

①②

EUROPEAN PATENT APPLICATION

②① Application number: **89118033.3**

⑤① Int. Cl.⁵: **B41M 5/26**

②② Date of filing: **29.09.89**

③③ Priority: **29.09.88 JP 246752/88**

④③ Date of publication of application:
04.04.90 Bulletin 90/14

⑥④ Designated Contracting States:
DE FR GB

⑦① Applicant: **mitsubishi Paper Mills, Ltd.**
4-2, Marunouchi 3-chome
Chiyoda-ku Tokyo(JP)

⑦② Inventor: **Goto, Atsuo**
Rarapouto Fujiyama 101 10-33,
Hanabatake-1-chome
Tsukuba-shi(JP)
Inventor: **Koike, Naomasa**
Tsuchiura Reiku Saido Haitzu 604 13-28,
Kawaguchi-
2-chome Tsuchiura-shi(JP)

⑦④ Representative: **Hansen, Bernd, Dr.rer.nat. et**
al
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4 Postfach 81 04 20
D-8000 München 81(DE)

⑤④ **Thermosensitive recording materials.**

⑤⑦ There is disclosed a thermosensitive recording material, comprising a support, a thermosensitive recording layer coated on said support and comprising a dye precursor and a color developer capable of developing a color of said dye precursor upon heating, and an undercoat layer composed of aggregated high polymer particles coated between said support and said thermosensitive recording layer.

EP 0 361 500 A2

THERMOSENSITIVE RECORDING MATERIALS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5

The present invention relates to thermosensitive recording materials having excellent thermal response and having minimized tailings or foreign matters adhered to a thermal head.

10 DISCUSSION ON RELATED ART

Thermosensitive recording materials are generally composed of a support having provided thereon a thermosensitive recording layer containing as major constituents an ordinarily colorless or slightly colored electron giving dye precursor and an electron receptive developer. Upon being heated by means of a thermal head, thermal pen or laser beam, the dye precursor instantaneously reacts with the developer to form a recorded image, as disclosed in Japanese Patent KOKOKU (Post Exam. Publication) Nos. 43-4160, 45-14039, etc. Because of the advantages of relatively simple design of devices, easy maintenance and making no noise, the recording devices employing such thermosensitive recording materials are being used in a wide field including recording instruments for measurements, facsimiles, printers, terminal devices for computers, labels, and automatic vending machines for railroad tickets and the like. Particularly in the field of facsimiles, demand for thermal sensitive mode has been greatly increasing and the performance of facsimiles has becoming high speed due to reduction in transmission costs. Facsimiles have reduced the cost and minimized the energy consumption. In response to such high speed and low energy performance required for facsimiles, high sensitivity has been demanded for thermosensitive recording materials. On the other hand, a dot density of thermal head was generally 8 lines/mm but has recently become a density as high as 16 lines/mm. In addition, a dot area has become small and, demands for printing small-sized characters in high image quality or printing characters with density gradation by Dither method have been increasing. Thus, good printability, namely, to obtain images faithfully reproduced from dots on a head has been much more demanded than ever.

Attempting to satisfy these requirements, adhesion between a recording sheet and a thermal head was improved by supercalendering to a strong degree but such a treatment resulted in defects of decreasing whiteness, i.e., so called background stain, and the like.

It is proposed in Japanese Patent Application KOKAI (Laid-Open) No. 56-27394 to provide an undercoat layer between a thermosensitive layer and the base paper. By the provision of an undercoat layer, high density images can be obtained in a small energy without any violent supercalendering and higher density can be achieved than before. It is believed that the provision of this undercoat layer would be effective for rendering the surface of a thermosensitive layer after coated smooth by filling up unevenness of a support to provide a smooth surface.

As described above, by the provision of undercoat layer, the higher density recording has been progressed than before. However, demands for much higher sensitivity and more improvement in the dot reproducibility in recent years cannot be coped simply with the provision of undercoat layer merely aiming at smoothening the surface.

