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(54) Thermal recording sheet.

(57) A thermal recording sheet having good dot reproducibility and image quality, with no sticking or adherence of residue comprises, in order, a substrate, an intermediate layer and a thermal color developing layer and contains in the intermediate layer particles of a cross-linked polymer having a particle diameter of 0.2 to 5.0 μm and an inorganic pigment having an oil absorption of less than 170 ml/100g in a weight ratio of 1 :1 to 1 :9.

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Technical Field

This invention relates to a thermal recording sheet which is superior in dynamic sensitivity, dot reproducibility, and image quality, without sticking and adherence of residue.

Background Technology

In general, in thermal recording sheets, a normally colorless or pale colored basic chromogenic dye and an organic color developer such as a phenolic substance are individually dispersed into fine particles, mixed, and a binder, a filler, a sensitivity improver, a slip agent, and other additives are added to obtain a coating color, which is coated on a substrate such as paper, synthetic paper, plastic films, cloths, and the like. The thermal recording sheet enables color recording by a momentary chemical reaction caused by heating with a thermal pen, a thermal head, a hot stamp, laser light, or the like.

These thermal recording sheets are applied in a variety of areas such as measurement recorders, computer terminal printers, facsimiles, automatic ticket vendors, and bar-code labels, however, with recent diversification and improvement of these recording devices, requirements to the thermal recording sheets have become stricter. For example, with increasing recording speed, it is required to obtain a high-concentration, sharp color image even with a small heat energy and, in addition, to have improved storage stability in terms of light resistance, weather resistance, and oil resistance.

Furthermore, with the diversification of market needs, demand is increasing for a thermal recording sheet which is superior in dot reproducibility and image quality over the energy regions from low energy to high energy.

On the other hand, a method is disclosed (Japanese Patent Laid-open Publication 2-307784) in which an intermediate layer containing polystyrene and a pigment having an oil absorption of less than 100 ml/100 g is introduced between a substrate and a thermal color developing layer to obtain a thermal recording paper with high density and reduced adherence of residue.

However, in this method, since polystyrene is a thermoplastic resin, it tends to increase adherence of residue to the thermal head and sticking, and is thus less practical.

Furthermore, there is disclosed a method (Japanese Patent Laid-open Publications 62-117787, 63-21180) in which, in order to apply heat from the thermal head to the thermal color developing layer, a heat insulating intermediate layer containing thermoplastic hollow fine particles is introduced to obtain a high density and sharp image.

Furthermore, there is disclosed a method (Japanese Patent Laid-open Publication 62-5886) in which a heat insulating intermediate layer containing thermoplastic hollow fine particles and an intermediate layer containing an inorganic or organic pigment are laminated between the substrate and the thermal color developing layer. However, even these methods are not practical because they involve problems in that the thermoplastic hollow fine particles themselves melt by heat, resulting in increased adherence of residue to the thermal head and sticking.

Therefore, it is a primary object of the present invention to provide a thermal recording sheet which is superior in dot reproducibility and image quality with reduced adherence of residue and sticking.

Disclosure of the Invention

In accordance with the present invention which solves all of the above problems, there is provided a thermal recording sheet having a thermal color developing layer containing a chromogenic agent and a color developer as main ingredients provided on a substrate, characterized in that an intermediate layer containing polymeric fine particles having a cross-linking structure with a particle diameter of 0.2 to 5.0 microns and an inorganic pigment having an oil absorption (according to JIS K5101) of less than 170 ml/100g in a ratio of 1:1 to 1:9.

Various substances are known as polymeric fine particles having such a cross-linking structure. In the present invention, it is desirable to use cross-linkable polymeric fine particles which have a particle diameter of 5 microns or less, more preferably 2 microns or less, and most preferably 0.2 to 1.0 micron. When those which have a particle diameter of 0.2 microns or less. When the particle diameter is 0.2 microns or less, spaces between particles in the intermediate layer become small, penetration into the substrate is increased, and it is impossible to obtain a thermal recording sheet which is the object of the present invention, resulting in considerable deterioration in quality such as sticking and adherence of residue.

On the other hand, when the particle diameter is 5.0 microns or more, voids between particles in the intermediate layer are large, which allow the ingredients of the thermal recording layer to penetrate into the intermediate layer, resulting in lowering the color developing sensitivity, sticking, and adherence of residue.

The polymeric fine particles having such a cross-linking structure used in the intermediate layer of the present invention are obtained by emulsion polymerization of a monomer mixture containing a cross-linkable monomer.

