Oct. 22, 1974 KINICHI ADACHI ET AL 3,843,384

HEAT-SENSITIVE TWO COLOR RECORDING PAPER

Filed June 12, 1972 6 Sheets-Sheet 1

FIG. 1

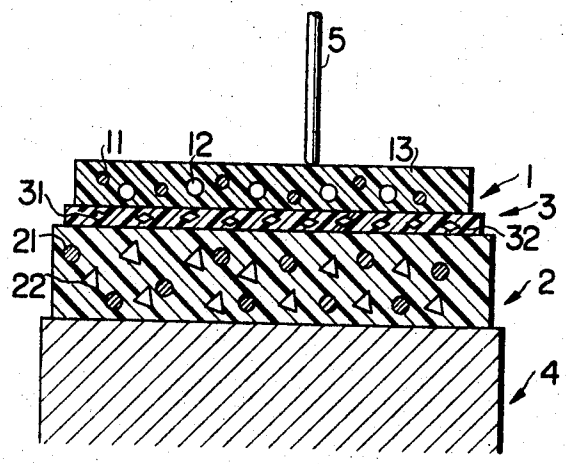
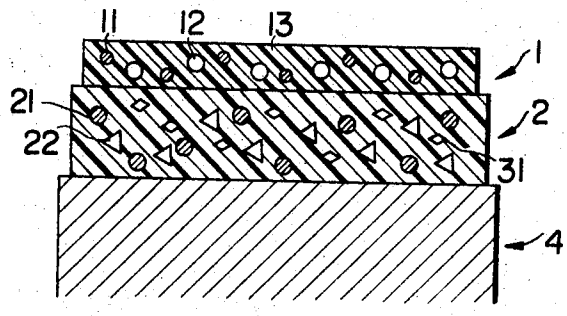


FIG. 2



HEAT-SENSITIVE TWO COLOR RECORDING PAPER

Filed June 12, 1972 6 Sheets-Sheet 2

FIG. 3

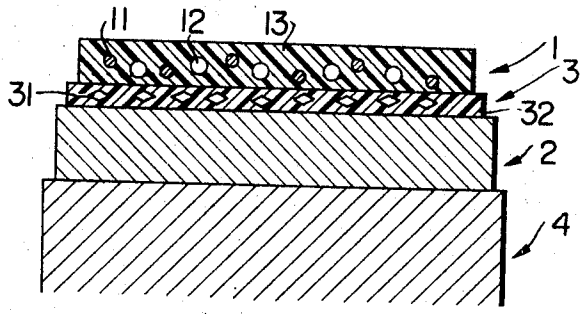


FIG. 4

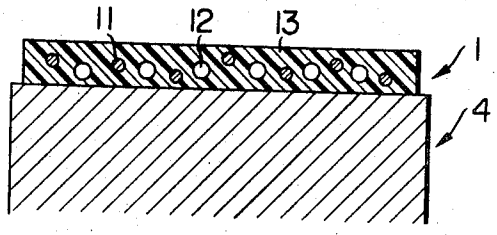


FIG. 5

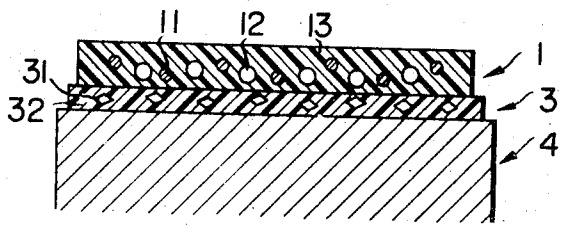


FIG. 6

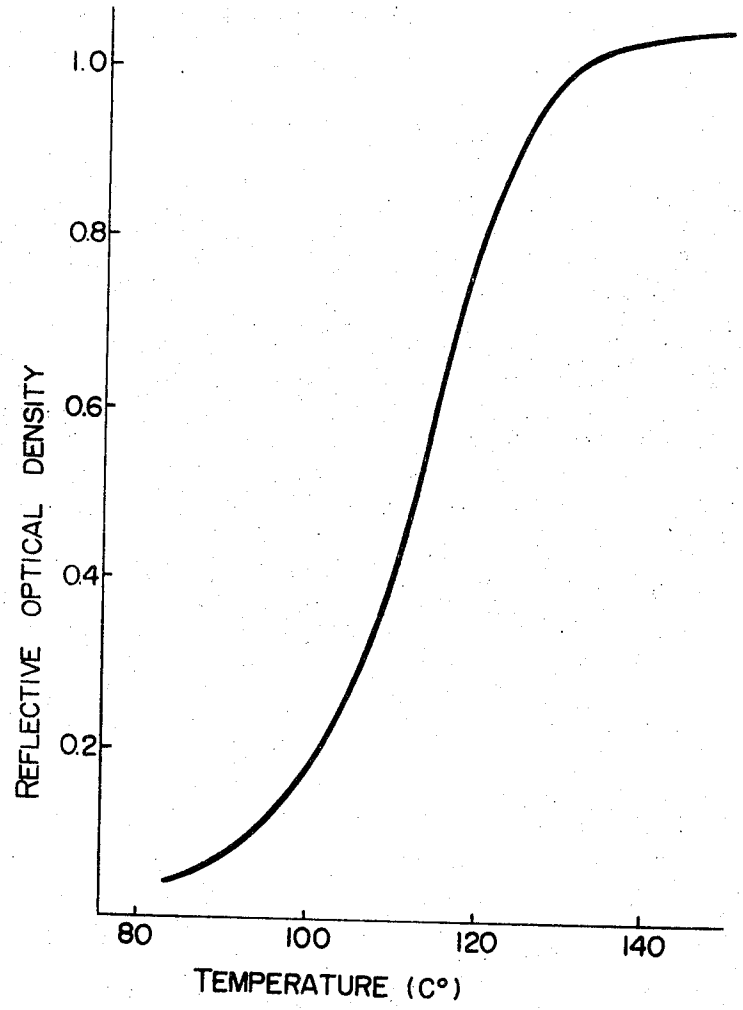

1.0
0.8
0.6
0.4
0.2
REFLECTIVE OPTICAL DENSITY
80
100
120
140
TEMPERATURE (C°)

FIG. 7

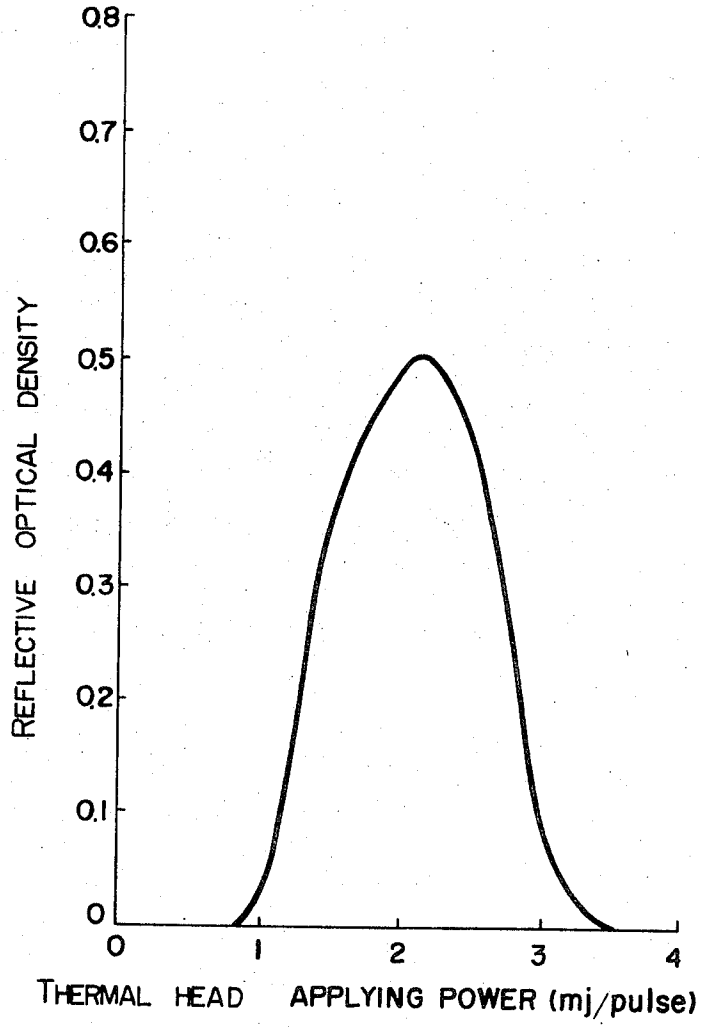

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
REFLECTIVE OPTICAL DENSITY
0
1
2
3
4
THERMAL HEAD APPLYING POWER (mj/pulse)

