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71 Applicant : **KANZAKI PAPER
MANUFACTURING CO., LTD.
7, Ogawa-cho 3-chome Kanda Chiyoda-ku
Tokyo-to (JP)**

72 Inventor : **Seki, Shigetoshi
No. 24-101, Hanayamahigashimachi 2-ban
Kita-ku, Kobe-shi, Hyogo (JP)
Inventor : Fuku, Terunobu
1-6-12-20-6, Higashi-Naruocho
Nishinomiya-shi, Hyogo (JP)
Inventor : Ishida, Koichi
9-8-207, Ohama-cho 2-chome
Amagasaki-shi Hyogo (JP)
Inventor : Takayama, Yukio
17-1-513, Tokuranishi 2-chome
Toyonaka-shi, Osaka (JP)**

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

54 **Heat-sensitive recording material useful for labels.**

57 A heat-sensitive recording material useful for labels has on a surface of a base sheet a heat-sensitive recording layer which comprises a colorless or pale colored basic chromogenic material and a color developer developing a color by contacting with the chromogenic material, and an adhesive layer on the back of the base sheet. There is formed, on the back or both surfaces of the base sheet, a coating layer which mainly comprises inorganic and/or organic pigments together with a binder and in which the K & N ink absorption is adjusted to from 5.0 g/m² to 10.0g/m² to improve the image-retainability and the plasticizer resistance of the heat-sensitive recording material.

HEAT-SENSITIVE RECORDING MATERIAL USEFUL FOR LABELSBackground of the Invention

5 This invention relates to a heat-sensitive recording material useful for labels, which is superior in image-retainability and stably produced without blocking, further in which the developed color images have a high PCS value when the back of the base sheet is printed.

There has 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 brought into contact with each other to produce color images. 10 These heat-sensitive recording materials are relatively cheap and the recording machines are compact and easily maintained. Therefore, they have been used not only as a recording medium of facsimiles, various calculator and the like, but also in the other various fields.

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

15 It is required for the heat-sensitive recording material to have good retainability of the recorded images. Therefore, in order to improve the image-retainability, there have been proposed such as the method of coating on the heat-sensitive recording layer an aqueous emulsion of a film-formable resin superior in chemical resistance (Japanese Laid-Open Patent Publication No.128347 of 1979), and the method of coating a water-soluble polymer, e.g., polyvinylalcohol and the like (Japanese Laid-Open Utility Model Publication No.125354 of 1981).

20 However, since heat-sensitive recording materials used as a label are frequently used in the state of sticking on a wrapping film confining a plasticizer, it is strongly required to prevent a discoloration generated by the affection of the plasticizer.

In general heat-sensitive recording materials, an adhesive layer is formed on the back of the base sheet and a release sheet base material is applied to the adhesive layer. As an adhesive agent of the adhesive layer, 25 there are generally used rubber type or acrylic type adhesive agents. When heat-sensitive recording materials for label in which a rubber type adhesive agent is used are sticking on a wrapping film containing a plasticizer, the plasticizer is easily migrated into the adhesive layer. Particularly, when the base sheet is paper, the plasticizer is penetrated into paper and further arrived in the heat-sensitive recording layer. As a result of it, the image-retainability of the heat-sensitive recording materials is very lowered.

30 In order to improve the problem, a back-coating layer mainly comprising a water-soluble polymer has been applied as described Japanese Laid-Open Utility Model Publication No.140461 of 1981. However, since the coating layer is inferior in water-resistance, when the back-coating layer is formed, a so-called "blocking phenomena" which is a phenomena of adhering the back-coating layer with the heat-sensitive recording layer in the winding step occurs to make the commercial value of a heat-sensitive recording material very low. Further, 35 as a method for preventing the blocking phenomena, there has been disclosed in Japanese Laid-Open Patent Publication No.32081 of 1987 that a colloidal silica is comprised in the back-coating layer. However, by this method, a substantial plasticizer resistance can not be obtained.

40 Further, when the back of a heat-sensitive recording material is printed to obtain a propaganda effect, a PCS value (namely, difference between optical densities of the recorded image and the background) of the heat-sensitive recording material inferior in opaqueness is lowered.