The cross-linkable monomer includes such monomers having at least two polymerizable unsaturated double bonds in one molecule such as trimethylolpropane-trimethacrylate, divinylbenzene, ethyleneglycoldiacrylate, and the like. The cross-linkable monomer is used in an amount of 0.5 to 1% by weight to a vinyl monomer mixture polymer which is described below.

In the present invention, an aromatic vinyl compound such as (meth)acrylic esters, vinylacetate, vinyl esters, vinylcyano compounds, halogenated vinyl compounds, styrene, α-methylstyrene, or vinyltoluene can be used as a vinyl monomer, and it is preferable to use styrene or methylmethacrylate as a main ingredient in view of heat resistance.

The polymeric fine particles having such a specific cross-linking structure are dispersed in a binder to obtain a solution, as will be described later. In this case, a latex-based binder gives a good coating color stability and endows the intermediate layer with an elasticity, and allows even contact with the thermal head, thereby remarkably improving the dot reproducibility.

The pigment used in combination with the polymeric fine particles having the specific cross-linking structure in the intermediate layer is an inorganic pigment having an oil absorption (according to JIS K5101) of 170 ml/100 g. This type of pigment includes alumina, magnesium hydroxide, calcium hydroxide, magnesium carbonate, zinc oxide, barium sulfate, silica, calcium carbonate, kaolin, calcined kaolin, diatomaceous earth, talc, titanium oxide, aluminum hydroxide, and the like. In this case, when the oil absorption is greater than 170 ml/100 g, the residue absorbing ability is improved, but the ingredients of the thermal recording layer tend to be absorbed into the intermediate layer in coating the thermal recording layer in coating the thermal recording layer, resulting in a deterioration in printing density and dot reproducibility.

The polymeric fine particles having the specific cross-linking structure and the inorganic pigment having an oil absorption of less than 170 ml/100 g are used in a ratio of 1:1 to 1:9 (weight ratio). A greater amount of the polymeric fine particles having the specific cross-linking structure than 1:1 tends to result in deterioration in dot reproducibility and image quality, sticking, and adherence of residue. A greater amount of inorganic pigment having an oil absorption of 170 ml/100 g than 1:9 tends to result in the dynamic sensitivity.

The amounts of the polymeric fine particles having the cross-linking structure and the inorganic pigment having an oil absorption of less than 170 ml/100 g used in the intermediate layer are not specifically limited, but it is desirable to use in amounts of typically 60 to 95 % by weight based on the total solids, preferably 70 to 90 % by weight. The coating amount is not specifically limited, but it is coated typically in an amount of 2 to 20 g/m^2, preferably 4 to 15 g/m^2.

In the present invention, the intermediate layer containing the fine particles having the cross-linking structure with a particle diameter of 0.2 to 5.0 microns and an inorganic pigment having an oil absorption (according to JIS K5101) of 170 ml/100 g in a ratio of 1:1 to 1:9 is coated on a substrate, and the thermal color developing layer is coated on top, followed by drying, to produce the thermal recording sheet of the present invention.

In the present invention, the combination of the chromogenic agent and the color developer is not specifically limited, but can be applied to various types of thermal recording sheets such as a leuco dye type color developing material comprising a basic colorless dye and an acid substance, a chelate type color developing material comprising iron salt of a higher fatty acid and stearyl gallate, a pigment type color developing material comprising an imino compound and an isocyanate compound, and the like, and the present invention includes these types of recording sheets.

However, the specific intermediate layer of the present invention provided on the substrate provides the best effect when the leuco dye type color developing material comprising a basic colorless dye and an acid substance is used.

In the present invention, examples of the color developer include bisphenols A, 4-hydroxybenzoic esters, 4-hydroxyphthalic diesters, phthalic monoesters, bis(hydroxyphenyl) sulfides, 4-hydroxyphenylarylsulfones, 4-hydroxyphenylarylsulfonates, 1,3-di[2-(hydroxyphenyl)-2-propyl]-benzenes, 4-hydroxybenzoyloxybenzoic esters, and bisphenolsulfones. These examples are shown below:

<u>Bisphenols A</u>

4,4'-Isopropylidene-diphenol (Bisphenol A)
4,4'-Cyclohexylidene-diphenol
p,p'-(1-Methyl-n-hexylidene)-diphenol
1,7-di(4-hydroxyphenylthio)-3,5-dioxaheptane

4-Hydroxybenzoic esters

Benzyl-4-hydroxybenzoate
Ethyl-4-hydroxybenzoate
Propyl-4-hydroxybenzoate
Isopropyl-4-hydroxybenzoate
Butyl-4-hydroxybenzoate
Isobutyl-4-hydroxybenzoate
Methylbenzyl-4-hydroxybenzoate