FIG. 8

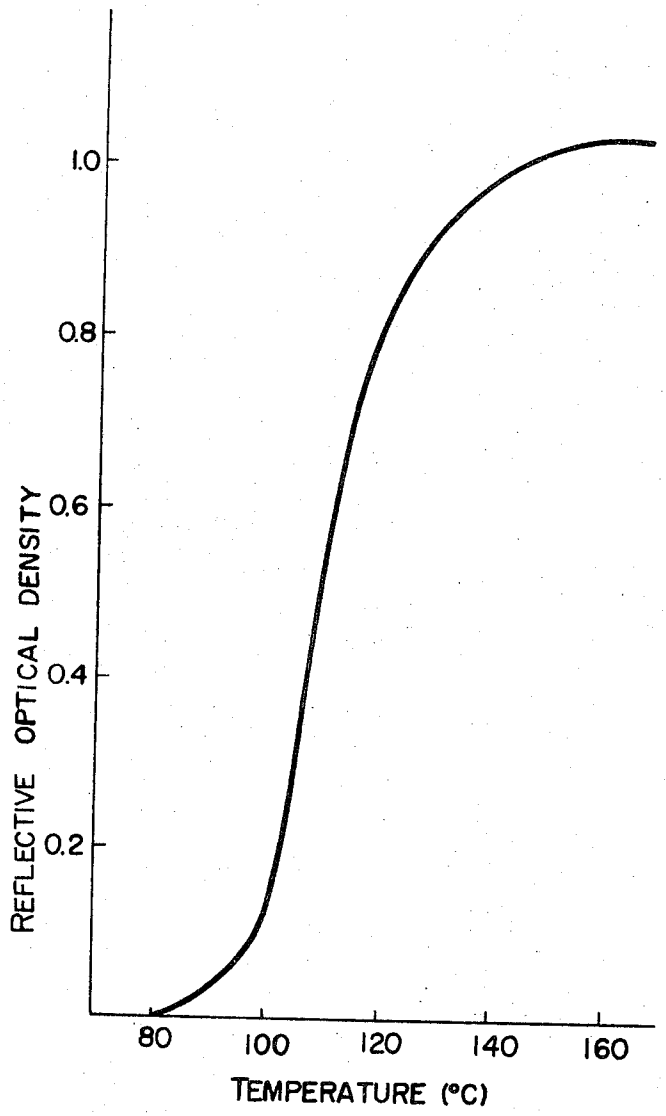

1.0
0.8
0.6
0.4
0.2
REFLECTIVE OPTICAL DENSITY
80
100
120
140
160
TEMPERATURE (°C)

FIG. 9b

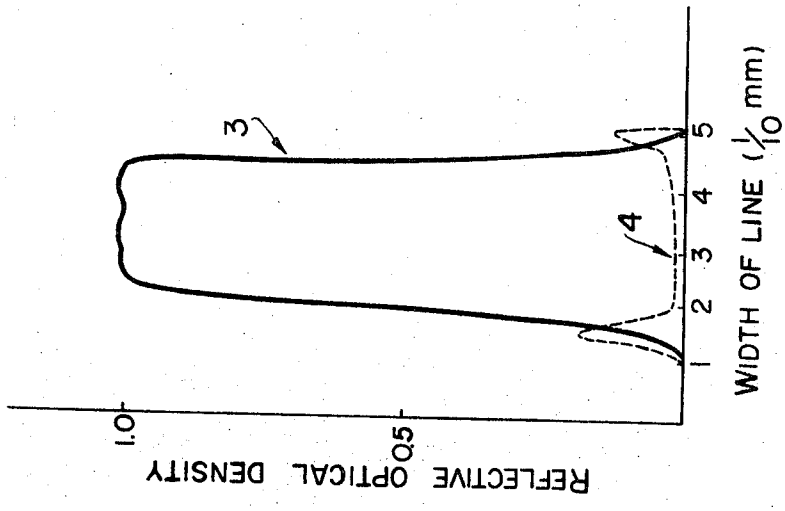
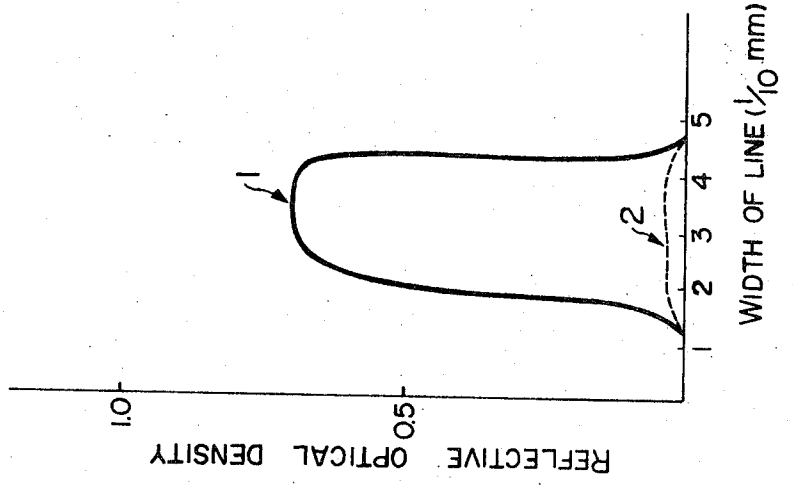

3
4
1
2
3
4
5
WIDTH OF LINE (1/10 mm)
1.0
0.5
REFLECTIVE OPTICAL DENSITY

FIG. 9a


1
2
1
2
3
4
5
WIDTH OF LINE (1/10 mm)
1.0
0.5
REFLECTIVE OPTICAL DENSITY

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3,843,384

HEAT-SENSITIVE TWO COLOR RECORDING PAPER

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Claims priority, application Japan, June 14, 1971, 46/42,341; Aug. 5, 1971, 46/59,395; Aug. 10, 1971, 46/60,752; Aug. 20, 1971, 46/63,815
Int. Cl. B41m 5/18
U.S. Cl. 117—36.9 13 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive two color recording paper having first and second layers which individually develop different colors due to difference in quantity of heat applied to the paper surface, in which the color-developing component of the first layer is composed of (i) a triphenylmethane or fluoran type dye base having in the molecule a reactive color-developing component of the lactone or lactam type and (ii) a phenolic substance or an organic acid. This recording paper contains polyether as a decolorizing agent for removing the color developed in the first layer, and the color of the first layer is removed at the time when the second layer develops a color, so that a clear two-colored record can be obtained.

This invention relates to heat-sensitive recording materials for use in information terminal machines such as, for example, facsimile, telegraphic machines, telewriters, electronic computers, various measuring machines and copying machines.

Recording materials which have heretofore been used in the above-mentioned machines are represented by conventional photographic materials, electrophotographic materials, electrostatic recording papers, electrolytic recording materials, diazo papers, etc. All these recording materials, however, require toners or developer and fixer at the image-forming step, so that the cleaning of recording machines and the supply of chemicals have been indispensable. Further, inks are used in the recording machines available at present, so that there have been such inconveniences from the standpoint of users that recording papers are stained with the inks, or solids formed due to vaporization of solvents used in the inks clog the ink-discharging holes of pens, with the result that figures to be recorded become thin or, in extreme cases, cannot be recorded. In order to overcome the above-mentioned drawbacks, many pressure-sensitive recording materials have come to be used. At present, however, the said recording materials are used as copying papers or teletyping papers in place of carbon papers, and thus are limited in uses.

On the other hand, many types of heat-sensitive recording materials have heretofore been proposed. Among these recording materials, those which have already been put into practical use or which will be practically used in the near future are as follows:

(1) A heat-sensitive sheet prepared by uniformly applying carbon or the like coloring pigment or dye powder onto a substrate, and coating on the resulting color layer a white and opaque thermofusible substance. This sheet is of such a type that the thermofusible substance on the surface is scribed with a thermal pen to expose the lower color layer. A recording material of this type has such drawbacks that wastes are formed and multi-color recording is impossible.

(2) A recording material of such a type that a color is formed by the formation of a complex compound of an electron donor with an electron acceptor. For example,

ferric stearate and pyrogallol are independently dispersed in a binder, and the thus treated binder is softened by application of heat, whereby the two compounds react with each other to form a complex compound which forms a color. The color developed in this case is dark brown.

(3) A recording material of such a type that Crystal Violet Lactone and a phenolic substance are dispersed as discontinuous particles into a thermoplastic substance such as polyvinyl alcohol or the like, and the binder is softened by application of heat. The color developed in this case is cobalt blue. While this type suggests a promising way of heat-sensitive recording materials, there is a problem in how to obtain a record having 2 or more colors.

As mentioned above, recording materials for terminal machines should satisfy such conditions that they can give clear records without any substantial trouble from the recording machines employed. In this respect, the heat-sensitive material of the above-mentioned type (3) is a preferable material, since it gives a clear image by mere application of a thermal head. However, high density informations have come to be required with the progress of society, and the demand for records having 2 or more colors is strong.

With an aim to satisfy the above demand, the present inventors made studies on the conventional heat-sensitive recording materials of this kind to find a heat-sensitive recording paper capable of forming clear two colors.

It is therefore an object of the present invention to provide a recording paper which develops, for example, a red color when recording is made by use of a thermal pen (or a thermal head) kept at a certain temperature, and which further develops, for example, a blue color when recording is made by use of a thermal pen kept at a higher temperature.

In the accompanying drawings, FIGS. 1 to 2 diagrammatically show the cross-sections of several recording papers of the present invention and FIGS. 4 and 5 show the cross-sections of recording papers for reference; FIGS. 6 and 8 are individually a color development sensitivity curve showing the relation between temperature and reflective optical density; FIG. 7 is a graph showing the relation between thermal head applying power and reflective optical density; and FIG. 9 is a graph showing the relation between width of line and reflective optical density.

