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

(57) In a heat-sensitive recording paper comprising a support coated with a heat-sensitive color-forming layer containing a color-forming dye material and a color developer, heat-sensitive color-forming layer contains parabenzylobiphenyl and 4,4'-thiobis(6-tertiary-butyl-3-methylphenyl) in order to develop highly sensitive heat-sensitive recording paper which would neither form color in non-image areas nor fade in image areas even when it was submerged in water.

EP 0 372 878 A2

HEAT-SENSITIVE RECORDING PAPER

The present invention relates to heat-sensitive recording paper. More particularly, it relates to heat-sensitive recording paper that has not only high sensitivity but also sufficient resistance to water to experience only limited fading of image even if it is submerged in water.

It has been known for many years that basic leuco dyes react with organic acid substances when fused upon heating, thereby forming color. Applications of this color-forming reaction to recording paper are also known and described in Japanese Patent Publication Nos. 43-4160 and 45-14039.

Such heat-sensitive recording paper finds use in a broad range of applications including measuring recorders, terminal printers such as word processors, facsimiles, automatic ticket venders and bar code labels. As these recording apparatus have become versatile in applications and their performance improved, the requirements to be satisfied by heat-sensitive recording paper have become strict. Stated specifically, with the recent increase in the adoption of the POS (point-of-sale) system at retail stores and supermarkets, it has become popular to use heat-sensitive recording paper on which bar codes, the weight of an item, its unit price, sales price and other information are to be recorded with a printer and this has given rise to the need for the development of heat-sensitive recording paper that will neither form color in non-image areas nor fade in image-areas even if they are placed in contact with overwrap films or exposed to sodium chloride or fluids such as oils, vinegars, soy sauce and water.

With a view to meeting this need, it has been proposed that a protective layer be provided by coating the surface of a heat-sensitive color-forming layer on ordinary paper with an aqueous emulsion of a resin having a film-forming capability and resistance to chemicals (Japanese Patent Public Disclosure No. 54-128347) or a water-soluble high-molecular weight compound such as polyvinyl alcohol (Japanese Utility Model Public Disclosure No. 56-125354). These methods are capable of preventing the color formation in non-image areas or fading in image areas even if the heat-sensitive recording paper is placed in contact with overwrap films or exposed to oils. However, if the heat-sensitive recording paper is submerged in water, the latter will penetrate into the paper either through the protective resin film or the protective layer made of a water-soluble high-molecular weight compound or from the unprotected edge or back side. Hence, it has been difficult to obtain satisfactory labels by these conventional methods.

More recently, a demand has arisen for the development of highly sensitive heat-sensitive recording paper because of the two major advantages it offers: first, it enables faster recording since heating with the thermal head can be shortened and because low power consumption suffices for producing satisfactory density; and second, it contributes to prolongation of the head's life by reducing the electric power that need be applied to the thermal head.

Another proposal that has been made in the prior art consists of incorporating benzylbiphenyls, alkyl benzylbiphenyls or hydrides thereof in a heat-sensitive color-forming layer (Japanese Patent Public Disclosure No. 60-82382). This method is effective in producing a highly sensitive record by rapid thermal response but the resulting image does not resist fading when submerged in water. Fading of image in water could be prevented by using two or more acidic substances in mixture but this method is also unsuitable for practical applications since it will cause extensive staining of the white background.

An object, therefore, of the present invention is to provide heat-sensitive recording paper that is capable of producing a record of high sensitivity, that will resist fading of image areas even if it is submerged in water, and that will experience only limited fogging in the white background.

As a result of intensive studies conducted in order to develop highly sensitive heat-sensitive recording paper that would neither form color in non-image areas nor fade in image areas even when it was submerged in water, the present inventor found that this objective could be attained by containing both parabenzylbiphenyl and 4,4'-thiobis(6-t-butyl-3-methylphenol) in a heat-sensitive color-forming layer. Stated more specifically, the heat-sensitive color-forming layer that contained these compounds had high sensitivity, did not form color in non-image areas or fade in image areas upon prolonged immersion in water, and experienced very limited fogging in the white background.

Common leuco dyes may be used in the heat-sensitive color-forming layer of the heat-sensitive recording paper of the present invention. Most common are fluoran-based leuco dyes which may be exemplified by the following:

- 3-diethylamino-6-methyl-7-anilino-fluoran;
- 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino-fluoran;
- 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran;
- 3-diethylamino-7-(ortho-chloroanilino)-fluoran;
- 3-diethylamino-7-(meta-trifluoromethylanilino)-fluoran;

3-diethylamino-6-methyl-7-(ortho,para-dimethylanilino)fluoran;
 3-pyrrolidino-6-methyl-7-anilinofluoran;
 3-piperidino-6-methyl-7-anilinofluoran; and
 3-dibutylamino-6-methyl-7-anilinofluoran;

5 Organic acidic substances that react with such leuco dyes upon heating to form a visible color must be solid at ambient temperatures and liquefy or vaporize at 50 °C and above in order to insure that the above-stated object of the present invention can be attained. Furthermore, the colored reaction product should not fade even if it is submerged in water. The present inventor found that 4,4'-thiobis(6-t-butyl-3-methylphenol) was very effective for this purpose. The effectiveness of this compound would be attributable to the
 10 following three facts: it is solid at ambient temperature; it liquefies or vaporizes at 164 °C; and it has a sulfur atom in its structure.