45 SUMMARY OF THE INVENTION

An object of the present invention is to provide thermosensitive recording materials having good thermal response and good dot reproducibility in response to requirements for higher sensitivity and improving dot reproducibility which could not be solved by the foregoing techniques as described above.

50

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The arrangement of the present invention is characterized in that aggregated high polymer particles are coated as an undercoat layer interposed between a support and a thermosensitive coating layer.

More specifically, the aggregated high polymer particles coated as the undercoat layer is considered to exhibit the effect of more effectively applying thermal energy to the thermosensitive layer by preventing the thermal energy from a thermal head from escaping to the outside of a system due to the thermally insulating property of porous particles as well as the effect to provide a smoother surface by smoothing the irregularities of the support like an undercoat layer to which only a pigment is coated. Further, it is considered that the elasticity of the porous particle layer improves the close contact property of the surface of a thermosensitive paper to the thermal head and exhibits an excellent dot reproducibility. These porous particles used in the present invention have an outside diameter of 5 μm or less, preferably have an outside diameter of 2 μm or less and most preferably have an outside diameter of 1 μm or less. When, however, the porous particles having an outside diameter greater than 5 μm are used, the thermosensitive recording layer having an excellent thermal response, which is an object of the present invention, cannot be provided.

In the present invention, aggregated high polymer particles can be provided by aggregating fine particles of a high polymer material to particles of the high polymer material emulsified to a diameter of about 0.05 μm - 0.5 μm serving as a core in a polymerizing process so that they have a diameter of 1 μm - 5 μm , the aggregated high polymer particles having an oil absorbing property of 50 - 200 ml/100 g and a specific surface area (BET) of 5 - 20 m^2/g .

These aggregated high polymer particles can provide a thermosensitive recording material which is particularly excellent in a thermal response when styrene-acryl copolymer resin is used. A typical example thereof is XMRP-170 made by Mitsui Toatsu Co., Ltd. or the like. Conventional styrene-acrylic copolymer particles are not porous and they cannot provide a sufficient effect of improving a thermal response because they are not porous.

In the first layer described above, it is also possible to incorporate other pigments in such an amount that does not interfere with the effect of aggregated high polymer particles. As such a pigment, mention may be made of a pigment ordinarily used for coated paper, etc., e.g., an organic pigment such as polyethylene, polystyrene, ethylene-vinyl acetate, urea-formaldehyde resin, etc.; diatomaceous earth, talc, kaolin, calcined kaolin, calcium carbonate, magnesium carbonate, titanium oxide, zinc oxide, silicon oxide, aluminum hydroxide, zinc hydroxide, barium sulfate, etc. They may be used singly or as admixture of two or more. An amount of the pigment described above to be used in combination is not particularly limited but preferably less than 50 wt% of the amount of the first layer.

Further in case that a thermosensitive recording layer is directly provided on the aggregated high polymer particle layer, a color forming component melted by thermal energy from a thermal head is absorbed into the hollow particle layer and colored images are shielded, sometimes resulting in rather decreasing image density or adherence of foreign matters onto the thermal head or sticking upon printing. For these reasons, it is believed that the provision of the oil-absorbing inorganic pigment layer further onto the porous particle layer as the second undercoat layer would not only prevent those defects but also act to render the surface smoother which was already smoothened by providing the first undercoat layer.

As the pigment used for the second undercoat layer of the present invention, those pigments generally used for coated paper, etc. can be used and are exemplified by calcium carbonate, kaolin, calcined kaolin, zinc oxide, titanium oxide, aluminum hydroxide, zinc hydroxide, barium sulfate, silicon oxide, etc. Of these, the pigments showing an oil absorbing amount of 70 ml/100 g or more, especially calcined kaolin and silicon oxide are preferred ones.