4-Hydroxyphthalic diesters

Dimethyl-4-hydroxyphthalate
Diisopropyl-4-hydroxyphthalate
Dibenzyl-4-hydroxyphthalate
Dihexyl-4-hydroxyphthalate

Phthalic monoesters

Monobenzylphthalate
Monocyclohexylphthalate
Monophenylphthalate
Monomethylphenylphthalate
Monoethylphenylphthalate
Monopropylbenzylphthalate
Monohalogenhenzylphthalate
Monoethoxybenzylphthalate

Bis-(hydroxyphenyl)-sulfides

Bis-(4-hydroxy-3-tert-butyl-6-methylphenyl)-sulfide
Bis-(4-hydroxy-2,5-dimethylphenyl)-sulfide
Bis-(4-hydroxy-2-methyl-5-ethylphenyl)-sulfide
Bis-(4-hydroxy-2-methyl-5-isopropylphenyl)-sulfide
Bis-(4-hydroxy-2,3-dimethylphenyl)-sulfide
Bis-(4-hydroxy-2,5-dimethylphenyl)-sulfide
Bis-(4-hydroxy-2,5-diisopropylphenyl)-sulfide
Bis-(4-hydroxy-2,3,6-trimethylphenyl)-sulfide
Bis-(2,4,5-trihydroxyphenyl)-sulfide
Bis-(4-hydroxy-2-cyclohexyl-5-methylphenyl)-sulfide
Bis-(2,3,4-trihydroxyphenyl)-sulfide
Bis-(4,5-dihydroxy-2-tert-butylphenyl)-sulfide
Bis-(4-hydroxy-2,5-diphenylphenyl)-sulfide
Bis-(4-hydroxy-2-tert-octyl-5-methylphenyl)-sulfide

4-Hydroxyphenylarylsulfones

4-Hydroxy-4'-isopropoxydiphenylsulfone
4-Hydroxy-4'-propoxydiphenylsulfone
4-Hydroxy-4'-n-butyloxydiphenylsulfone
4-Hydroxy-4'-n-propoxydiphenylsulfone

4-Hydroxyphenylarylsulfonates

4-Hydroxyphenylbenzenesulfonate
4-Hydroxyphenyl-p-toluylsulfonate
4-Hydroxyphenylmethylenesulfonate
4-Hydroxyphenyl-p-chlorobenzenesulfonate

4-Hydroxyphenyl-p-tert-butylbenzenesulfonate
4-Hydroxypllenyl-p-isopropoxybenzenesulfonate
4-Hydroxyphenyl-1'-naphthalenesulfonate
4-Hydroxyphenyl-2'-naphthalenesulfonate

1,3-Di[2-(hydroxyphenyl)-2-propyl]-benzenes

1,3-Di[2-(4-hydroxyphenyl)-2-propyl]-benzene
1,3-Di[2-(4-hydroxy-3-alkylphenyl-2-propyl]-benzene
1,3-Di[2-(2,4-dihydroxyphenyl)-2-propyl]-benzene
1,3-Di[2-(4-hydroxy-5-methylphenyl)-2-propyl]-benzene

Resorcinols

1,3-Dihydroxy-6(α,α-dimethylbenzyl)-benzene

4-Hydroxybenzoyloxybenzoic esters

Benzyl-4-hydroxybenzoyloxybenzoate
Methyl-4-hydroxybenzoyloxybenzoate
Ethyl-4-hydroxybenzoyloxybenzoate
Propyl-4-hydroxybenzoyloxybenzoate
Butyl-4-hydroxybenzoyloxybenzoate
Isopropyl-4-hydroxybenzoyloxybenzoate
tert-Butyl-4-hydroxybenzoyloxybenzoate
Hexyl-4-hydroxybenzoyloxybenzoate
Octyl-4-hydroxybenzoyloxybenzoate
Nonyl-4-hydroxybenzoyloxybenzoate
Cyclohexyl-4-hydroxybenzoyloxybenzoate
β-Phenethyl-4-hydroxybenzoyloxybenzoate
Phenyl-4-hydroxybenzoyloxybenzoate
α-Naphthyl-4-hydroxybenzoyloxybenzoate
β-Naphthyl-4-hydroxybenzoyloxybenzoate
sec-Butyl-4-hydroxybenzoyloxybenzoate

Bisphenolsulfones (I)