Therefore, it is an object of the present invention to provide a heat-sensitive recording material useful for labels, which is superior in plasticizer-resistance and can be produced without a substantial "blocking phenomena", and in which the recorded images has a high PCS value when the back is printed.

45 Summary of the Invention

The heat-sensitive recording material according to the present invention has a heat-sensitive recording layer which comprises a colorless or pale colored basic chromogenic material and a color developer developing a color by contacting with the chromogenic material on a surface of the base sheet, and an adhesive layer on 50 the back of the base sheet. On the back or both surfaces of the base sheet, a coating layer mainly comprising inorganic and/or organic pigments together with a binder is formed, and K & N ink absorption of the coating layer is adjusted to from 5.0 g/m² to 10.0 g/m².

55 Detailed Description of the Invention

The most important features of the present invention are the formation of a coating layer which mainly com-

prises inorganic and/or organic pigments together with a binder on the back or both surfaces of the base sheet, and the adjustment of K & N ink absorption of the coating layer to from 5.0 g/m² to 10.0 g/m², preferably to from 5.0 g/m² to 7.0 g/m².

When the coating layer has a K & N ink absorption of more than 10.0 g/m², the plasticizer resistance of the heat-sensitive recording material becomes very bad.

The K & N ink used in the present invention is a colored ink only used for measuring ink absorption of paper. The measuring method generally comprises the steps of coating the K & N ink in excess on the whole surface of a coated paper, allowing it to stand for 2 minutes at the room temperature, substantially wiping the excess amount of the ink from the surface with a gauze, waste or the like, and then examining the variation of the whiteness as a measure of the ink-absorption of paper.

The K & N ink absorption in the present invention is defined as an absorbed ink-amount per square meter which is obtained by measuring the ink amount absorbed in paper after the above treatment.

It has been found that the calculated K & N ink absorption is mutually related with the plasticizer resistance of heat-sensitive recording materials. Namely, when the heat-sensitive recording material is inferior in plasticizer resistance, the ink absorption becomes larger. On the contrary, a film-like surface which is very superior in plasticizer resistance shows a very low ink absorption.

However, although a very remarkably film-like treated surface has a low K & N ink absorption, it has the following problems ; such as that, when a back-printing is applied, the printed pattern is seen through the paper, and that the contrast between the recorded images and the background becomes bad to lower the so-called PCS value. Generally, as to heat-sensitive recording materials, a PCS value of at least 0.9 is preferred, because the contrast becomes very bad when the PCS value is less than 0.85. Further, in order to maintain such a PCS value, it is preferred to adjust the K & N ink absorption to at least 5.0 g/m², more preferably to at least 6.0 g/m².

Accordingly, the K & N ink absorption useful in the present invention is 5.0 g/m² to 10.0g/m², preferably 6.0 g/m² to 10.0g/m² and the most preferably 6.0 g/m² to 7.0g/m².

The method for evaluation of PCS value will be described hereinafter.

The heat-sensitive recording materials according to the present invention are not obtained by merely using paper in which the plasticizer resistance is improved by making the K & N ink absorption lower. It is necessary in the present invention to add pigments in the coating layer applied on the back or both surfaces of the base sheet to prevent a lowering of the PCS value depending on a remarkable lowering of the K & N ink absorption and to prevent the occurrence of a blocking phenomena. Further, as the pigments added in the coating layer, there are preferably used, in consideration of the K & N ink absorption, those having an oil absorption of less than 50 ml/100 g, more preferably 10 to 40 ml/100 g, which is measured by JIS K-5101.

As the pigments, there are exemplified inorganic pigments such as kaolin, clay, calcium carbonate, aluminum hydroxide, silicon oxide, calcined clay and the like ; and organic pigments such as styrene microballs, polyamide powder, polyethylene powder, urea-formaldehyde resin filler, raw starch particles and the like. The other pigments may be used. Those pigments may be used either solely or in combination.