The porous particles as the first layer in the present invention are effective when they are coated in a coverage of 1 g/m^2 or more. However, if the porous particles are coated in an excessively large amount, properties as paper are rather injured than improving that of thermosensitive. For example, as the coated layer is thickened, the base paper is thinned to make its whole thickness even. This would result in a problem of flexural rigidity. A coverage of 3 to 15 g/m^2 is thus preferred. In order to exhibit the function as the second layer without injuring the effect of the first layer, a coverage of 1 to 10 g/m^2 of oil-absorbing inorganic pigment of the second layer is most preferred. Where a coverage in the second layer is large, the thermal transfer becomes poor so that the heat insulating properties and elasticity of the first layer are not sufficiently utilizable in some occasion.

By providing a thermosensitive layer on the thus provided undercoat layer, desired properties can be obtained.

Dye precursors used in the present invention are not particularly limited so long as they are generally used for pressure-sensitive recording paper or thermosensitive recording paper. Specific examples include the following dye precursors.

(1) Triarylmethane compounds:

3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (Crystal Violet lactone), 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-(p-dimethylaminophenyl)-3-(2-phenylindol-3-yl)phthalide, 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-5-dimethylaminophthalide, 3,3-bis(2-phenylindol-3-yl)-5-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrol-2-yl)-6-dimethylaminophthalide, etc.

(2) Diphenylmethane compounds:

4,4'-bis-dimethylaminophenyl benzhydryl benzyl ether, N-halophenyl leuco Auramine, 2,4,5-trichlorophenyl leuco Auramine, etc.

(3) Xanthene compounds:

Rhodamine B anilinolactam, Rhodamine B p-chloroanilinolactam, 3-diethylamino-7-dibenzylaminofluorane, 3-diethylamino-7-octylaminofluorane, 3-diethylamino-7-phenylfluorane, 3-diethylamino-7-chlorofluorane, 3-diethylamino-6-chloro-7-methylfluorane, 3-diethylamino-7-(3,4-dichloroanilino)fluorane, 3-diethylamino-7-(2-chloroanilino)fluorane, 3-diethylamino-6-methyl-7-anilinofluorane, 3-(N-ethyl-N-tolyl)amino-6-methyl-7-anilinofluorane, 3-piperazine-6-methyl-7-anilinofluorane, 3-(N-ethyl-N-tolyl)amino-6-methyl-7-phenetylfluorane, 3-diethylamino-7-(4-nitroanilino)fluorane, 3-dibutylamino-6-methyl-7-anilinofluorane, 3-(N-methyl-N-propyl)amino-6-methyl-7-anilinofluorane, 3-(N-ethyl-N-isoamyl)amino-6-methyl-7-anilinofluorane, 3-(N-methyl-N-cyclohexyl)amino-6-methyl-7-anilinofluorane, 3-(N-ethyl-N-tetrahydrofuryl)amino-6-methyl-7-anilinofluorane, etc.

(4) Thiazine compounds:

benzoyl leuco methylene blue, p-nitrobenzoyl leuco methylene blue, etc.

(5) Spiro compounds:

3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3,3'-dichloro-spiro-dinaphthopyran, 3-benzylspiro-dinaphthopyran, 3-methylnaphtho-(3-methoxybenzo)spiro-pyran, 3-propyl-spiro-benzopyran, etc. These dye precursors can be used singly or as admixtures of two or more.