As seen in FIG. 1 for example, the recording paper of the present invention is composed of a first heat-sensitive recording material layer **1** which develops a color by the reaction of a triphenylmethane or fluoran type dye base (hereinafter referred to as "color-forming dye") having in the molecule a reactive color-developing component of the lactone or lactam type with a phenolic substance or an organic acid (hereinafter referred to as "color-forming agent"); a second heat-sensitive recording material layer **2** which develops a color by the reaction of a diazo compound with an azo coupler; a layer **3** disposed between the said two layers **1** and **2** which contains a decolorizing agent for removing the color of the color-forming substance contained in the first layer **1**; and a substrate **4**. In FIG. 1 **4** is a recording thermal head. In the first layer, the color-forming dye **11** and the color-forming agent **12** have independently been dispersed as discontinuous particles into a film-forming binder **13**, which is solid at normal temperature but is softened when heat is applied thereto. Accordingly, when the binder is heated by applying a certain quantity of heat to the surface of the recording material, the color-forming dye reacts with the color-forming agent to develop a color. In the second layer, the diazo compound **21** and the azo coupler **22** have independently been dispersed as discontinuous particles into

a film-forming binder **23**, which is solid at normal temperature but is softened when heat is applied thereto. Accordingly, when the said binder is heated by applying a certain quantity of heat to the surface of the recording paper, the two compounds react with each other to develop a color different from the color of the first layer.

The recording materials constituting the above-mentioned first and second layers have individually been known as heat-sensitive recording materials of this kind. However, the recording paper of the present invention is characterized in that a thermofusible polyether is used as the decolorizing agent for the color-developing substance of the first layer. In the case of the recording paper of the present invention, therefore, the quantity of heat (hereinafter referred to as "heat A") necessary to develop the color of the first layer and the quantity of heat (hereinafter referred to as "heat B") necessary to develop the color of the second layer are in such a relation as to satisfy the inequality $A<B$. Further, the said decolorization agent is substantially solid at normal temperature, but is fused and fluidized when the heat B is applied to the paper surface. That is, when the quantity of heat applied to the paper surface in order to fluidize the decoloring agent is deemed as heat C, the heats A, B and C are in such a relation as to satisfy the inequality $A<C\leqq B$.

The quantities of heat applied to these layers **1**, **2** and **3** are dependent on the temperature of the recording thermal head **5** to be contacted with the paper surface, the time of contact of the thermal head with the paper surface, and the thermal conductivity of the paper from the surface of each layer. For example, in the case of the recording paper of such a construction as shown in FIG. 1, the quantity of heat applied to the first layer **1** is greater than the quantity of heat applied to the second layer **2**, even though the temperature of the thermal head and the time of contact of thermal head with the paper surface are definite. In the above case, the temperature of the first layer is higher than that of the second layer. Accordingly, the color forming temperature of the second layer is not always required to be higher than that of the first layer. Generally, however, the color forming temperature of the second layer is made higher than that of the first layer.

The color formation mechanism of the first layer and the mechanism of removing the color formed in the first layer with the polyether in the inter layer are explained below.

The fact that a leuco dye base of the triphenylmethane type such as Crystal Violet Lactone forms a color by reaction with a phenolic substance such as phenol or cresol or with an inorganic or organic acid has been clarified by O. Fischer et al. [Berichte der Deutschen Chemischen Gesellschaft, *42*, 2934–2935 (1909)]. Further, a leuco dye base of the fluoran type also shows the same property as above. It is said that the mechanism of the above-mentioned reaction is such that the electron attractive acid attracts the electrons of amine of the dye base, whereby the dye base is ionized to form a color. When the above-mentioned kind of color-forming dye and color-forming agent are contacted with each other, they react in the above manner to form a color. In this case, either one or both of the color-forming dye and color-forming agent may be dissolved in a thermoplastic substance such as polyvinyl alcohol or the like.

Since the above-mentioned color-forming dye forms a color due to such ionization as mentioned above, no color is formed in the presence of a polar solvent or the like substance which disturbs the ionization. In the present invention, the fact that the color-forming dye brings about no color formation reaction in the presence of a polyether is utilized, so that in case the second layer is desired to be made visible, the color formed in the first layer is removed by the polyether to make the second layer clearly visible. Concretely, the first heat-sensitive recording material layer shown in FIG. 1, which has developed a color by the reaction of a leuco dye base of the triphenylmethane or fluoran type with a phenolic substance or an organic acid, is decolored by a polyether or the like substance, as explained above. Accordingly, the recording paper of such a construction as shown in FIG. 1 can develop two brilliant colors by varying the quantity of heat applied.

The recording paper of the present invention is such that in forming the color of the second layer, the color formed in the first layer is removed by means of the polyether, as mentioned above, to obtain a color which has not been migrated with the color of the first layer. Accordingly, the color forming reaction of the second layer should not be affected by the polyether.

In the case of the recording paper shown in FIG. 1, the combination of a diazo compound and an azo coupler is used as the color-forming component of the second layer. When heat is applied to the recording paper, the film-forming binder, which separates the said two components from each other, is softened, with the result that the two components contact with each other and bring about a coupling reaction to form a color. Accordingly, the second layer is different in color forming mechanism from the first layer which forms a color due to ionization of dye base, and the color forming reaction of the second layer is not affected at all by the polyether.

As components which are not affected by polyether and usable as color-forming components of the second layer, there are combinations of electron acceptors and electron donors, in addition to the combination mentioned above.

Alternatively, the recording paper of the present invention may have such a construction as shown in FIG. 3. That is, the second layer **2** is a previously colored layer, and the inter layer **3** is composed of a thermoplastic polymer or wax **32**, which itself can form a transparent thin layer, and a polyether **31** as the decolorizing agent. The said polyether has been dispersed as particles into said polymer or wax so as to form a dispersed layer, and the thus formed inter layer **3** has been used to cover the colored layer, i.e. the second layer **2**. At the time of developing the color of the second layer **2**, the inter layer **3** is fused by application of heat so that the color image formed in the first layer is decolored by the polyether and, at the same time, the second layer is made visible.

Further, as the color-forming component of the second layer **2**, there may be used, like in the case of the first layer **1**, a triphenylmethane or fluoran type dye base having in the molecule a reactive color-forming component of the lactone or lactam type. In this case, however, the color of the second layer is also removed by the polyether, so that the amount of the color-developing substance in the second layer should be made larger than that in the first layer. The amount of the color-developing substance in the second layer is at least 5 parts by weight per part by weight of the color forming substance in the first layer. When the above-mentioned amount is employed, the second layer can sufficiently develop a clear color even when the polyether is used in an amount sufficient to remove the color of the first layer. In case such procedure is adopted, it is desirable to bring the recording paper into such a construction that the inter layer **3** is incorporated with the polyether and is disposed between the first and second layers, as shown in FIG. 1.

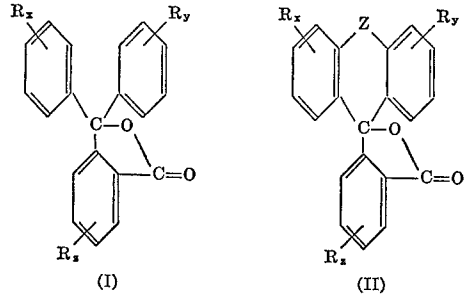
As to the polyether as the decolorizing agent, FIG. 1 shows the case where the inter layer **3**, which has been formed by dispersing particles of the polyether **31** in the thermoplastic binder **32** is disposed between the first and second layers. As shown in FIG. 2, however, it is also possible that the inter layer **3** is omitted, and the polyether **31** is dispersed in the second layer **2**.

Various materials used in the present invention are exemplified below.

1. First heat-sensitive recording material

It has already been clarified that a leuco dye of the triphenylmethane type such as Crystal Violet Lactone develops a brilliant color by reaction with clay, an inorganic acid, a phenolic substance or an organic acid. In order to apply such color-forming phenomenon to reocrding, there has been adopted a process in which a leuco compound of dye and a phenolic substance or an organic acid are independently dispersed in a physical manner into a binder. Further, it has been found that a dye base of the fluoran type is effectively usable in the present invention as a novel color-forming agent.

(a) Color-forming dye: Generally, a triphenylmethane type leuco dye base represented by the formula (I) shown below or a fluoran type dye base represented by the formula (II) shown below is used.



(I) (II)

wherein R_x, R_y and R_z are individually a hydrogen atom, a hydroxy group, a halogen atom, an alkyl group, a nitro group, an amino group, a dialkylamino group, a monoalkylamino group or an aryl group; and Z is an oxygen or sulfur atom necessary to form a heterocyclic group.