The binders contained in the coating layer are not particularly limited. Among them, there are included proteins such as casein and the like ; starches such as cationic starch, phosphoric esterified starch, oxidized starch and the like ; cellulose derivatives such as hydroxyethylcellulose, carboxymethylcellulose and the like ; gum arabic, polyvinyl alcohol, carboxy-group modified polyvinyl alcohol, acetoacetyl-group modified polyvinyl alcohol, salts of diisobutyrenemaleic anhydride copolymer, salts of styrene-maleic anhydride copolymer, urea resins, melamine resins, amide resins and the like. Further, with considering the printability such as surface strength, the preferable binders are those having a glass transition temperature of 30 °C or less, particularly from -30 °C to 0 °C, such as latexes of conjugated diene polymers, e.g., styrene-butadiene copolymer, methylmethacrylate-butadiene copolymer and the like ; acrylic polymers, e.g., homopolymer or copolymer of acrylic esters and/or methacrylic esters ; vinyl polymers, e.g., ethylene-vinyl acetate copolymer and the like.

The binders are preferably used in an amount of 8 to 40 % by weight, more preferably 10 to 30 % by weight with respect to the total solid amount of the coating composition. When the amount is more than 40 %, the drying speed of the ink (namely, ink set) is inferior, and when the amount is less than 8 %, the surface strength is lowered.

Further, if necessary, the coating composition may include various kinds of additives such as dispersing agents, e.g., sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl alcohol sulfate, metal salts of fatty acids and the like ; lubricants, e.g., zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and the like ; ultraviolet ray absorbers, e.g., benzophenone compounds and the like ; antifoaming agents ; fluorescent dyes ; coloring dyes and the like.

As the coating methods, there may be used various known methods. The coating composition is applied on the base sheet with use of such as an air-knife coater, blade coater, bar coater, roll coater, gravure coater, curtain coater or the like, and dried.

The amount of the applied coating composition is not also particularly limited, but it is generally controlled within the range of 3 to 30 g/m², preferably 5 to 15 g/m² on dry basis.

5 In order to obtain the desired advantages of the present invention, it is important to prepare the coating layer which has a K&N ink absorption of 5.0 g/m² to 10.0 g/m² by controlling the used materials, mixed ratio, coated amount and the like.

As the basic chromogenic materials used in the present invention, there are exemplified various well-known colorless or pale colored basic chromogenic materials. For example, triallylmethane compounds such as 3,3-
10 bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)-
phthalide, 3,3-bis(1,2-dimethylindole-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindole-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazole-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindole-3-yl)-6-
15 dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrole-3-yl)-6-dimethylaminophthalide and the like ; diphenylmethane compounds such as 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halophenyl-leuco-
coauramine, N-2,4,5-trichlorophenyl-leucoauramine and the like ; thiazine compounds such as benzoyl-leuco-
methylene blue, p-nitrobenzoyl-leucomethylene blue and the like ; spiro compounds such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-
20 dinaphthopyran-, 3-methyl-naphtho-(6'-methoxybenzo)spiropyran, 3-propyl-spiro-dibenzopyran and the like ;
lactam compounds such as Rhodamine-B anilinolactam, Rhodamine(p-nitroanilino)lactam, Rhodamine(o-chloro-
anilino)lactam and the like ; and fluoran compounds such as 3-dimethylamino-7-methoxyfluoran, 3-
diethylamino-6-methoxyfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethyla-
25 mino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-
diethylamino-7-(N-acetyl-N-methylamino)fluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-
dibenzylaminofluoran, 3-diethylamino-7-(N-methyl-N-benzylamino)fluoran, 3-diethylamino-7-N-chloroethyl-N-
methylaminofluoran, 3-diethylamino-7-N-diethylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylami-
30 nofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran, 3-diethylamino-6-methyl-7-phenylaminof-
luoran, 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-phenylaminof-
luoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-dibuty-
35 lamino-7-(o-chlorophenylamino)fluoran, 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, 3-diethylamino-
7-(o-fluorophenylamino)fluoran, 3-dibutylamino-7-(o-fluorophenylamino) fluoran, 3-dibutylamino-6-methyl-7-
phenylaminofluoran, 3-(N-methyl-N-n-amy)amino-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-n-amy)ami-
no-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-iso-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-ethylhexyl)amino-6-methyl-7-phenylaminofluoran, and the like. The basic chromogenic mate-
40 rials may be used either solely or in combination.