As dye developers used in the present invention, electron accepting compounds generally employed for thermosensitive paper are used; in particular, phenol derivatives, aromatic carboxylic acid derivatives or metal compounds thereof, N,N'-diarylthiourea derivatives, etc. are used. Among them, particularly preferred ones are phenol derivatives. Specific examples are p-phenylphenol, p-hydroxyacetophenone, 4-hydroxy-4'-methyl-diphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, 4-hydroxy-4'-benzenesulfonyloxydiphenylsulfone, 1,1-bis(p-hydroxyphenyl)propane, 1,1-bis(p-hydroxyphenyl)pentane, 1,1-bis(p-hydroxyphenyl)hexane, 1,1-bis(p-hydroxyphenyl)cyclohexane, 2,2-bis(p-hydroxyphenyl)propane, 2,2-bis(p-hydroxyphenyl)butane, 2,2-bis(p-hydroxyphenyl)hexane, 1,1-bis(p-hydroxyphenyl)-2-ethylhexane, 2,2-bis(3-chloro-4-hydroxyphenyl)propane, 1,1-bis(p-hydroxyphenyl)-1-phenylethane, 1,3-di[2-(p-hydroxyphenyl)-2-propyl]benzene, 1,3-di[2-(3,4-dihydroxyphenyl)-2-propyl]benzene, 1,4-di[2-(p-hydroxyphenyl)-2-propyl]benzene, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenylsulfone, 3,3'-dichloro-4,4'-dihydroxydiphenylsulfone, 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone, 3,3'-dichloro-4,4'-dihydroxydiphenylsulfide, methyl 2,2-bis(4-hydroxyphenyl)acetate, butyl 2,2-bis(4-hydroxyphenyl)acetate, 4,4'-thiobis(2-t-butyl-5-methylphenol), bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, 3,4-dihydroxy-4'-methyl-diphenylsulfone, benzyl p-hydroxybenzoate, chlorobenzyl p-hydroxybenzoate, propyl p-hydroxybenzoate, butyl p-hydroxybenzoate, dimethyl 4-hydroxyphthalate, benzyl gallate, stearyl gallate, salicylanilide, 5-chlorosalicylanilide, etc.

In addition, the thermosensitive layer may also contain as pigments diatomaceous earth, talc, kaolin, calcined kaolin, calcium carbonate, magnesium carbonate, titanium oxide, zinc oxide, silicon oxide, aluminum hydroxide, urea-formalin resin, etc.; may further contain waxes such as N-hydroxymethylstearic amide, stearic amide, palmitic amide, etc.; naphthol derivatives such as 2-benzoyloxynaphthalene, etc.;

biphenyl derivatives such as p-benzylbiphenyl, 4-allyloxybiphenyl, etc.; polyether compounds such as 1,2-bis(3-methylphenoxy)ethane, 2,2'-bis(4-methoxyphenoxy)diethyl ether, bis(4-methoxyphenyl)ether, etc.; carbonate or oxalate diester derivatives such as diphenyl carbonate, dibenzyl oxalate, di(p-fluorobenzyl) oxalate, etc.

In addition, there may be incorporated, for purposes of preventing head abrasion, prevention of sticking, etc., higher fatty acid metal salts such as zinc stearate, calcium stearate, etc.; waxes such as paraffin, oxidized paraffin, polyethylene, oxidized polyethylene, stearic amide, castor wax, etc.; dispersing agents such as sodium dioctylsulfosuccinate, etc.; UV absorbing agents of benzophenone type, benzotriazole type, etc. and further surface active agents, fluorescent dyes, etc., if necessary and desired.

In the present invention, as adhesives used for the first undercoat layer, second undercoat layer and thermosensitive recording layer used in the present invention, various adhesives generally used are usable. Examples of the adhesives include water soluble adhesives such as starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, polyvinyl alcohol, modified polyvinyl alcohol, sodium polyacrylate, acrylic amide/acrylate copolymer, acrylamide/acrylate/methacrylate ternary copolymer, alkali salts of styrene/maleic anhydride copolymer, alkali salts of ethylene/maleic anhydride copolymer, etc.; latexes such as polyvinyl acetate, polyurethane, polyacrylates, styrene/butadiene copolymer, acrylonitrile/butadiene copolymer, methyl acrylate/butadiene copolymer, ethylene/vinyl acetate copolymer, etc. As the support used in the present invention, paper is mainly used. Non-woven cloth, a plastic film, synthetic paper, metal foil and the like or a composite sheet obtained by combining them may optionally be employed.