Typical examples of the above-mentioned compound are as follows:

Compounds of the formula (I):

3,3-Bis(p-dimethylaminophenyl)-phthalide
3,3-Bis(p-dimethylaminophenyl)-6-dimethylamino-phthalide [Crystal Violet Lactone]
3,3-Bis(p-dimethylaminophenyl)-6-nitrophthalide
3,3-Bis((p-dimethylaminophenyl)-6-monomethylamino-phthalide
3,3-Bis(p-dimethylaminophenyl)-6-chlorophthalide
3,3-Bis-(p-dimethylaminophenyl)-6-ethoxyphthalide
3,3-Bis(p-dimethylaminophenyl)-6-diethylamino-phthalide

Compounds of the formula (II):

3-Dimethylamino-6-methoxyfluoran
7-Acetamino-3-dimethylaminofluoran
3-Dimethylamino-5,7-dimethylfluoran
3-Diethylamino-5,7-dimethylfluoran
3,6-Bis-β-methoxyethoxyfluoran
3,6-Bis-β-cyanoethoxyfluoran

Other lactam compounds:

9-p-Nitroanilino-3,6-bis(diethylamino)-9-xanthenyl-6-benzoic acid lactam [Rhodamine lactam]
9-Nitroamino-3,6-bis(dimethylamino)-9-thioxanthenyl-6-benzoic acid lactam

The above-mentioned dye bases are effective as color-forming dyes. They are scarcely soluble in water and in benzene, toluene, n-hexane, xylene, ligroin and the like organic solvents which are non-polar or extremely low in polarity, and can be pulverized into particles of less than 10 microns.

(b) Color-forming agent: As the color-forming agent which reacts with the color-forming dye mentioned in the preceding item (a) to form a dye, a phenolic substance or an organic acid is preferable. It is desirable for dye formation that said phenolic substance or organic acid is solid at normal temperature and melts or gasifies at above 50° C. Examples of such phenolic substance and organic acid are as follows:

(1) Phenolic substances:

4-tert-Butylphenol
4-Phenylphenol
4-Hydroxydiphenoxide
α-Naphthol
Methyl-4-hydroxybenzoate
β-Naphthol
4-Hydroxyacetophenone
4-tert-Octyl catechol
2,2'-Dihydroxydiphenyl
2,2'-Methylenebis(4-chlorophenol)
4,4'-Isopropylidene diphenol [Bisphenol A]
4,4'-Isopropylidenbis(2-chlorophenol)
4,4'-Isopropylidenebis(2,6-dibromophenol)
4,4'-Isopropylidenebis(2,6-dichlorophenol)
4,4'-Isopropylidenebis(2-methylphenol)
4,4'-sec-Isobutylidene diphenol
4,4'-Cyclohexylidene diphenol
2,2'-Thiobis(4,6-dichlorophenol)
Hydroquinone
Pyrogallol
Phologlucine
Phloroglucinolcarboxylic acid

(2) Organic acids:

p-Hydroxybenzoic acid
m-Hydroxybenzoic acid
o-Hydroxybenzoic acid
Boric acid
Tartaric acid
Oxalic acid
Maleic acid
Citric acid
Succinic acid
Gallic acid
1-Hydroxy-2-naphthenic acid
2-Hydroxy-p-toluyl acid

(c) Binder: When a dispersion formed by merely dispersing the aforesaid color-forming dye and color-forming agent in water or in a non-polar or slightly polar organic solvent is coated on a substrate, the resulting recording paper becomes high in fog or suffers from peeling and thus is low in practicality. It is therefore necessary to use a binder which can disperse and fix said color-forming dye and color-forming agent as discontinuous particles at normal temperature. Due to its inherent property, the binder is softened or melted when heat is applied thereto, whereby the formation of dye is promoted. Examples of such binder are as follows:

(1) Water-soluble binders:

Polyvinyl alcohol
Polyacrylic acid
Hydroxyethyl cellulose
Polyacrylamide
Carboxymethyl cellulose
Methoxycellulose
Polyvinyl pyrrolidone
Gelatin
Starch

These are preferable binders which are dissolved in or swelled with water to provide tackiness.

(2) Binders soluble in non-polar or slightly polar organic solvents:

Natural rubber
Synthetic rubbers
Chlorinated rubbers
Alkyl resins
Styrene-butadiene copolymers
Polybutyl methacrylate

These binders disperse and fix the aforesaid color-forming dyes and color-forming agents as discontinuous particles at temperatures below the heat recording temperature and, at the same time, play the role of adhering them to substrates. It is desirable to use a binder which is not easily discolored by heat.

(d) Other additives: In order to enhance the recording paper in whiteness and printability and to prevent the adhesion of thermal head, there may be used talc, titanium oxide, zinc oxide, calcium carbonate or the like. Further, in order to carry out the formation of dye at a sharp temperature, there may be used urea, thiourea, acetanilide, phthalic anhydride or the like thermofusible substance

which can melt the aforesaid color-forming dye and color-forming agent at the time of melting.

2. Decolorizing agent

It is said that the formation mechanism of a color by use of the aforesaid color-forming agent and color-forming dye is such that an electron attractive acid attracts the electrons of amine of a dye base, thereby bringing about the ionization of the dye base. Accordingly, no color is developed in the presence of a polar solvent or the like substance which disturbs the ionization of dye base. The present invention utilizes the fact that a substance, which has developed a color by use of the said color-forming dye and color-forming agent, is decolored in the presence of a polyether.

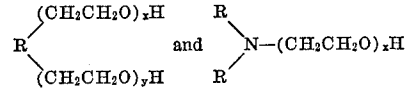
A polyether having such decolorizing effect is represented by the general formula,

$$\text{-(M-O-)}_x$$

wherein x is an integer of 1 or more, and M is a methylene or polymethylene group or a derivative thereof.

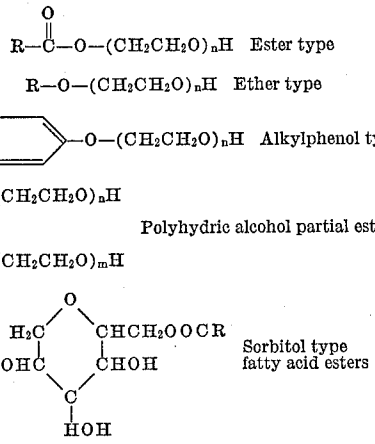
Typical examples of such polyether are as follows:

(1) Polyoxydecamethylene
(2) Polyoxymethylene
(3) Polyethylene oxide
(4) Trimethylene oxide polymers
(5) 1,3-Dioxolan polymers
(6) Alkylamine type cationic surface active agents represented by the following general formulas:



wherein R and R' are individually a fatty acid chain, and x and y are individually an integer of 1 or more.

Polyethylene glycol type nonionic surface active agents represented by the following general formulas:



wherein R is a fatty acid chain, and n and m are individually an integer of 1 or more.

Typical examples of the above-mentioned polyethers are as follows:

Polyoxyethylene alkylamine
Polyoxyethylene oleyl ether
Polyoxyethylene cetyl ether
Polyoxyethylene alkylallyl ethers
Polyoxyethylene glycol monolaurate
Polyoxyethylene glycol monostearate
Sorbitan monolaurate
Sorbitan monopalmitate
Sorbitan monostearate
Polyoxyethylene sorbitan monostearate
Polyoxyethylene sorbitan monooleate
Polyoxyethylene alkylamides
Polyoxyethylene dodecylmercaptan ether
Polyalkylene glycol derivatives

In addition to the above-mentioned decolorizing agents, compounds having the skeleton

in the molecules can be used as decolorizing agents in the present invention.

It is desirable that the binders are solid at normal temperature. According to the capsulating technique at present, however, binders in the form of liquids may also be successfully used so far as the wall materials of capsules are suitably selected.

3. Second heat-sensitive recording material

The first heat-sensitive recording material is decolorized with a decolorizer, but the second heat-sensitive recording material should not be decolorized with a decolorizer. It is therefore desirable that the second color-forming layer is composed of a substance which develops a color by application of heat larger in quantity than the heat required for decolorizing the first layer. Preferable examples of the above-mentioned substance are such combinations of electron acceptors and electron donors as mentioned below.

	Electron acceptor	Electron donor
(1)	Metal salts of long chain fatty acids (e.g., ferric stearate and ferric myristate).	Phenols (e.g., ammonium salts of tannic, gallic and salicylic acids).
(2)	Heavy metal salts of organic acids (e.g., Ni, Co, Pb, Cu, Fe, Hg and Ag salts of acetic, stearic and palmitic acids).	Alkaline earth metal salts (e.g., CaS, SrS and BaS).
(3)	Organic chelates (e.g., thiodiphenyl carbazide and diphenyl carbazone).	Sulfur compounds (e.g., sodium tetrathionate, sodium thiosulfate and thiourea).
(4)	Heavy metal salts of oxalic acid (e.g., Ag, Pb, Hg and Th salts).	Sulfur compounds (e.g., sodium tetrathionate, sodium thiosulfate and thiourea).
(5)	Noble metal salts of organic acids (e.g., silver oxalate and mercury oxalate).	Organo-polyhydroxy compounds (e.g., polyhydroxy alcohol, glycerin and glycol).
(6)	Noble metal salts of organic acids (e.g., silver behenate and silver stearate).	Aromatic organic reducing agents (e.g., protocatechuic acid, spiroindane and hydroquinone).
(7)	Aliphatic ferric salts (e.g., ferric stearate).	Aromatic polyhydroxy compounds (e.g., 3,4-dihydroxy tetraphenyl methane).
(8)	Metal salts of organic acids (e.g., silver behenate and acidic silver phthalate).	Cyclic organic reducing agents (e.g., protocatechuic acid and 2,3-dihydroxy-benzoic acid).
(9)	Lead salts of organic acids (e.g., lead caproate and lead behenate).	Thiourea derivatives (e.g., ethylene thiourea and N-dodecyl thiourea).
(10)	Grignard type organometallic compounds.	Sulfur compounds.