Parabenzylbiphenyl which is the other essential component of the heat-sensitive color-forming layer works as an accelerator of color formation. Presumably, it will cause a melting point dropping effect when present in combination with the organic acidic substance and react with the leuco dye at a temperature that
 15 is lower than the melting point of either compound. Further, the incorporation of this parabenzylbiphenyl will contribute to the accomplishment of a higher sensitivity and a higher degree of whiteness in the background.

The 4,4'-thiobis(6-t-butyl-3-methylphenol) and parabenzylbiphenyl are generally used with the leuco dye in such amounts that 0.5 - 10 parts by weight of 4,4'-thiobis(6-t-butyl-3-methylphenyl) and 0.2 - 10 parts by
 20 weight of parabenzylbiphenyl are combined with one part by weight of the leuco dye.

Organic or inorganic pigments commonly employed in coating and other applications may be used as fillers in the heat-sensitive recording paper of the present invention. Typical examples include calcium carbonate, clay, calcined clay, aluminum hydroxide, talc, magnesium carbonate, silica, polystyrene particles and a urea-formaldehyde resin powder. Suitable binders may be selected from among the following: water-
 25 soluble resins such as various polyvinyl alcohols, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, styrene-acrylic copolymer, isobutylene-maleic acid copolymer and starches; and aqueous emulsions of styrene-butadiene copolymer, vinyl acetate copolymers, ethylene-vinyl acetate copolymer, etc. Desirably, binders of high water resistance are selected and these may be used in combination with either themselves or crosslinking agents. Various waxes may also be incorporated in order to provide greater ease
 30 in coating operations.

Supports that can be used in the present invention may be selected from among paper, plastic films, synthetic paper, and any other suitable materials.

If desired, the heat-sensitive recording paper of the present invention may be provided with conventional protective layers that are effective in preventing color formation in non-image areas or fading in image
 35 areas due to contact with packaging films or exposure to oils. Such protective layers may be made of film-forming water-soluble resins or chemical resistant aqueous emulsions. The pigments already described above, lubricants and crosslinking agents may also be used for the purpose of antiblocking or increasing the strength of water-resistant films having good slip properties.

The following examples and comparative examples are provided for the purpose of further illustrating
 40 the present invention but are in no way to be taken as limiting.

Preparation of Coating Solutions for Heat-Sensitive Color-Forming Layer:

45 Solutions A - D were prepared by pulverizing compositions having the recipes shown below with a sand grinder until an average particle size of 1.0 μm was attained.

Solution A	
3-dibutylamino-6-methyl-7-anilinofluoran	200 parts
Polyvinyl alcohol (10% aq. sol.)	200 parts
Water	600 parts

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Solution B	
4,4'-thiobis(6-tertiary-butyl-3-methylphenol) ("Yoshinox SR" of Yoshitomi Pharmaceutical Ind., Ltd.)	100 parts
Parabenzylbiphenyl ("PBBP" of Nippon Steel Chemical Co., Ltd.)	100 parts
Calcium carbonate ("Brilliant 15" of Shiraishi Kogyo K.K.)	100 parts
Polyvinyl alcohol (10% aq. sol.)	200 parts
Water	500 parts

Solution C	
4,4'-isopropylidenediphenol ("Bisphenol A" of Mitsui Toatsu Chemicals, Inc.)	100 parts
Stearylamine	100 parts
Calcium carbonate ("Brilliant 15" of Shiraishi Kogyo K.K.)	100 parts
Polyvinyl alcohol (10% aq. sol.)	200 parts
Water	500 parts

Solution D	
4,4'-isopropylidenediphenol ("Bisphenol A" of Mitsui Toatsu Chemicals, Inc.)	50 parts
4,4'-Cyclohexylidenediphenol ("Antigen W" of Sumitomo Chemical Co., Ltd.)	50 parts
Stearylamine	100 parts
Calcium carbonate ("Brilliant 15" of Shiraishi Kogyo K.K.)	100 parts
Polyvinyl alcohol (10% aq. sol.)	200 parts
Water	500 parts

Example 1

Solution A (100 parts by weight), Solution B (400 parts by weight), a styrene-butadiene copolymer latex (50% solids; 500 parts by weight) and a zinc stearate emulsion (20% solids; 625 parts by weight) were mixed to form a coating solution for heat-sensitive color-forming layer. This solution was applied onto fine paper (basis weight, 50 g/m²) in a dry coating weight of 5 g/m² and dried to prepare heat-sensitive recording paper.