As the developers which develop a color by contacting with the above basic chromogenic materials, there have been known various kinds of inorganic or organic acidic compounds. For example, there are included inor-
40 ganic acidic compounds such as activated clay, attapulgit, 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'-isopropylide-
nebis(2-tert-butylphenol), 4,4'-sec-butylidenediphenol, 4-phenylphenol, 4,4'-isopropylidenediphenol, 2,2-bis(4-
45 hydroxyphenyl)-4-methylpentane, 2,2'-methylenebis(4-chlorophenol), hydroquinone, 4,4'-cyclohexyldenedi-
phenol, 4,4'-dihydroxydiphenylsulfide, hydroquinone monobenzyl ether, 4-hydroxy-benzophenone, 2,4-dihyd-
roxybenzophenone, 2,4,4'-tri-hydroxybenzophenone, 2,2',4,4'tetrahydroxybenzophenone, dimethyl 4-hydro-
xyphthalate, methyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, sec-butyl 4-hydroxybenzoate, pentyl 4-
hydroxybenzoate, phenyl 4-hydroxybenzoate, benzyl 4-hydroxybenzoate, tolyl 4-hydroxybenzoate,
50 chlorophenyl 4-hydroxybenzoate, phenylpropyl 4-hydroxybenzoate, phenethyl 4-hydroxybenzoate, p-
chlorobenzyl 4-hydroxybenzoate, p-methoxybenzyl 4-hydroxybenzoate, novolak phenol resin, phenol polym-
ers 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-hyd-
roxybenzoic acid, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-(α -methylbenzyl)salicylic acid, 3-chloro-
55 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 ; 4-hydroxydiphenylsulfone derivatives such as 4,4'-dihyd-
roxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, bis(3-allyl-4-
hydroxyphenyl)sulfone, 4-hydroxy-4'-methylidiphenylsulfone, 3,4-dihydroxydiphenylsulfone, 3,4-dihydroxy-4'-
methylidiphenylsulfone and the like ; sulfide derivatives such as bis(3-tert-butyl-4-hydroxy-6-methylphenyl)sul-
fide, bis(2-methyl-4-hydroxy-6-tert-butylphenyl)sulfide, 4,4'-methylenebis(oxyethylenethio)diphenol, 1,5-di(4-
hydroxyphenylthio)-3-oxapentane and the like ; and salts of the above phenolic compounds or aromatic

carboxylic acids with polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin and nickel ; and organic acidic compounds such as antipyrine complex of zinc thiocyanate and the like.

5 The used ratio of the basic chromogenic materials and the color developer may be suitably selected depending on the kind of the basic chromogenic material and the color developer, and accordingly is not particularly limited. However, the used amount of the color developer is generally within the range of 1 to 50 parts by weight, preferably 2 to 10 parts by weight, per one part by weight of the basic chromogenic materials.

10 The coating composition comprising those above materials is generally prepared by dispersing simultaneously or separately the chromogenic material and the color developer in water as the dispersion medium with use of a mixer or pulverizer such as ball mill, attritor, sand mill or the like.

15 As the binders contained in the coating composition, there are exemplified starches, hydroxyethylcellulose, methylcellulose, carboxymethylcellulose, gelatin, casein, gum arabic, polyvinyl alcohol, carboxyl-group modified polyvinyl alcohol, acetoacetyl-group modified polyvinyl alcohol, salts of diisobutylene-maleic anhydride copolymer, salts of styrene-maleic anhydride copolymer, salts of ethylene-acrylic acid copolymer, salts of styrene-acrylic acid copolymer, styrenebutadiene copolymer emulsions, urea resin, melamine resin, amide resin and the like.

20 Further, if necessary, the coating composition may include various kinds of additives such as dispersing agents, e.g., sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl alcohol sulfate, metal salts of fatty acids and the like ; zinc stearate or calcium stearate ; waxes, e.g., polyethylene wax, carnauba wax, paraffin wax, ester wax and the like ; ultraviolet ray absorbers, e.g., benzophenone compounds and the like ; antifoaming agents ; fluorescent dyes ; coloring dyes and the like.

25 Additionally, various pigments may be added. Among the pigments, there are included such as inorganic pigments, e.g., kaolin, clay, calcium carbonate, calcined clay, calcined kaolin, titanium dioxide, diatom earth, fire-grain anhydrous silica, activated clay and the like ; and organic pigments, e.g., styrene microball, Nylon powder, polyethylene powder, urea-formaldehyde resin filler, raw starch powder and the like.