Bis-(3-1-butyl-4-hydroxy-6-methylphenyl)-sulfone
Bis-(3-ethyl-4-hydroxyphenyl)-sulfone
Bis-(3-propyl-4-hydroxyphenyl)-sulfone
Bis-(3-methyl-4-hydroxyphenyl)-sulfone
Bis-(3-isopropyl-4-hydroxyphenyl)-sulfone
Bis-(2-ethyl-4-hydroxyphenyl)-sulfone
Bis(3-chloro-4-hydroxyphenyl)-sulfone
Bis-(2,3-dimethyl-4-hydroxyphenyl)-sulfone
Bis-(2,5-dimethyl-4-hydroxyphenyl)-sulfone
Bis-(3-methoxy-4-hydroxyphenyl)-sulfone
4-Hydroxyphenyl-2'-ethyl-4'-hydroxyphenylsulfone
4-Hydroxyphenyl-2'-isopropyl-4'-hydroxyphenylsulfone
4-Hydroxyphenyl-3'-isopropyl-4'-hydroxyphenylsulfone
4-Hydroxyphenyl-3'-sec-butyl-4'-hydroxyphenylsulfone
3-Chloro-4-hyydroxyphenyl-3'-isopropyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-aminophenyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-isopropylphenyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-octylphenyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-chloro-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-methyl-4'-hydroxyphenylsulfone

2-Hydroxy-5-t-butylphenyl-3'-isopropyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-chloro-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-methyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-isopropyl-4'-hydroxyphenylsulfone
2-Hydroxy-5-t-butylphenyl-3'-methyl-4'-hydroxyphenylsulfone

Bisphenolsulfones (II)

4,4'-Sulfonyldiphenol
2,4'-Sulfonyldiphenol
3,3'-Dichloro-4,4'-sulfonyldiphenol
3,3, -Dibromo-4 ,4, -sulfonyldiphenol
3,3',5,5'-Tetrabromo-4,4'-sulfonyldiphenol
3,3'-Diamino-4,4'-sulfonyldiphenol

Others

p-tert-Butylphenol
2,4-Dihydroxybenzophenone
Novolac type phenolic resin
4-Hydroxyacetophenone
p-Phenylphenol
Benzyl-4-hydroxyphenylacetate
p-Benzylphenol

The basic colorless dye used in the present invention is not specifically limited, however, it is preferable to use triphenylmethane-type dyes, fluorane-type dyes, fluorene-type dyes, divinyl-type dyes, or the like, and practical examples of these dyes are shown below.

Triphenylmethane-type leuco dye

3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide [Crystal Violet Lactone]

Fluorane-type leuco dyes (I)

3-Diethylamino-6-methyl-7-anilinofluorane
3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluorane
3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluorane
3-Diethylamino-6-methyl-7-(o,p-dimethylanilino)fluorane
3-Pyrrolidino-6-methyl-7-anilinofluorane
3-Piperidino-6-methyl-7-anilinofluorane
3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluorane
3-Diethylamino-7-(m-trifluoromethylanilino)fluorane
3-N-n-Dibutylamino-6-methyl-7-anilinofluorane
3-N-n-Dibutylamino-7-(o-chloroanilino)fluorane
3-(N-ethyl-N-tetrahdrofurfurylamino)6-methyl-7-anilinofluorane
3-Dibutylamino-6-methyl-7-(o,p-dimethylanilino)fluorane
3-(N-methyl-N-propylamino)-6-methyl-7-anilinofluorane
3-diethylamino-6-chloro-7-anilinofluorane
3-Dibutylamino-7-(o-chloroanilino)fluorane
3-Diethylamino-7-(o-chloroanilino)fluorane.
3-Diethylamino-6-methyl-7-(m-methylanilino)fluorane
3-n-Dibutylamino-6-methyl-7-(m-methylanilino)fluorane
3-Diethylamino-6-methyl-chlorofluorane
3-Diethylamino-6-methyl-fluorane
3-Cyclohexylamino-6-chlorofluorane
3-Diethylamino-benzo[a]-fluorane
3-n-Dipentylamino-6-methyl-7-anilinofluorane

2-(4-Oxo-hexyl)-3-dimethylamino-6-methyl-7-anilinofluorane
2-(4-Oxo-hexyl)-3-diethylamino-6-methyl-7-anilinofluorane
2-(4-Oxo-hexyl)-3-dipropylamino-6-methyl-7-anilinofluorane

Fluorene-type leuco dyes

3,6,6'-tris(dimethylamino)spiro[fluorene-9,3'-phthalide
3,6,6'-tris(diethylamino)spiro[fluorene-9,3'-phthalide

Fluorane-type leuco dyes (II)

