_3 is one of the groups represented by the above formulae (2) to (8).

(2) A heat-sensitive recording material according to Claim 1, in which said coating layer is a heat-sensitive recording layer, and said chromogenic material and said color developer together with said epoxy resin being comprised in said recording layer.

(3) A heat-sensitive recording material according to Claim 1, in which said coating layer comprises a heat-sensitive recording layer and a protective layer applied on said recording layer, said chromogenic material and said color developer together with said epoxy resin being comprised in said recording layer.

(4) A heat-sensitive recording material according to Claim 1, 2 or 3, in which a primer layer is applied on said base sheet and said recording layer is formed on said primer coating layer.

(5) A heat-sensitive recording material according to Claim 1, in which said coating layer comprises a heat-sensitive recording layer and a protective layer applied on said recording layer, said chromogenic material and said color developer being comprised in said recording layer and said epoxy resin being comprised in said protective layer.

(6) A heat-sensitive recording material according to Claim 1, in which said epoxy resin is at least one selected from the group consisting of 1,4-di(glycidyoxy)benzene, 1,4-diglycidyl phthalate and 1-phenoxy-14-glycidyoxy-3,6,9,12-tetraoxatetradecane.

(7) A heat-sensitive recording material according to Claim 6, in which said epoxy resin is at least one selected from the group consisting of 1,4-di(glycidyoxy)benzene and 1,4-diglycidyl phthalate.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8649

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.5)
A	PATENT ABSTRACTS OF JAPAN vol. 4, no. 132 (M-32)(614) 17 September 1980 & JP-A-55 087 596 (RICOH K.K.) 2 July 1980 * abstract *	1-7	B41M5/30
A	----- PATENT ABSTRACTS OF JAPAN vol. 13, no. 588 (M-912)(3936) 25 December 1989 & JP-A-01 247 192 (NIPPON KAYAKU K.K.) 3 October 1989 * abstract *	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 JANUARY 1992	Examiner BACON A. J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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