30 Sensitizers may be used simultaneously, if necessary. Among the sensitizers, there are included fatty acid amides such as caproic acid amide, capric acid amide, stearic acid amide, oleic acid amide, erucic acid amide, linolic acid amide, linoleic acid amide, N-mehtylstearic acid amide, benzanilide, linolic acid anilide, N-ethylcapric acid amide, N-butylallic acid amide, N-octadecyl acetamide, N-olein acetamide, N-oleyl benzoamide, N-stearyl cyclohexylamide, polyethyleneglycol, 1-benzyloxynaphthalene, 2-benzyloxynaphthalene, phenyl 1-hydroxynaphthoate, 1,2-diphenoxyethane, 1,4-diphenoxybutane, 1,2-bis(3-methylphenoxy)ethane, 1,2-bis(4-methoxyphenoxy)ethane, 1-phenoxy-2-(4-chlorophenoxy)ethane, 1-phenoxy-2-(4-methoxyphenoxy)ethane, 1-(2-methylphenoxy)-2-(4-methoxyphenoxy)ethane, dibenzyl telephthalate, dibenzyl oxalate, di(4-methylbenzyl) oxalate, benzyl p-benzyloxybenzoate, p-benzylbiphenyl, 1, 5-bis(p-methoxyphenoxy)-3-oxapentane, 1,4-bis(2-vinyloxyethoxy) benzene, p-biphenyl p-tolyl ether, benzyl p-methylthiophenyl ether and the like.

35 The usage amount of the sensitizer is not particularly limited, however, it is generally preferable to adjust the amount within the range of not more than 4 parts by weight per one part by weight of the color developer.

40 Further, methods for forming the recording layer are not particularly limited. It may be formed by coating the coating composition on a base sheet with a coating method such as air-knife coating, rod-blade coating, pure-blade coating, short dwell coating, and drying it. The amount of the applied coating composition is particularly limited, but generally adjusted within the range of 2 to 12 g/m², preferably 3 to 10 g/m².

45 On the heat sensitive recording materials according to the invention, a protective layer is preferably applied. As a water-soluble or water-dispersible polymer used for forming the protective layer, there are exemplified polyvinyl alcohol, carboxyl-group modified polyvinyl alcohol, acetoacetyl-group modified polyvinyl alcohol, silicon-containing modified polyvinyl alcohol, hydroxyethylcellulose, methylcellulose, carboxymethylcellulose, starch and the derivatives, casein, sodium alginate, polyvinyl pyrrolidone, polyacrylic amide, salts of styrene-maleic anhydride copolymer, polyurethane resin, urea resin, melamine resin, polyamide resin, epichlorohydrinated polyamide resin, styrene-butadiene copolymer emulsion, styrene-acrylic acid ester type emulsion, acrylic acid ester type emulsion and the like. The polymers may be used solely or in combination.

50 Among them, acetoacetyl-group modified polyvinyl alcohol and silicon-containing modified polyvinyl alcohol are particularly preferred because of forming a strong resin film.

55 Further, pigments may be added in the protective layer. As the pigments, there are exemplified 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, calcined clay, colloidal silica and the like ; organic pigments such as styrene microballs, Nylon powder, polyethylene powder, urea-formaldehyde resin filler, raw starch powder and the like. The usage amount of the pigments is preferable to be adjusted within the range of 20 to 500 parts by weight per 100 parts by weight of the binders.

Further, there may be added in the coating composition for the protective layer, if desired, various known additives such as lubricants, e.g., zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin

wax and ester wax ; surface-active agents, e.g., sodium dioctylsulfosuccinate ; anti-foaming agent and the like.

To further improve the water-resistance, there may be added a hardener, such as glyoxal, boric acid, dialdehyde starch, epoxy type compounds and the like.

Thus prepared coating composition may be applied on the heat-sensitive recording layer by a coater. The coated amount of the composition is generally controlled within the range of 1 to 20 g/m², preferably 2 to 10 g/m² on dry basis, because the image-retainability is not substantially improved and a thermal head sticking easily occurs if the coated amount is less than 1 g/m², and on the other hand the recording sensitivity of the heat-sensitive recording material is lowered if the coated amount is more than 20 g/m².