2-Methyl-6-p-(p-dimetylaminophenyl)aminoanilinofluorane
2-Methoxy-6-p-(p-dimetylaminophenyl)aminoanilinofluorane
2-Chloro-3-methyl-6-p-(p-dimetylaminophenyl)aminoanilinofluorane
2-Chloro-6-p-(p-dimetylaminophenyl)aminoanilinofluorane
2-Nitro-6-p-(p-diethylaminophenyl)aminoanilinofluorane
2-Amino-6-p-(p-diethylaminophenyl)aminoanilinofluorane
2-Diethylamino-6-p-(p-diethylaminophenyl)aminoanilinofluorane
2-Phenyl-6-methyl-6-p-(p-phenylaminophenyl)aminoanilinofluorane
2-Benzyl-6-p-(p-phenylaminophenyl)aminoanilinofluorane
2-Hydroxy-6-p-(p-phenylaminophenyl)aminoanilinofluorane
3-Methyl-6-p-(p-dimethylaminophenyl)aminoanilinofluorane
3-Diethyamino-6-p-(p-diethylaminophenyl)aminoanilinofluorane
3-Diethyamino-6-p-(p-dibutylaminophenyl)aminoanilino-fluorane

Divinyl-type leuco dyes

3,3-Bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-ethenyl]-4,5,6,7-tetrabromophthalide
3,3-Bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-ethenyl]-4,5,6,7-tetrachlorophthalide
3,3-Bis-[1,1-bis(4-pyrrolidinophenyl)ethylene-2-yl]-4,5,6,7-tetrabromophthalide
3,3-Bis-[1-(4-methoxyphenyl)-1-(4-pyrrolidinophenyl)-ethylen-2-yl]-4,5,6,7-tetrachlorophthalide

Others

1,1-Bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-dinitrileethane
1,1-Bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2-β-naphthoylethane
1,1-Bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-diacetylethane
Dimethyl-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-methylmalonate

These dyes can be used alone or as mixtures of two or more.

Furthermore, as a sensitizer, fatty acid amides such as stearamide, palmitamide, or the like; ethylenebisamide, montan wax, polyethylene wax, dibenzyl terephthalate, benzyl p-benzyloxybenzoate, di-p-tolylcarbonate, p-benzylbiphenyl, phenyl-α-naphthylcarbonate, 1,4-diethoxynaphthalene, phenyl-1-hydroxy-2-naphthoate, 1,2-di-(3-methylphenoxy) ethane, di(p-methylbenzyl)oxalate, β-benzyloxynaphthalene, 4-biphenyl-p-tolylether, o-xylylene-bis-(phenylether), 4-(m-methylphenoxymethyl)biphenyl, or the like can be added.

In the present invention, the binder used in the intermediate and the thermal recording layer can be completely-hydrolyzed polyvinylalcohol with a polymerization degree of 200 to 1,900, partially-hydrolyzed polyvinylalcohol, carboxy-modified polyvinylalcohol, amide-modified polyvinylalcohol, sulfonic acid-modified polyvinylalcohol, butyral-modified polyvinylalcohol, and other modified polyvinylalcohols, hydroxyethylcellulose, methylcellulose, carboxymethylcellulose, styrene-maleic anhydride copolymer, styrene-butadiene copolymer, styrene-acrylate copolymer, acrylonitrile-butadiene copolymer; cellulose derivatives such as ethylcellulose and acetylcellulose; polyvinylchloride, polyvinylacetate, polyacrylamide, polyacrylic esters, polyvinylbutyral, polystyrene and its copolymers, polyamide resins, silicone resins, petroleum resins, terpene resins, ketone resins, coumarone resins, starch, starch derivatives, and casein. These polymeric substances are used in the state emulsified in water or other solvents, or can be used in combination according to the quality requirements.

In the present invention, it is also possible to add known stabilizers based on metal salts (Ca, Zn) of p-nitrobenzoic acid or metal salts (Ca, Zn) of monobenzylphthalate as much as the effect of the present invention is not impaired.

The pigment used in the present invention can be inorganic fillers such as alumina, magnesium hydroxide, calcium hydroxide, magnesium carbonate, zinc oxide, barium sulfate, silica, calcium carbonate, kaolin, calcined kaolin, diatomaceous earth, talc, titanium oxide, aluminum hydroxide, or the like, and organic pigments such as urea-formaldehyde resins, styrene-methacrylic acid copolymer, polystyrene resins, and amino resin fillers.

In addition to the above, it is possible to use releasing agents such as fatty acid metal salts, slip agents such as wax, benzophenone- or triazole-based ultraviolet absorbers, water resistant agents such as glyoxal, dispersants, defoamers, and the like.