Alternatively, the second heat-sensitive recording material is composed mainly of at least one compound selected from diazo compounds and azo type diazo compounds, an azo coupler and a binder.

(a) Diazo compounds and azo type diazo compounds: It is desirable that these compounds are stable to light and is slightly colored or white or colorless.

(1) Diazobenzenes having the substituents m-CH_3, p-Cl, p-Ph, p-NO_2, m-NO_2, o-Cl, o-CH_3 and p-N=N-Ph, wherein m, p and o before the substituents represent the positions of substitution, and Ph represents a phenyl group.

Examples of the above compounds are as follows:

1-Daizo-2-nitro-4-chlorobenzene·½ $ZnCl_2$
1-Diazo-2-methyl-4-chlorobenzene·½ $ZnCl_2$
1-Diazo-2-chlorobenzene·½ $ZnCl_2$

(2) Azo type diazo compounds:

4-Amino-3-nitroanisole hydrochloride·½ $ZnCl_2$
o-Nitroaniline·$ZnCl_2$
4-Chloro-2-nitroaniline·$ZnCl_2$
Stable diazonium compounds of 4-chloro-2-trifluoromethylaniline
Stable diazonium compounds of 2,6-dichloro-p-phenylenediamine
p-Nitroaniline

(b) Azo couplers: (Compounds forming azo dyes by reaction with diazo compounds or azo type diazo compounds)

3-Hydroxy-2-naphthanilide
3-Hydroxy-2-naphtho-o-toluidide
3-Hydroxy-2-naphtho-2-ethoxyanilide
3-Hydroxy-2-naphtho-o-anisidide
1,3,5-Hydroxybenzene
3,5-Diethoxyphenol
3-Acetamidophenol
1,3,5-Resorcyclic acid anilide
4,4',6,6'-Tetrahydroxyphenyl
1-Hydroxynaphthalene
2-Hydroxynaphthalene-4-sulfonic acid
2-Hydroxynaphthalene-3,6-disulfonic acid
2-Hydroxy-2-naphthoic acid diethanolamide
5,5'-Dimethyl-1,3-cyclohexanedione
Cyanoacetanilide
3-Hydroxy-2-naphthoic acid-3'-morpholino propylamide

(c) Binders: Since azo dye-forming components comprising the aforesaid diazo compounds or azo type diazo compounds and azo couplers are water soluble, it is preferable to use binders which are soluble in non-polar or slightly polar organic solvents. Examples of such binders include natural rubber, synthetic rubbers, chlorinated rubbers, alkyd resins, polystyrene, styrene-butadiene copolymers, polymethyl methacrylate, ethyl cellulose, nitrocellulose and polyvinyl carbazole.

(d) Other additives: Additives are used in order to prolong the second heat-sensitive recording material in life and to make brilliant the thermally formed colors. For example, a basic substance such as ammonium carbonate, ammonium salicylate, urea, thiourea or amine takes part in the thermal color-forming of the material, and an organic acid such as palmitic acid, stearic acid, hydroquinone, resorcinol, salicylic acid, tartaric acid, citric acid or p-hydroxybenzoic acid, or a phenolic acid has effect of enhancing the material in storage stability.

It is also possible to bring the recording paper of the present invention to such a construction that the second layer is composed of a colored layer and the inter layer, which covers the second layer, is composed of a light-scattering layer in which has been dispersed the aforesaid decolorizing agent in the form of particles, so that at the time of color formation, the inter layer is melted to remove the color developed in the first layer and, at the same time, to make the second layer visible. In the colored layer, it is ideal to use a pigment or dye having a color which is complementary to the color to be developed in the first layer. Further, when the binder used is a water-soluble polymer, not only the binder is easily applicable to the paper surface, but also the production cost of recording paper can advantageously be reduced.

Examples of the pigment or dye to be used in the colored layer include carbon black (black), Benzidine Yellow (yellow), Chrome Vermilion (orange), Lake Red C (red), Toluidine Red (red), Phthalocyanine Blue (blue), Phthalocyanine green (green), Methyl Violet, Methylene Blue, Auramine O, Fuchsine NB, Congo Red and Acid Violet.

Evaluation method for investigating the effect of the present invention is as mentioned below.

A heat-sensitive recording sheet is colored for decolored by means of a metal stamp bed capable of being maintained at a definite temperature, and the colored or decolored image is represented by a reflective optical density (hereinafter referred to as "R.O.D."), whereby a relative comparison can conveniently be made. In the evaluation according to the present invention, the recording was effected by use of a column-shaped stainless steel-made stamp having an end diameter of 10 mm. which had a heating portion in the interior, and a thermal head having silicon oxide film resistors as heat-generating members, and the R.O.D. was measured by means of Automatic Equilibrium Densitometer NLM VI manufactured by Narumi Co. and Microdensitometer manufactured by Konishiroku Co. The filter used was a gelatin filter produced by Kodak Co.

Referential Example 1

200 Parts by weight of an aqueous solution containing 10% by weight of a polyvinyl alcohol (PVA 205 produced by Kurare Co.) was mixed with 35 parts by weight of 3,3-bis(p-dimethylaminophenyl) - 6-dimethylaminophthalide as a color-forming dye, and the resulting mixture was pulverized in a ball mill for more than 1 hour to obtain a dispersion (hereinafter referred to as "liquid A"). In the liquid A, the color-forming dye had scarcely dissolved and had been dispersed in the form of fine particles of less than 5 microns.

On the other hand, 200 parts by weight of an aqueous solution containing 10% by weight of polyvinyl alcohol was mixed with 35 parts by weight of bisphenol A as a color-forming agent, and the resulting mixture was pulverized in a ball mill for more than 1 hour to prepare a liquid B. In the liquid B, the color-forming agent had been dispersed in the form of fine particles of less than 5 microns.

Subsequently, 1 part by weight of the liquid A was mixed with 20 parts by weight of the liquid B by use of a homogenizing mixer. In the mixed liquid comprisng the liquids A and B, the color-forming dye and the color-forming agent had individually been dispersed as fine particles and had individually been surrounded by the polyvinyl alcohol, so that it may be said that there was no direct contact between the two particles. The thus obtained mixed liquid was coated by use of a wire bar on a white paper of 70 g./m.^{2}, air-dried and then dried at a temperature of 40° to 45° C., on a photographic ferro plate to prepare a heat-sensitive one color recording paper. The amount of the coated mixture after drying was 5 g./m.^{2}. The thus prepared recording paper had such a construction as shown in FIG. 4. The recording paper was colored by means of a stamp type color tester, whereby a clear blue image was obtained. When stamp temperatures are plotted on a horizontal axis and R.O.D. values on a vertical axis, there is obtained a curve corresponding to the H-D curve (characteristic curve) which is generally used in the photography. The temperature giving an R.O.D. of fog (D_f)+0.1 is referred to as color forming sensitivity and is represented by Ts_1. In this example, the said temperature Ts_1 was 85° C., the maximum density D-max was 1.35, and the R.O.D. of fog (D_f) was 0.04 (refer to FIG. 6).

The recorded image thus obtained was sufficiently visible even when allowed to stand in a room for 6 months.

Referential Example 2

A recording sheet of the construction as shown in FIG. 5:

In this case also, the same liquids A and B as in Referential Example 1 were used. In addition to said liquids, however, a liquid C was prepared by dissolving 10 parts by weight of polyethylene glycol (#6,000, produced by Nippon Yushi Co.) in 90 parts by weight of water.

The liquid C was coated by means of a wire bar on a white paper of 70 g./m.^{2}, air-dried and then dried at a temperature of 40° to 45° C. by use of a photographic ferro plate to form a layer on the paper. Subsequently, the same mixed liquid comprising the liquids A and B as in Referential Example 1 was coated by means of a wire bar on the above-mentioned layer, air-dried and then dried at 40° to 45° C. by use of a photographic ferro plate to prepare a recording sheet. The thus prepared recording sheet was recorded by means of a thermal recorder using a silicon oxide film resistor. The recording was

effected at a pen speed of 300 mm./sec. and the measurement of R.O.D. was conducted by use of Micro-densitometer manufactured by Konishiroku Co. As the result, a blue color initiated to develop at an energy of 1.5 mj. (milli-joules), reached maximum (D-max=0.6) at 2.0 mj., gradually disappeared thereafter, and completely disappeared at 3.0 mj. (refer to FIG. 7).

represented by T_{D1}, and the R.O.D. value at that time was represented by D_{D1}.