Furthermore, there may be added various kinds of well-known technique for producing the heat-sensitive recording material, such as formation of an under-coating layer between the heat-sensitive layer and the base sheet having a specific coating layer of the present invention. As the base sheet, papers such as paper and synthetic paper are mainly used.

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 Formation of a specific coating layer of the present invention :

The following composition was coated in the weight of an amount of 10 g/m² on dry basis on a surface of a base sheet of 40 g/m² and dried to form a back-coating layer on a surface of the base sheet.

calcium carbonate (oil absorption: 35 ml/100g)	100 parts
styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C solid amount: 50 %)	35 parts
water	160 parts

② Preparation of dispersion A :

The following composition was pulverized by a sand mill, and the pulverization was continued until an average particle size of 3 μ m.

3-(N-ethy-N-isoamyl)amino-6-methyl-7-phenylfluoran	10 parts
5% aqueous solution of methylcellulose	5 parts
water	40 parts

③ Preparation of dispersion B :

The following composition was pulverized by a sand mill, and the pulverization was continued until an average particle size of 3 μ m.

4,4'-isopropylidenediphenol	30 parts
5% aqueous solution of methylcellulose	5 parts
water	80 parts

④ Preparation of dispersion C :

The following composition was pulverized by a sand mill, and the pulverization was continued until an average particle size of 3 μ m.

	1,2-di(3-methylphenoxy)ethane	20 parts
5	5% aqueous solution of methylcellulose	5 parts
	water	55 parts

⑤ Formation of a recording layer :

10 The following composition was mixed with stirring to prepare a coating composition.

	dispersion A	55 parts
	dispersion B	115 parts
	dispersion C	80 parts
15	10% aqueous solution of polyvinyl alcohol	80 parts
	calcium carbonate	35 parts

The coating composition was coated in the weight of an amount of 6 g/m² on dry basis on the other surface of the base sheet having the back-coating layer, and dried to form a recording layer on the base sheet.

20 ⑥ Formation of a protective layer :

The following composition was mixed with stirring to prepare a protective coating composition.

25	10% aqueous solution of acetoacetyl-modified polyvinyl alcohol	200 parts
	calcium carbonate	100 parts
30	water	100 parts

The coating composition was coated in the weight of an amount of 5 g/m² on dry basis on the recording layer, dried and calendered to obtain a heat-sensitive recording material having a protective layer on the recording layer.

35 Example 2

40 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that vinyl chloride-ethylene copolymer emulsion (glass transition temperature : 20 °C , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion to prepare the coating composition in the step ①.

Example 3

45 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that vinyl acetate-ethylene-vinyl chloride copolymer emulsion (glass transition temperature : 0°C , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion to prepare the coating composition in the step ①.

Example 4

50 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that acrylic acid ester copolymer emulsion (glass transition temperature : 15°C , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion to prepare the coating composition in the step ①.

Example 5

55 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that kaolin (oil absorption : 30 ml/100g) was used instead of calcium carbonate to prepare the coating composition in the step ①.

Example 6

5 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the following coating composition was used as the coating composition of the step ① ;

10	kaolin (oil absorption: 30 ml/100g)	50 parts
	calcium carbonate (oil absorption: 35 ml/100g)	50 parts
	styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C ,	
15	solid amount: 50 %)	25 parts
	10 % aqueous solution of oxidized starch	63 parts
20	water	100 parts.

Example 7

25 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that aluminum hydroxide (oil absorption 35 ml/100g) was used instead of calcium carbonate to prepare the coating composition in the step ① .

Example 8

30 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the coating composition in the step ① was coated in the weight of an amount of 10 g/m² on dry basis on each of the back and front surfaces of the base sheet.

Example 9

35 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that styrene-butadiene copolymer emulsion (glass transition temperature : 33 °C , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion (glass transition temperature : -6 °C , solid amount : 50 %) to prepare the coating composition in the step ① .

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Example 10

45 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that vinyl acetate-ethylene-vinyl chloride copolymer emulsion (glass transition temperature : 50 °C) , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion (glass transition temperature : -6 °C , solid amount : 50 %) to prepare the coating composition in the step ① .