The amounts of the organic color developer and the basic colorless dye used in the present invention and the types and amounts of other constituents are determined according to the required properties and recording adaptability, and are not specifically limited, but it is usually preferable to use 1 to 8 parts of the organic color developer and 1 to 20 parts of the filler to 1 part of the basic colorless dye, and the binder is used in an amount of 10 to 25% of the total solid.

The coating color of the above composition can be coated on any type of substrate such as paper, synthetic paper, plastic films, non-woven fabrics, or the like to obtain the objective thermal recording sheet.

Furthermore, the sheet can be provided on the thermal color developing layer with an overcoating layer comprising a polymeric substance containing a pigment, or on the substrate with a back coating layer comprising a polymeric substance, to improve the storage stability.

The organic color developer, the basic colorless dye, and the materials which are added as needed are dispersed by a dispersing machine such as a ball mill, an attriter, a sand grinder, or the like, or by an appropriate emulsifying apparatus to a particle diameter of several microns or less, and mixed with the binder and various additives according to the purpose to obtain a coating color.

In the thermal recording sheet of the present invention, the formation method of the intermediate layer and the recording layer is not specifically limited, but these layers can be formed by a conventional method known in the art, and off-machine coaters or on-machine coaters provided with an air knife coater, a rod blade coater, a bill blade coater, a roll coater, or the like can be appropriately selected.

Furthermore, after the intermediate layer and the recording layer are coated and dried, the individual layer can be smoothed as needed by a super-calender or the like.

In the present invention, the reason why the effect of the present invention is obtained by providing the intermediate layer is considered as follows:

In the present invention, the intermediate layer containing polymeric fine particles having the specific cross-linking structure and the inorganic pigment having an oil absorption of 170 ml/100 g is provided between the substrate and the thermal color developing layer. With this arrangement, the pigment mixture mutually functions, and the intermediate layer containing the pigment fills and smooths microscopic irregularities on the surface of the base paper to suppress penetration of the coating color of thermal recording layer which is subsequently coated, thereby obtaining a heat insulating layer having a high void ratio and enabling uniform coating of the thermal recording layer.

Furthermore, since the polymeric fine particles having the specific cross-linking structure of the present invention are low in thermal conductivity, the intermediate layer itself containing the particles is also low in the conductivity, the heat energy supplied from the thermal head can be effectively used for color developing. Moreover, the cross-linking-structured polymeric fine particles are also superior in heat resistance, sticking and adherence of residue is prevented. Thus, improved dynamic sensitivity, dot reproducibility, and image quality, and prevention of sticking and adherence of residue are achieved.

Best Mode for Practicing the Invention

The present invention will now be described with reference to the examples. In the description, part means part by weight.

[Example 1 (Test Nos. 1-5)]

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU 201-S, Mitsui Toatsu)	X
Calcined kaolin (tradename: ANSILEX, ENGEL HARD, oil absorption: 90ml/100 g)	Y
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

The above compositions were blended to obtain various coating colors for the intermediate layer. These coating colors were coated on fine paper with a substance of 50 g/m^2 to a dry coating amount of 8 g/m^2 and dried.

(Formation of the thermal color developing layer)	
Solution A (color developer dispersion)	Part
4,4'-Isopropylidene-diphenol	6.0
10% Aqueous polyvinylalcohol solution	18.8
Water	11.2
Solution B (dye dispersion)	
3-N-n-dibutylamino-6-methyl-7-anilinofluorane	2.0
10% aqueous polyvinylalcohol solution	4.6
Water	2.6
Solution C (sensitizer dispersion)	
4-Biphenyl-p-tolylether	4.0
10% aqueous polyvinylalcohol solution	5.0
Water	3.0

The above dispersions were individually ground by a sand grinder to an average particle diameter of 1 micron. Then, the dispersions were mixed in the following ratio to obtain a coating color.

Solution A	36.0 parts
Solution B	9.2
Solution C	12.0
Kaolin clay (50% dispersion)	12.0

The above thermal color developing layer coating color was coated on top of the intermediate layer obtained above to a dry coating amount of 6.0 g/m^2 and dried. The resulting sheet was super-calendered to a smoothness of 700-800 seconds to obtain a thermal recording sheet.