TABLE 1

Referential example number	First heat-sensitive recording material: Color-forming dye	Color forming agent	Binding	Decolorization layer: Decolorizing agent	Liquid	Characteristics: T_{S1} (° C.)	T_{D1} (° C.)	D_{D1}	$D_{max\text{-}1}$	D_{f1}	Color
3-1	3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide.	Chloroglycine carboxylic acid.	Hydroxyethyl cellulose.	Polyethylene glycol.	C-2	60	110	0.12	1.13	0.06	Bluish purple.
3-2	3,6-dimethylfluoran	2,2'-Di hydroxy diphenyl.	Polyvinyl alcohol.	Polyoxyethylene oleyl ether.	C-2	63	110	0.08	0.60	0.02	Red.
3-3	9-p-nitroanilino-3,6-bis(diethylamino)-9-xanthenyl-o-benzoic acid lactam.	Gallic acid	Styrene-butadiene copolymer.	Polyethylene glycol.	C-1	105	130	0.09	0.75	0.06	Blue.
3-4	3,3-bis(p-dimethylaminophenyl) phthalide.	β-Naphthol	Gelatin	Sorbitan monostearate.	C-2	67	110	0.09	0.90	0.07	Bluish green.
3-5	3,7-bis(diethylamino)-fluoran.	Methyl-4-hydroxybenzoate.	Starch	Polyoxyethylene sorbitan mono-oleate.	C-2	65	120	0.25	0.98	0.11	Black.
3-6	3-dimethylamino-phenyl-5,7-dimethyl-fluoran.	p-Hydroxybenzoic acid.	Polyvinyl alcohol.	Polyethylene glycol monostearate.	C-1	90	130	0.07	0.70	0.03	Red.
3-7	3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide.	4,4'-isopropylidene pylidene dipehnol.	do	Polyethylene glycol.	C-2	87	115	0.10	1.25	0.06	Bluish purple.

Referential Example 3

Another embodiment of recording sheets prepared by using other combinations of color-forming dyes and color-forming agents, binders and decolorizing agents:

Liquids A and B corresponding to those in Referential Example 1 were prepared by use of the components shown below.

Liquid A:	Parts by weight
10% Binder solution	200
Color-forming dye	35
Liquid B:	
10% Binder solution	200
Color-forming agent	35

These liquids were individually pulverized and dispersed by means of a ball mill for more than 1 hour, and were mixed with each other immediately before use by means of a homogenizing mixer. The mixing ratio of liquid A to liquid B was 1:20 by weight.

On the other hand, liquids C–1 and C–2 were prepared by use of the components shown below.

Liquid C–1:	Parts by weight
Decolorizing agent	10
Water	90
Liquid C–2:	
Decolorizing agent	20
Polystyrene	20
1:1 Mixed solution of toluene and benzene	70

The liquid C–2 was prepared by pulverizing in a ball mill for more than 1 hour a mixture comprising 20 parts by weight of a polystyrene (Picolastic D 150, produced by Esso Standard Oil Co.), 70 parts by weight of a 1:1 mixed solution of toluene and benzene, and 20 parts by weight of a decolorizing agent. The above-mentioned 3 kinds of liquids were individually coated on a coating paper of 70 g./m.^{2} and then dried to prepare a heat-sensitive recording paper. Thereafter, the thus prepared recording paper was colored or decolored by use of a stamp type color-forming tester to measure such characteristics as mentioned in Referential Example 1.

The results obtained were as set forth in Table 1, in which the temperature for complete decolorization was

Procedure for preparing only the second heat-sensitive recording material by use of an electron donor and an electron acceptor:

500 Parts by weight of a toluene-methanol mixed solution containing 20% by weight of polyvinyl butyral is equally divided into two to prepare liquids D and E. The liquid D is mixed with 25 parts by weight of an electron donor, and the liquid E is mixed with 25 parts by weight of an electron acceptor, and the resulting mixtures are individually pulverized by means of a ball mill for at least 2 hours. The thus prepared electron donor dispersion and electron acceptor dispersion are mixed with each other in a weight ratio of 1:1.

Referential Example 4

According to the above-mentioned procedure, liquids D and E were prepared by using ferric stearate as the electron acceptor and gallic acid as the electron donor. The two liquids were mixed with each other in a ratio of 1:1, and the resulting mixture was coated on a paper and sufficiently dried to obtain a recording paper. The thus obtained recording paper was colored by means of the stamp type color tester used in Referential Example 1, whereby a deep black color was obtained. The color formation sensitive curve of the recording paper was as shown in FIG. 8.

Example 1

A second color layer-forming material containing cadminium stearate as an electron donor and diphenylcarbazone as an electron acceptor was coated on a high quality paper of 80 microns in thickness, and then gradually dried at about 80° C. to form a second color layer on the paper. Thereafter, an inter layer-forming material containing polyethylene glycol was coated on the above-mentioned layer and then dried to form an inter layer. Subsequently, the mixed liquid prepared in Referential Example 1 was coated on the inter layer and then gradually dried to obtain a recording paper. The weights of the first color layer, the inter layer and the second color layer were 2 g./m.^{2}, 0.2 g./m.^{2} and 5 g./m.^{2}, respectively.

The thus obtained recording paper was recorded by means of a recorder using a thermal head, whereby the first layer formed a blue color when thermal head temperature was 85° to 90° C., and the second layer formed a red color when the thermal head temperature became more than 125° C. More particularly, the blue color was formed at 85° to 90° C. and completely disappeared at 110° to 120° C., and only the red color of the second layer

was formed at above 125° C. Subsequently, the two color recording paper was subjected to recording by means of a thermal printer using silicon oxide film resistors, whereby a blue color was formed at an imput energy of 7 mj./dot. The thus formed blue and red colors were sufficiently stable to storage.

Example 2

A recording paper was prepared in the same manner as in Example 1, except that 3-dimethylamino-5,7-dimethylfluoran and bisphenol A were used as the color-forming components of the first layer, polypropylene glycol was used as the inter layer material, and ferric stearate, gallic acid and titanium oxide were used as the color-forming components of the second layer. This recording paper was subjected to recording by use of thermal head kept at 95° C. and 130° C., whereby a brilliant red color was formed at 95° C. and a black color migrated with no red color was formed at 130° C.

Examples 3–8

Recording papers were prepared in the same manner as in Example 1, except that the components of individual layers were as shown in Table 2, and were subjected to the same recording as in Example 1. The results obtained were as set forth in Table 2.

Example 10

Diphenylcarbazole as an electron acceptor, cadmium stearate as an electron donor and polypropylene glycol as a decolorizing agent were treated in the same manner as in Example 9 to prepare a liquid. This liquid was coated on the same paper as in Example 9 and then sufficiently dried to form a layer on the paper. Subsequently, a liquid containing Leuco Crystal Violet as a color-forming dye and bisphenol A as a color-forming agent was coated on the above-mentioned layer and then sufficiently dried to obtain a recording paper. The thus obtained recording paper was subjected to recording by use of a 2 pen type thermal recorder, which had been so designed that a definite energy could always be applied to the paper by use of silicon oxide film resistors. As the result, a brilliant blue color was recorded on the first low energy side and a brilliant red color was recorded on the high energy side. Further, when the said recorded was operated at a speed of 2 cm./hr. to 300 mm./sec., definite red and blue colors could always be recorded.

Example 11

Combinations of second layer-constituting materials comprising several diazo components:

TABLE 2

Example number	Color-forming components of the first layer	Decolorizing agent of the inter layer	Color-forming components of the second layer	Developed colors	
				Fist layer	Second layer
3	Crystal violet lactone bisphenol A.	Sorbitan monostearate	Ferric stearate gallic acid	Blue	Black.
4	do	Polyoxyethylene oleyl ether	Nickel acetate calcium sulfide	do	Do.
5	3-dimethylamino-5 7-dimethyl-fluoran 4-hydroxybenzoate.	Polyethylene glycol	Ferric stearate octadecly ferrocyanide	Red	Blue.
6	do	Polyethylene glycol mono-stearate.	Cesium stearate 4-methoxy-1-hydroxy diphenyl.	do	Do.
7	Crystal violet lactone bisphenol A.	Polyethylene glycol	Silver hehenate procatechuic acid	Blue	Red.
8	do	Polypropylene glycol	N-Dodecylthiourea guanidyl carbonate lead p-toluene-sulfonate.	do	Black.

Example 9

200 Parts by weight of a 1:1 mixed liquid of the liquids D and E prepared in Referential Example 4 was mixed with 50 parts by weight of a liquid prepared by dispersing 10 parts by weight of polyethylene glycol in 100 parts by weight of toluene, and the resulting mixed liquid was sufficiently stirred. This liquid was coated on a high quality paper of 80 microns in thickness in a proportion of 7 g./m.^{2} and then dried to form a layer on said paper. On the other hand, a liquid was prepared in the same manner as in Referential Example 1 by use of 1,3,6-bis-β-methoxyethoxyfluoran as a color-forming dye and bis-phenol A as a color-forming agent. This liquid was coated on the above-mentioned layer in a proportion of 2 g./m.^{2}, sufficiently dried and then finished by use of a calender roll to prepare a recording paper. The thus prepared recording paper was subjected to recording by use of a head made of silicon oxide film resistors arranged in one line in the horizontal direction and 7 lines in the vertical direction.

When the speed was 45 characters/sec., a brillant red color was recorded at an energy of 6 mj./dot and a brilliant black color was recorded at an energy of 10 mg./dot. The thus obtained record could be stored stably without any change.

Liquid F: Parts by weight

Diazo compound	5
10% Binder solution	100

Liquid G:

Diazo coupler	15
10% Binder solution	100

Each of liquids F and G of the above compositions were individually pulverized for more than 10 hours by means of a ball mill having an inner volume of 200 ml. to form dispersions. The size of each dispersed particle after the pulverization was 0.1 to 5 microns. Each 100 parts by weight of the dispersions were mixed with each other by means of a homogenizing mixer. Subsequently, the mixed dispersion was coated on a paper, air-dried and then dried by use of a photographic ferro bed to prepare a recording material. The amount of the dispersion coated was 3.5 to 10 g./m.^{2}. The thus prepared recording paper was tested by use of a stamp type color forming tester. The results obtained were as set forth in Table 3.