Example 11

50 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that acrylic acid ester copolymer emulsion (glass transition temperature : 45 °C , solid amount : 50 %) was used instead of styrene-butadiene copolymer emulsion (glass transition temperature : -6 °C , solid amount : 50%) to prepare the coating composition in the step ① .

55 Example 12

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the following composition was used as the coating composition in the step ① ;

5	calcined talc (oil absorption: 80 ml/100g)	100 parts
	styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C ,	
	solid amount: 50 %)	160 parts
10	water	160 parts.

Example 13

15 Heat-sensitive recording material was obtained in the same manner as in Example 1 except that the following composition was used as the coating composition in the step ① ;

20	calcium carbonate (oil absorption: 35 ml/100g)	100 parts
	styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C ,	
	solid amount: 50 %)	16 parts
25	water	150 parts.

Example 14

30 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the following composition was used as the coating composition in the step ① ;

35	calcium carbonate (oil absorption: 35 ml/100g)	100 parts
	styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C ,	
	solid amount: 50 %)	140 parts
40	water	160 parts.

Example 15

45 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the following composition was used as the coating composition in the step ① ;

50	calcium carbonate (oil absorption: 35 ml/100g)	100 parts
	styrene-butadiene copolymer emulsion (glass transition temperature: -6 °C ,	
	solid amount: 50 %)	16 parts
55	20 % aqueous solution of polyvinyl alcohol	125 parts
	water	90 parts.

Comparative Example 1

5 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that calcined kaolin (oil absorption : 80 ml/100g) was used instead of calcium carbonate to prepare the coating composition in the step ①.

Comparative Example 2

10 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that calcined talc (oil absorption : 80 ml/100g) was used instead of calcium carbonate to prepare the coating composition in the step ①.

15 Comparative Example 3

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that 10 % aqueous solution of aceto-acetylated polyvinyl alcohol was used instead of the coating composition in the step ①.

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Comparative Example 4

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that the mixture of styrene-methyl acrylate copolymer emulsion (solid amount :45 %) and 30 % aqueous dispersion of colloidal silica in the ratio of 2 : 1 was used instead of the coating composition in the step ①.

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Comparative Example 5

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that a styrene-butadiene copolymer emulsion (glass transition temperature : -6 °C , solid amount : 50 %) was used instead of the coating composition in the step ①.

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The properties of thus obtained heat-sensitive recording materials in Examples and Comparative Examples were evaluated by the following methods. The results are shown in Table 1.

35 [K & N ink absorption]

K & N ink is coated in excess on the back surface of a heat-sensitive recording material, and allowed to stand for 2 minutes at the room temperature. Then the excess ink is substantially wiped with a gauze and immediately the heat-sensitive recording material is weighed to calculate the absorbed amount of the ink (g/m²).

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[Plasticizer resistance]

The heat-sensitive recording material is pressed by a hot plate heated at 120°C for 5 seconds under 4 kg/cm² to record color images and a rubber binder (ECOMELT L-302 manufactured by ECOMELT AG) is coated on the back surface of the recorded material in the weight of an amount of 20 g/m². Then a polyvinylidene chloride film manufactured by Mitsui Toatsu Chemicals, Inc. is wrapped threefold around a polypropylene pipe having a diameter of 40mm. The recorded material is put on the outer surface in the manner as the color images are exposed outward and further a polyethylene film which does not contain a plasticizer is wrapped threefold around the recorded material. The resultant material is allowed to stand at 40 °C for 24 hours, and then the image density of the color images is measured. Plasticizer resistance is evaluated by the discoloration degree of the color images as follows ;

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- ⊙ : Discoloration is not substantially appreciated.
- : Discoloration is slightly appreciated but can be neglected.
- x : Discoloration is remarkably appreciated so as to make the practical use impossible.

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[Blocking resistance]

0.05 ml of water is dropped on the surface of a heat-sensitive recording material and the back surface of the heat-sensitive recording material is piled on the water-dropped surface. After one hour, the adhesiveness is evaluated by peeling the surfaces.