Example 2

Heat-sensitive recording paper was prepared as in Example 1 except that the heat-sensitive color-forming layer was coated with a protective layer that was formed from a coating solution having the recipe shown below and which was deposited in a dry weight of 3.0 g/m².

Coating Solution for Protective Layer	
Polyvinyl alcohol (10% aq. sol.) (polymerization degree, 1100; saponification degree, 98.5%)	100 parts
Calcined clay (Ansilex 93, Engelhard Corp.)	6 parts
20% zinc stearate emulsion	2 parts
Glyoxal (40% aq. sol.)	1 part

These ingredients were dispersed with a sand grinder to prepare the coating solution for protective layer.

Comparative Example 1

Solution A (100 parts by weight), Solution C (400 parts by weight), a styrene-butadiene copolymer latex (50% solids; 500 parts by weight) and a zinc stearate emulsion (20% solids; 625 parts by weight) were mixed to form a coating solution for heat-sensitive color-forming layer. This solution was applied onto fine paper (basis weight, 50 g/m²) in a dry coating weight of 5 g/m² and dried to prepare heat-sensitive recording paper.

Comparative Example 2

Heat-sensitive recording paper was prepared as in Comparative Example 1 except that the heat-sensitive color-forming layer was coated with a protective layer that was formed from a coating solution having the recipe shown below and which was deposited in a dry weight of 3.0 g/m².

Coating Solution for Protective Layer	
Polyvinyl alcohol (10% aq. sol.) (polymerization degree, 1100; saponification degree, 98.5%)	100 parts
Calcined clay (Ansilex 93, Engelhard Corp.)	6 parts
20% zinc stearate emulsion	2 parts
Glyoxal (40% aq. sol.)	1 part

Comparative Example 3

Solution A (100 parts by weight), Solution D (400 parts by weight), a styrene-butadiene copolymer latex (50% solids; 500 parts by weight) and a zinc stearate emulsion (20% solids; 625 parts by weight) were mixed to form a coating solution for heat-sensitive color-forming layer. This solution was applied onto fine paper (basis weight, 50 g/m²) in a dry coating weight of 5 g/m² and dried to prepare heat-sensitive recording paper.

Comparative Example 4

Heat-sensitive recording paper was prepared as in Comparative Example 3 except that the heat-sensitive color-forming layer was coated with a protective layer that was formed from a coating solution having the recipe shown in Comparative Example 2 and which was deposited in a dry weight of 3.0 g/m².

The samples of heat-sensitive recording paper prepared in Examples 1 and 2 and in Comparative Examples 1 - 4 were supercalendered to a surface smoothness of 300 seconds as measured by an Oji-Bekk method (JIS P-8123). The thus finished products were evaluated for their performance and the results are shown in Table 1. The evaluation tests were conducted by the following methods:

Whiteness

Measured with a Hunter whiteness meter (equipped with a blue filter) in accordance with JIS K-8123.

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Sensitivity for Color Formation

Recording was conducted with a facsimile testing machine (product of Matsushita Electronic Parts Co., Ltd.) having a thermal head capable of main scanning at a density of 8 dots/mm. The other recording conditions were as follows: head voltage, 16 V; current application time, 20 ms./line; and sub-scanning density, 3.85 lines/mm. Thereafter, the obtained color density was measured with a Macbeth reflection densitometer (RD 514).

15 Water Resistance

After recording under the conditions described above, the heat-sensitive recording paper was submerged in tap water (40 °C) for 24 hours, recovered, dried with air and subjected to measurements of the densities in image and non-image areas with a Macbeth reflection densitometer (RD 514).

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Table 1

25			Example		Comparative Example			
			1	2	1	2	3	4
30	Water resistance of recorded area	Before testing	1.33	1.30	1.02	1.00	1.05	1.04
		After testing	1.30	1.28	0.14	0.18	0.72	0.75
		Color retention	97%	98%	14%	18%	69%	72%
	Water resistance of white background	Before testing	0.09	0.10	0.11	0.11	0.25	0.29
		After testing	0.10	0.10	0.11	0.12	0.30	0.32
35	Degree of whiteness		82%	78%	75%	70%	65%	60%
	Sensitivity for color formation		1.33	1.30	1.02	1.00	1.05	1.04

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The above data show that the present invention enables the preparation of a heat-sensitive recording material that has good balance between various aspects such as whiteness, sensitivity for color formation and water resistance in both image and non-image areas.

45 **Claims**

1. Heat-sensitive recording paper comprising a support coated with a heat-sensitive color-forming layer containing a color-forming dye material and a color developer, said heat-sensitive color-forming layer containing parabenzylobiphenyl and 4,4'-thiobis(6-tertiary-butyl-3-methylphenol) as essential ingredients.

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