(E) Examples

Next, the present invention will be described in more detail by referring to the examples.

Parts and % shown below are all based on weight. Numeral values representing coated amounts or coverages are dry weights, unless otherwise indicated.

Example 1

(1) Preparation of Suspension A (coating liquid for the first layer)

A mixture having the following composition was stirred to prepare a coating liquid for the first layer.

XMRP-100 (porous particle emulsion composed of styrene-acryl copolymer resin made by Mitsui Toatsu Kagaku K.K.; particle diameter: about 1.0 μ m, solid content: 40%)	100 parts
Styrene-Butadiene copolymer latex (50% aqueous dispersion)	20 parts
Water	20 parts

(2) Preparation of Suspension B (coating liquid for the second layer)

A mixture having the following composition was stirred to prepare a coating liquid for the second layer.

ANSILEX (calcined kaolin made by Engelhardt Co., Ltd.)	100 parts
Styrene-Butadiene copolymer latex (50% aqueous dispersion)	24 parts
MS4600 (Phosphoric acid ester starch made by Nihon Shokuhin K.K.; 10% aqueous solution)	60 parts
Water	52 parts

(3) Preparation of Thermosensitive Suspension

A mixture having the following composition was ground into a mean grain diameter of about 1 μm with a sand grinder to prepare [Suspension C] and [Suspension d], respectively.

[Suspension C]	
3-dibutyl amino-6-methyl-7-anilino-fluorane	40 parts
Aqueous solution containing 10% polyvinyl alcohol	20 parts
Water	40 parts

[Suspension D]	
Bisphenol A	50 parts
Benzoyloxy naphthalene	50 parts
Aqueous solution containing 10% polyvinyl alcohol	50 parts
Water	100 parts

Then, a thermosensitive suspension was prepared in the following formulation, using the prepared [Suspension C] and [Suspension D].

[Suspension C]	50 parts
[Suspension D]	250 parts
Zinc stearate (40% dispersion)	25 parts
Aqueous solution containing 10% polyvinyl alcohol	216 parts
Calcium carbonate	50 parts
Water	417 parts

Each of the thus prepared coating suspensions was coated onto a base paper weighing 40 g/m² in the following coverages with a Mayor bar to prepare a thermosensitive recording material.

First layer	8 g/m ²
Second layer	3 g/m ²
Thermosensitive layer	5.5 g/m ²

Example 2

A thermosensitive layer was prepared in a manner similar to Example 1 except that a coating liquid for the first layer was prepared by stirring a mixture having the following composition and coated in a coverage of 8 g/m².

5	MXRP-140 (porous particle emulsion composed of styrene-acryl copolymer resin made by Mitsui Toatsu Kagaku K.K.; particle diameter: about 0.5 μ m, solid content: 40%)	100 parts
	Styrene-Butadiene copolymer latex (50% aqueous dispersion)	20 parts
	Water	

10

Example 3

15 A thermosensitive recording material was prepared in a manner similar to Example 1 except that a coating liquid for the first layer was prepared by stirring a mixture having the following composition and coated in a coverage of 8 g/m².

20	XM RP-170 (porous particle emulsion composed of styrene-acryl copolymer resin made by Mitsui Toatsu Kagaku K.K.; particle diameter: about 0.9 μ m, solid content: 40%)	100 parts
	Styrene-Butadiene copolymer latex (50% aqueous dispersion)	10 parts
	Water	20 parts

25

30 Example 4

A thermosensitive recording material was prepared in such a manner that the coating liquid for the first layer used in Example 1 was coated in a coverage of 8 g/m², no coating was effected to the second layer and the thermosensitive suspension was directly coated like Example 1.

35

Example 5

40 A thermosensitive recording material was prepared in a manner similar to Example 1 except that 100 parts of Ultra White-90 (kaolin for the purpose of coating, made by Engelhardt Co., Ltd.) were used in place of 100 parts of ANSILEX in the preparation of Suspension B (coating liquid for the second layer) used in Example 1.