[Example 2 (Test Nos. 6-10)]

In the formation of the intermediate layer, the same procedure as Example 1 was used, except that the intermediate layer of the following composition was provided, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU 201-S, Mitsui Toatsu)	X
Silicon dioxide (tradename: NIPSIL E-743, Nippon Silica, oil absorption: 165 ml/100 g)	Y
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Example 3 (Test Nos. 11-15)]

In the formation of the intermediate layer, the same procedure as Example 1 was used, except that the intermediate layer of the following composition was provided, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU OPP-100, Mitsui Toatsu)	X
Calcined kaolin (tradename: ANSILEX, ENGEL HARD, oil absorption: 90ml/100 g)	Y
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Example 4 (Test Nos. 16-20)]

In the formation of the intermediate layer, the same procedure as Example 1 was used, except that the intermediate layer of the following composition was provided, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU OPP-100, Mitsui Toatsu)	X
Silicon dioxide (tradename: NIPSIL E-743, Nippon Silica)	Y
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Comparative Example 1]

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU 201-S, Mitsui Toatsu)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

The above compositions were blended to obtain an intermediate layer coating color. The coating color was coated on fine paper with a substance of 50 g/m^2 to a dry coating amount of 8 g/m^2 and dried.

(Formation of the thermal color developing layer)

Solution A (color developer dispersion)	Part
4,4'-Isopropylidene-diphenol	6.0
10% Aqueous polyvinylalcohol solution	18.8
Water	11.2
Solution B (dye dispersion)	
3-N-n-dibutylamino-6-methyl-7-anilinofluorane	2.0
10% aqueous polyvinylalcohol solution	4.6
Water	2.6
Solution C (sensitizer dispersion)	
4-Biphenyl-p-tolylether	4.0
10% aqueous polyvinylalcohol solution	5.0
Water	3.0

The above dispersions were individually ground by a sand grinder to an average particle diameter of 1 micron. Then, the dispersions were mixed in the following ratio to obtain a coating color.

Solution A	36.0 parts
Solution B	9.2
Solution C	12.0
Kaolin clay (50% dispersion)	12.0

The above thermal color developing layer coating color was coated on top of the intermediate layer obtained above to a dry coating amount of 6.0 g/m^2 and dried. The resulting sheet was super-calendered to a smoothness of 700-800 seconds to obtain a thermal recording sheet.

[Comparative Example 2]

In the formation of the intermediate layer, the same procedure as Comparative Example 1 was used, except that the intermediate layer of the following composition was formed on fine paper with a substance of 50 g/m^2 to a dry amount of 8 g/m^2 and dried, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Styrene-based polymeric fine particles having cross-linking structure (tradename: GLOSSDERU OPP-100, Mitsui Toatsu)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Comparative Example 3]

In the formation of the intermediate layer, the same procedure as Comparative Example 1 was used, except that the intermediate layer of the following composition was formed on fine paper with a substance of 50 g/m^2 to a dry amount of 8 g/m^2 and dried, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Calcined kaolin (tradename: ANSILEX, ENGEL HARD, oil absorption: 90ml/100 g)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Comparative Example 4]

In the formation of the intermediate layer, the same procedure as Comparative Example 1 was used, except that the intermediate layer of the following composition was formed on fine paper with a substance of 50 g/m^2 to a dry amount of 8 g/m^2 and dried, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Silicon dioxide (tradename: NIPSIL E-743, Nippon Silica)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Comparative Example 5]

In the formation of the intermediate layer, the same procedure as Comparative Example 1 was used, except that the intermediate layer of the following composition was formed on fine paper with a substance of 50 g/m^2 to a dry amount of 8 g/m^2 and dried, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Styrene-acrylic copolymer hollow fine particles (tradename: LOPAQUE OP-62, Rohm & Haas)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

[Comparative Example 6]

In the formation of the intermediate layer, the same procedure as Comparative Example 1 was used, except that the intermediate layer of the following composition was formed on fine paper with a substance of 50 g/m^2 to a dry amount of 8 g/m^2 and dried, to obtain a thermal recording sheet.

(Formation of the intermediate layer)	Part
Polystyrene-fine particles (tradename: L8801, Asahi Kasei)	100
Styrene-butadiene copolymer latex (solid content: 48%)	11
10% Aqueous polyvinylalcohol solution	5

The thermal recording sheets obtained in the above Examples and Comparative Examples were tested for the properties. The test results are summarized in Table 1 and Table 2. As can be seen from Examples 1-4 in Table 1 and Table 2, the best effects are obtained when the polymeric fine particles having the cross-linking structure and the inorganic pigment having an oil absorption of less than 170 ml/100 g are used in a ratio of 1:1 to 1:9 (weight ratio). When the content of the polymeric fine particles having the cross-linking structure is greater than the ratio of 1:1, deterioration in dot reproducibility and image quality, sticking, and adherence of grounds result, and when the content of the inorganic pigment having an oil absorption of less than 170 ml/100 g is greater than the ratio of 1:9, a considerable reduction occurs in the dynamic sensitivity.