- : No adhesion.
- x : Adhesion

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[PCS value]

10 A black ink (New Champion F Gloss manufactured by Dai Nihon Ink Chemical Corp.) is printed on the back surface of a heat-sensitive recording material by RI Printing Tester. The heat-sensitive recording material is pressed by a hot plate heated at 120 °C for 5 seconds under 4 kg/cm² to record color images. The color density of the recorded images and the background is measured by Macbeth densitometer RD-100R manufactured by Macbeth Corp. PCS value is calculated by the following equation.

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$$\text{PCS value} = \frac{\text{density of recorded images} - \text{density of background}}{\text{density of recorded images}}$$

[Ink set property]

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A black ink (New Champion F Gloss manufactured by Dai Nihon Ink Chemical Corp.) is printed on the back surface of a heat-sensitive recording material by RI Printing Tester and immediately the back surface without printed images is put on the printed back surface and pressed by a roller several times. The ink transfer is evaluated with naked eyes as follows ;

- 25
- ⊙ : Ink transfer is not substantially appreciated.
 - : Ink transfer is slightly appreciated.
 - Δ : Ink transfer is substantially appreciated.
 - x : Ink transfer is very remarkably appreciated.

30 [Surface strength]

35 It is also evaluated by RI printing applicability. A test ink for paper (Printing Ink SD Super Deluxe 50 Beni manufactured by Toka Sikiso Kabushiki Kaisha) is printed on the back surface of a heat-sensitive recording material by RI Printing Tester and the state of picking (surface-peeling off) is observed and evaluated as follows :

- ⊙ : Picking is not substantially appreciated.
- : Picking is slightly appreciated.
- Δ : Picking is substantially appreciated.

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Table 1

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	K&N ink absorption g/m ²	plasticizer resistance	blocking resistance	PCS value (%)	ink set	surface strength
<u>Examples</u>						
1	6.2	◎	○	0.94	◎	◎
2	6.6	◎	○	0.94	●	○
3	6.3	◎	○	0.94	◎	●
4	6.5	◎	○	0.93	◎	○
5	6.0	◎	○	0.94	◎	●
6	6.6	◎	○	0.94	◎	◎
7	6.3	◎	○	0.93	◎	◎
8	6.2	◎	○	0.96	◎	◎
9	6.7	◎	○	0.92	●	△
10	6.6	◎	○	0.93	◎	△
11	6.8	◎	○	0.92	◎	△
12	7.3	○	○	0.90	○	○
13	9.6	○	○	0.96	◎	△
14	5.7	◎	○	0.91	△	◎
15	7.2	○	○	0.94	◎	△
<u>Comparative Examples</u>						
1	13.8	x	○	0.95	◎	△
2	10.9	x	○	0.94	◎	△
3	4.5	◎	x	0.78	x	◎
4	11.9	x	○	0.84	◎	△
5	4.9	◎	x	0.82	x	◎

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As shown in Table 1, each of the heat-sensitive recording materials according to the present invention is superior in both of plasticizer resistance and blocking resistance, and further indicates a high PCS value when a back-printing is applied.

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Claims

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1. A heat-sensitive recording material useful for labels, which has on a surface of a base sheet a heat-sensitive recording layer which comprises a colorless or pale colored basic chromogenic material and a color developer which develops a color by contacting with the chromogenic material, and an adhesive layer on the back of the base sheet, characterized in that a coating layer mainly comprising inorganic and/or organic pigments together with a binder is formed on the back or both surfaces of the base sheet, and K & N ink absorption of the coating layer is adjusted to from 5.0 g/m² to 10.0g/m².
2. A heat-sensitive recording material as defined in Claim 1, wherein the K & N ink absorption is from 6.0 g/m² to 10.0g/m².
3. A heat-sensitive recording material as defined in Claim 1 or 2, wherein the oil absorption of the inorganic and/or organic pigments measured by JIS K-5101 is less than 50 ml/100g.
4. A heat-sensitive recording material as defined in anyone of Claims 1 to 3, wherein the binder is a latex of polymer having a glass transition temperature of 30 °C or less.
5. A heat-sensitive recording material as defined in anyone of Claims 1 to 4, wherein the solid content of the binder is from 8 % to 40 % by weight per the total solid amount of the coating layer

6. A heat-sensitive recording material as defined in anyone of Claims 1 to 5, wherein the coating layer is formed in an amount of from 3 g/m² to 30 g/m² on dry basis.

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