45 Comparative Example 1

A thermosensitive recording material for the comparative study was prepared by directly coating the thermosensitive coating liquid prepared in Example 1 in a coverage of 5.5 g/m² without coating the coating liquids for the first and second layers prepared in Example 1.

50

Comparative Example 2

55 A thermosensitive recording material for the comparative study was prepared by directly coating the coating liquid for the second layer prepared in Example 1 on a base paper in a coverage of 8 g/m² and then coating the thermosensitive suspension prepared in Example 1 in a coverage of 5.5 g/m² thereon without coating the coating liquid for the first layer prepared in Example 1.

Comparative Example 3

A thermosensitive recording material for the comparative study was prepared by directly coating the coating liquid for the second layer prepared in Example 1 on a base paper in a coverage of 11 g/m² and then coating the thermosensitive suspension prepared in Example 1 to the amount of 5.5 g/m² thereon without coating the coating liquid for the first layer prepared in Example 1.

Comparative Example 4

A thermosensitive recording material was prepared in a manner similar to Example 1 except that a coating liquid for the first layer was prepared by stirring a mixture having the following composition and coated in a coverage of 8 g/m².

Spherical particle emulsion composed of styrene-acryl copolymer resin (particle diameter: about 1.0 μm, solid content: 40%)	100 parts
Styrene-Butadiene copolymer latex (50% aqueous dispersion)	10 parts
Water	20 parts

Comparative Example 5

In Comparative Example 4, a thermosensitive recording material was prepared by directly coating the thermosensitive suspension after coating the coating liquid for the first layer in a coverage of 8 g/m² without coating the second layer.

The thermosensitive recording materials prepared as described above were treated by a supercalendering so as to have complied with a Beck's degree of smoothness varied between 400 and 500 seconds. And these materials were compared with respect to recording density, printability and degree of adhering tailings or foreign matters using a FIII facsimile test machine. The test machine was (TH-PMD) manufactured by Okura Denki Co., Ltd. Printing was performed using with a thermal head showing its dot density of 8 dots/mm and its head resistance of 185 ohm at a head voltage of 15 V, for its load time of 0.10 ms and 0.12 ms. The recording density was measured with Macbeth RD-918 reflection densitometer. These results are shown in Table 1.

Table 1

	sensitivity		printability	tailings
	0.10 ms	0.12 ms		
Example 1	0.86	1.22	○	○
2	0.86	1.23	○	○
3	0.95	1.29	○	○
4	0.77	1.10	○ ~ Δ	○ ~ Δ
5	0.80	1.14	○	○ ~ Δ
Comparative Example 1	0.34	0.57	X	X
2	0.56	0.97	Δ	○
3	0.61	1.01	Δ	○
4	0.70	1.09	Δ	○
5	0.58	0.95	Δ	Δ
○ good				
○ ~ Δ relatively good				
Δ no good				
X bad				

Claims

1. A thermosensitive recording material, comprising a support, a thermosensitive recording layer coated on said support and comprising a dye precursor and a color developer capable of developing a color of said dye precursor upon heating, and an undercoat layer composed of aggregated high polymer particles coated between said support and said thermosensitive recording layer.

2. A thermosensitive recording layer according to claim 1, wherein said aggregated high polymer particles are composed of styrene-acryl copolymer resin.

3. A thermosensitive recording layer according to claim 1, wherein a second undercoat layer mainly composed of a pigment is further coated between said thermosensitive layer and the first undercoat layer.

4. A thermosensitive recording layer according to claim 3, wherein said pigment of said second undercoat layer is composed of an oil-absorbing inorganic pigment.

5. A thermosensitive recording layer according to claim 1, wherein an oil absorbing amount of said oil-absorbing pigment is at least 70 ml/100 g.