Table 1 Test Results

Test No.	Pigment (part)		Dynamic color developing density (1)	Dot reproducibility (2)	Sticking (3)	Residue adherence (4)	Total evaluation (5)
	X	Y					
Example 1							
1	66.5	33.3	1.05	△	△	△	△
2	50.0	50.0	1.05	○	○	○	○
3	25.0	75.0	1.02	○	○	○	○
4	10.0	90.0	1.00	○	○	○	○
5	5.6	94.4	0.89	△	○	○	△
Example 2							
6	66.6	33.3	1.05	△	△	△	△
7	50.0	50.0	1.04	○	○	○	○
8	25.0	75.0	1.02	○	○	○	○
9	10.0	90.0	1.01	○	○	○	○
10	5.6	94.4	0.88	△	○	○	△
Example 3							
11	66.6	33.3	1.06	△	△	△	△
12	50.0	50.0	1.06	○	○	○	○
13	25.0	75.0	1.03	○	○	○	○

Table 2 Test Results

Test No.	Pigment (part)		Dynamic color developing density (1)	Dot reproducibility (2)	Sticking (3)	Residue adherence (4)	Total evaluation (5)
	X	Y					
Example 4							
14	10.0	90.0	1.01	○	○	○	○
15	5.6	94.4	0.87	△	○	○	△
16	66.6	33.3	1.08	△	△	△	△
17	50.0	50.0	1.07	○	○	○	○
18	25.0	75.0	1.05	○	○	○	○
19	10.0	90.0	1.01	○	○	○	○
20	5.6	94.4	0.86	△	○	○	△
Comparative Example							
1 21	-	-	0.84	×	×	×	×
2 22	-	-	0.85	×	×	×	×
3 23	-	-	0.91	○	○	△	×
4 24	-	-	0.89	○	○	△	×
5 25	-	-	1.07	×	×	×	×
6 26	-	-	0.85	×	×	×	×

Note (1): Dynamic color developing density: Image density recorded using the Matsushita Denso Thermal Facsimile UF-1000 at a voltage of 14.7V, a resistance of 360Ω, a pulse width of 0.82 ms, and an applied energy of 0.37 mj/dot is measured by a Macbeth densitometer (RD-914, an amber filter used).

Note (2): Dot reproducibility: Printed dot shape of the image dynamic-recorded by the method (1) is visually observed.

Note (3): Sticking: Image recorded using the Matsushita Denso Thermal Facsimile UF-22, GII communication mode, (test environment: 22°C, 65%) is visually observed.

Note (4): Residue adherence: 20 sheets of a vertical line document (B4) are recorded using the Matsushita Denso Thermal Facsimile UF-60 copy mode, and the amount of residue adhered to the thermal head is visually determined.

Note (5): Total evaluation: the dynamic color developing density, dot reproducibility, sticking, and residue adherence are collectively evaluated.

The effects of the present invention are as follows:
(1) With superior heat response, a sharp, high-density image can be obtained even in high-speed, high-density recording (high sensitivity).
(2) Superior dot reproducibility and image quality.
(3) No sticking or residue adherence occurs during thermal printing.

Claims

1. A thermal recording sheet comprising, in order, a substrate, an intermediate layer and a thermal color developing layer containing a chromogenic agent and a color developer as main ingredients, characterized in that the intermediate layer contains particles of a cross-linked polymer having a particle diameter of 0.2 to 5.0 μm and an inorganic pigment having an oil absorption according to JIS K5101 of less than 170 ml/lOOg in a weight ratio of 1:1 to 1:9.

2. A sheet according to claim 1 wherein the polymer is a styrene-based resin.

3. A sheet according to claim 1 wherein the polymer is a copolymer of a cross-linkable monomer and a vinyl monomer.

4. A sheet according to claim 3 wherein the polymer particles are obtainable by the emulsion polymerization

of a monomer mixture containing the cross-linking monomer.

5. A sheet according to claim 3 or 4 wherein said cross-linkable monomer has two polymerizable unsaturated bonds in a molecule.

6. A sheet according to claim 5 wherein the cross-linkable monomer is selected from trimethylolpropanemethacrylate, divinylbenzene and ethyleneglycol-diacrylate.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 3616

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,D	EP-A-0 399 785 (OJI PAPER COMPANY) * page 2, line 35 - page 3, line 8 * & JP-A-02 307 784 (OJI YUKA GOSEISHI COMPANY LIMITED) -----	1-6	B41M5/40
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 JUNE 1993	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
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E : earlier patent document, but published on, or after the filing date
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