TABLE 3

Example number	Second layer-constituting materials			Characteristics			
	Diazo compound	Azo coupler	Binder	Ts_2 (° C.)	$D_{max.2}$	Df_2	Developed color
11-1	1-diazo-2-methyl-4-chlorobenzene· ½ $ZnCl_2$.	1,3,5-hydroxybenzene	Ethyl cellulose	125	0.76	0.07	Reddish purple.
11-2	4-chloro-2-nitroaniline	3-hydroxy-2-naphthol-O-toluidide.	Ethylene-butadiene copolymer.	107	0.65	0.05	Turkish red.
11-3	4-chloro-2,2'-trichloromethyl aniline diazonium.	3-hydroxy-2-naphthanilide	Polystyrene	127	0.85	0.08	Red.
11-4	4-amino-3-nitroanisole hydrochloride· ½ $ZnCl_2$.	3-hydroxy-2-naphtho-O-anilide.	do	123	0.98	0.13	Bordeaux.

In Table 3, Ts_2 is a color forming sensitivity. $D_{max.2}$ is a maximum density, and Df_2 is a fog density.

Several examples concerning the constructions of heat-sensitive two color recording sheets are mentioned below. These are the constructions shown in FIGS. 1 and 2, and, in practice, there may be thought out many combinations by varying the coating order.

Example 12

A recording sheet was prepared b use of the materials described in Example 11–1, and polyethylene glycol dispersed in a toluene solution of polystyrene was coated thereon in a proportion of 2 g./m.^{2} to form a layer on the sheet. Subsequently, a color-forming component comprising Crystal Violet Lactone and 2,2'-dihydroxydiphenyl was coated on the above-mentioned layer in a proportion of 2.5 g./m.^{2} to prepare a heat-sensitive two color recording sheet. This recording sheet was tested in characteristics by means of a stamp type color forming tester to obtain the results shown below.

Ts_1=61° C. T_{D1}=105° C.
Ts_2=113° C. Df_0=0.08
$D_{max.1}$=1.05 D_{D1}=0.12
$D_{max.2}$=0.56

(Df_0 is the fog density of un-colored portion of the recording sheet.)

The color of the first recording material was a brilliant bluish purple color (a cobalt color), and that of the second recording material was a reddish orange color.

Example 13

Recording sheet of the construction (FIG. 2) comprising a first recording material and a second recording material incorporated with a decolorizing agent:

15 Parts by weight of polyethylene glycol was added to each of the liquids F and G used in Example 11–1, and the resulting mixture was pulverized for more than 10 hours by means of a ball mill having an inner volume of 200 ml. The size of each dispersed particle was 0.1 to 5 microns. After the pulverization, each 50 parts by weight of the liquids F and G were quickly mixed with each other by means of a homogenizing mixer, and the resulting mixed liquid was coated on a paper of 70 g./m.^{2}, air-dried and then dried by use of a ferro bed to form a layer. Subsequently, an equal amount of the first color-forming component of Example 12 was coated on said layer, and then air-dried to prepare a recording sheet. The thus prepared recording sheet was investigated in characteristics by means of a stamp type color forming tester to obtain entirely the same results as in Example 12.

Example 14

Recording sheets of the construction shown in FIG. 1: Using such components as in Table 4, heat-sensitive two color recording sheets were prepared in the same manner as in Example 12. The characteristics of the recording sheets were as set forth in Table 4.

TABLE 4

Example number	First layer	Decolorizing agent	Second layer	Characteristics: Ts_1 (° C.)	T_{D1} (° C.)	Ts_2 (° C.)	$D_{max.1}$	$D_{max.2}$	Df_0	First color	Second color
14–1	3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide. β-Naphthol. Styrene-butadiene copolymer.	Sorbitan monostearate.	4-chloro-2-hitroaniline. 3-hydroxy-2-naphthol-0-toluidide. Ethylene-butadiene copolymer.	67	110	107	0.88	0.63	0.09	Bluish green.	Turkish red.
14–2	3,6-dimethylfluoran. 2,2'-dihydroxy-diphenyl. Polyvinyl alcohol.	Polyoxyethylene oleyl ether.	4-amino-3-nitroanisole hydrochloride·½ $ZnCl_2$. 3-hydroxy-2-naphtho-0-anilide. Polystyrene.	63	108	125	0.61	0.90	0.15	Red	Bordeaux.
14–3	3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide. 4,4'-isopropylidene diphenol. Polyvinyl alcohol.	Polyethylene glycol.	4-chloro-2,2'-trichloromethylaniline diazonium. 3-hydroxy-2-naphtho-O-anilide. Polystyrene.	85	115	130	1.20	0.80	0.10	Bluish purple.	Reddish orange.
14–4	do	Polyethylene glycol mopostearate.	do	86	115	130	1.15	0.72	0.15	do	Do.
14–5	3-dimethylamino-phenyl-5,7-dimethylfluoran.	Polypropylene glycol.	1-diazo-2-methyl-4-chloro-benzene·½ $ZnCl_2$. 1,3,5-hydroxy-benzene. Ethyl cellulose.	90	130	125	0.65	0.75	0.13	Red	Brownish purple.
14–5	p.Hydroxybenzoic acid. Polyvinyl alcohol.										

Example 15

In the same manner as in Referential Example 1, an emulsion was prepared by use of Rhodamine Lactam as a color-forming dye and p-hydroxybenzoic acid as a color-forming agent. The emulsion was coated on a white paper of 70 g./m.^{2} and then dried to form a layer on the paper. The amount of the coated emulsion after drying was 7 g./m.^{2}. The thus coated paper was subjected to a calender roll to make the surface thereof sufficiently smooth, and then the liquid C–2 used in Referential Example 2 was coated on the paper surface and then dried to form a layer thereon. The amount of the coated liquid after drying was 0.42 g./m.^{2}. On the other hand, an emulsion was prepared in the same manner as in Referential Example 1 by use of Crystal Violet Lactone as a color-forming dye and bisphenol A as a color-forming agent. This emulsion was coated on the above-mentioned layer and then dried to obtain a recording paper. The amount of the coated emulsion after drying was 1 g./m.^{2}.

The thus obtained recording paper was subjected to recording by use of a thermal recorder having silicon oxide films resisters as heat-generating members and under a speed condition of 200 m./sec., whereby a blue color could be recorded at 1.5 mj. and a red color at 2.5 mj. Subsequently, the first and second colors were measured in reflective optical density by means of Konishiroku Microdensitometer using a filter. The results obtained were shown in Fig. 9, wherein the vertical axis shows the reflective optical density, and the horizontal axis shows the width of line.

Fig. 9–(A) is a graph showing the reflective optical densities of the first color formed at 1.5 mj., in which the solid line **1** represents the reflective optical densities of the first color when measured by use of a red filter (Ratten No. 25 produced by Kodak Co.), and the dotted line **2** represents those of a red color component detected in a more or less amount in the first color when measured by use of a blue filter (Ratten No. 55 produced by Kodak Co.). Visually,

the first color is a substantially complete blue color, though a more or less amount of red color was detected by the densitometer.

Fig. 9–(B) is a graph showing the reflective optical densities of the second color formed at 2.5 mj., in which the solid line 3 represents the reflective optical densities of the second color when measured by use of the above-mentioned blue filter, and the dotted line 4 represents those of a blue color component detected in a more or less amount in the second color when measured by use of the above-mentioned red filter. Visually, the second color is a substantially brilliant red color, though a more or less amount of blue color was detected by the densitometer on both sides of the recorded curve of the red color.

In the above manner, two brilliant colors could be recorded. The thus recorded colors were sufficiently stable to storage.

Further, the above-mentioned recording paper was subjected to recording by use of a head comprising silicon oxide film resistors of 7 dots and under a speed condition of 45 characters/sec., whereby a blue color could be recorded at 6 mj., and a brilliant red color at 10 mj.

Example 16

On a paper were successively coated in this order 5 g./m.^{2} of a second color-forming component comprising gallic acid and Leuco Crystal Violet Lactone, 0.3 g./m.^{2} of the decolorizing agent used in Example 15, and 1 g./m.^{2} of a first color-developing component comprising 2,2'-dihydroxybenzoate and 3,6-dimethylfluoran. Subsequently, the coated paper was sufficiently dried to obtain a recording paper. This recording paper was subjected to recording by use of the same recorder as in Example 15, whereby two brilliant red and blue colors could be recorded as the first and second colors, respectively.

Example 17

Recording papers were prepared in the same manner as in Example 15, and then subjected to recording at a speed of 60 mm./sec., using silicon oxide film resistors. The results obtained were as set forth in Table 5, in which the color formation temperatures are temperatures of the heating portions of the silicon oxide film resistors.

The above-mentioned black coating layer was formed by coating on the paper a mixture of 100 parts by weight of an aqueous solution containing 4% by weight of polyvinyl alcohol and 10 parts by weight of carbon black. The polyvinyl alcohol acted as a binder for the pigment particles. The thickness of the black coating layer was made about 2 microns.

The above-mentioned opaque light-scattering particle layer of a fusible material was formed in such a manner that 30 parts by weight of polyethylene glycol (average molecular weight 7,000) and 100 parts by weight of a solution comprising acetone and toluene in a volume ratio of 1:1 were mixed with 25 parts by weight of a 10 wt. percent solution of nitrocellulose in a 1:1 mixed solvent of acetone and toluene, and the resulting mixture was coated on the above-mentioned black layer and then sufficiently dried with hot air at below 50° C. The thickness of the light-scattering particle layer was about 3 microns.

The black color of the aforesaid black layer had been protected substantially completely with the said light-scattering particle layer, and hence was not visible.

The thus obtained recording paper was subjected to recording at a speed of 60 mm./sec. by means of the aforesaid recorder using silicon oxide film resistors, whereby a black color could be recorded at an input energy of 1.8 mj.

Further, the recording paper was tested in color formation by use of the aforesaid stamp type color forming tester, whereby a black color initiated to develop at 75° C. and reached the maximum density at 90° C. More particularly, the opaque layer initiated to be made transparent at 75° C. and was completely made transparent at 90° C. to make the lower colored layer visible. In this case, the fog density (density prior to recording) was 0.1.

Example 19

5 Parts by weight of fuchsine was dissolved in 100 parts by weight of water. 10 Parts by weight of the resulting solution was mixed with 30 parts by weight of a 4% aqueous polyvinyl alcohol solution, and the mixed solution was coated on a base paper to form a colored

TABLE 5

Example number	Color-forming components of the first layer	Decolorizing agent of the inter layer	Color-forming components of the second layer	Ratio in amount of color-forming components: First layer	Ratio in amount of color-forming components: Second layer	Color formation temperatures and colors: First layer	Color formation temperatures and colors: Second layer
17-1	Leuco crystal violet lactone, β-naphthol.	Polyoxyethylene alkylamide.	Rhodamine lactam, p-hydroxybenzoic acid.	1	7	135° C., Blue	200° C., red.
17-2	Leuco crystal violet lactone, 2,2-dihydroxydiphenyl.	do	do	1	10	do	Do.
17-3	Leuco crystal violet lactone, bisphenol A.	Polyethylene glycol	do	1	5	140° C., blue	215° C., red.
17-4	Rhodamine lactam, bisphenol A.	Polyoxyethylene alkylallyl ether.	Leuco crystal violet, lactone, gallic acid.	1	8	140° C., red	230° C., blue.
17-5	do	Polyethylene glycol	do	1	7	do	225° C., blue.
17-6	do	Polyoxymethylene	do	1	10	do	220° C., blue.
17-7	Leuco crystal violet lactone, bisphenol A.	do	Rhodamine lactam, p-hydroxybenzoic acid.	1	10	135° C., blue	215° C., red.

Two brilliant colors could be recorded also on a recording paper prepared by successively coating on a base paper in this order (i) a previously colored dye or pigment and a binder, (ii) polyether and polyethylene glycol derivatives dispersed as light-scattering particles into a thermoplastic polymer capable of forming by itself a transparent thin layer, and (iii) a color-forming substance comprising a leuco dye base of the triphenylmethane type, a dye of the fluoran type and a phenolic substance.

Example 18

Onto a continuous sheet-like paper of 75 microns in thickness were successively formed a black sub-coating layer and an opaque light-scattering particle layer (inter layer) of an inherently fusible material.

layer. On the other hand, 30 parts by weight of polypropylene glycol, 10 parts by weight of nitrocellulose, 30 parts by weight of hydrogenated fatty oil wax and 10 parts by weight of talc were added to 150 parts by weight of a mixed solution of acetone and toluene, and the resulting mixture was kneaded by means of a ball mill to form a dispersion. 10 Parts by weight of this dispersion was mixed with 10 parts by weight of a 1:1 mixed solution of acetone and toluene, and then coated on the surface of the aforesaid colored layer to form an opaque light-scattering layer. The thickness of the light-scattering layer after thorough drying was 4 microns. Subsequently, a color-forming component comprising Leuco Crystal Violet Lactone as a color-forming dye and 2,2'-dihydroxydiphenyl as a color-forming agent was coated on the above-mentioned light-scattering layer. The thus coated

paper was dried to prepare a recording paper. This recording paper was subjected to recording at a pen speed of 60 mm./sec. by use of a recorder having silicon oxide film resistors as heat-generating members. The first color, i.e. blue color, was formed at a thermal head temperature of 120° C. and disappeared at 150° C., and, at the same time, a red color initiated to be made visible and reached the maximum density at 200° C. These two colors were brilliant colors which had not been migrated with each other. Of these two colors, the first color was somewhat low in stability. However, a first color which had been formed in a recording material having a thermoplastic resin layer disposed between the light-scattering layer and the first layer, was quite excellent in stability.

Example 20

Using such components and materials as shown in Table 6, two color recording papers were prepared in the same manner as in Example 19. According to the procedure described in Example 19, the recording papers were measured in color formation temperatures and colors of the second and first layers. The results obtained were as set forth in Table 6.

TABLE 6

Example number	Color-forming components of the first layer	Inter layer-constituting materials: Binder	Inter layer-constituting materials: Decolorizing agent	Inter layer-constituting materials: Additives	Coloring pigment of the second layer	Color formation temperatures and colors: First layer	Color formation temperatures and colors: Second layer
20-1	Leuco crystal violet lactone, 2,2'-methylenebis(4-chlorophenol).	Nitro-cellulose.	Polyethylene gly col	Talc	Lake red C	102° C., blue	150° C., red.
20-2	Leuco crystal violet lactone, bisphenol A.	Ethyl cellulose.	Polyethylene glycol monostearate.	Talc, hydro-genated fatty oil wax.	Carbon black	108° C., blue	145° C., black.
20-3	Rhodamine lactam, bisphenol A.	Styrene polymer.	Polyoxyethylene alkylallyl ether.	do	Phthalocyanine blue.	100° C., red	145° C., blue.
20-4	Rhodamine lactam, 4-hydroxyacetophenone.	Nitro-cellulose.	Polyethylene glycol.	do	Carbon black	90° C., red	140° C., black.

What is claimed is:

1. A heat-sensitive two color recording paper which has a layer of a first heat-sensitive recording material prepared by dispersing, as discontinuous particles into a film-forming binder, a triphenylmethane or fluoran type non-colored dye base having in the molecule a reactive color-developing component of the lactone or lactam type, and a phenolic substance or an organic acid, said layer developing a color at the time of application of heat, by formation of a color-developing substance, and a layer of a second heat-sensitive recording material capable of developing at the time of application of heat a color different from the color of the aforesaid first layer, and which contains as a decolorizing agent for the color-developing substance contained in the first layer a thermofusible polyether which is substantially solid at normal temperature.

2. A heat-sensitive two color recording paper according to Claim 1, wherein the quantity of heat A necessary to develop the color of the first layer, the quantity of heat B necessary to form the color of the second layer, and the quantity of heat C necessary to fluidize the thermofusible polyether are in such a relation as to satisfy the inequality $A<C\leqq B$.

3. A heat-sensitive two color recording paper according to Claim 1, wherein the second layer has such a construction that an electron donor and an electron acceptor have been used as color-forming components and have been dispersed as discontinuous particles into the film-forming binder.

4. A heat-sensitive two color recording paper according to Claim 1, wherein the second layer has such a construction that a diazo compound and an azo coupler have been used as color-forming components and have been dispersed as discontinuous particles into the film-forming binder.

5. A heat-sensitive two color recording paper according to Claim 1, wherein the polyether has been dispersed in the film-forming binder and disposed as an inter layer between the first layer and the second layer.

6. A heat-sensitive two color recording paper according to Claim 1, wherein the polyether has been dispersed in the second layer.

7. A heat-sensitive two color recording paper according to Claim 5, wherein the second layer is a previously colored layer, and the inter layer has been so constructed as to act as a protective layer for the second layer so that, by application of heat, the inter layer becomes substantially transparent to make the second layer visible.

8. A heat-sensitive two color recording paper according to Claim 5, wherein the second layer is a layer composed of a triphenylmethane or fluoran type non-colored dye base having in the molecule a reactive color-forming component of the lactam or lactone type and of a phenolic acid substance or an organic acid which have been dispersed as discontinuous particles in the film-forming binder, the amount of said color-forming component being at least 5 parts by weight per part by weight of the color-forming substance of the first layer.

9. In a heat-sensitive two color recording paper of two layers which individually develop different colors due to a difference in the quality of heat applied to the paper surface and which has a layer of a first heat-sensitive recording material prepared by dispersing, as discontinuous particles into a film-forming binder, a triphenylmethane or fluoran-type non-colored dye base having in the molecule a reactive color-developing component of the lactone or lactam type, and a phenolic substance or an organic acid, said layer developing a color at the time of application of heat, and a layer of a second heat-sensitive recording material capable of developing at the time of application of heat a color different from the color of the aforesaid first layer, the improvement which comprises employing in said recording paper a decolorizing agent for the color-developing substance formed in the first layer a thermofusible polyether which is substantially solid at normal temperature.

10. The heat-sensitive two color recording paper of claim 9 wherein said triphenylmethane or fluoran type non-colored dye base is selected from the group consisting of

3,3-bis(p-dimethylaminophenyl)-phthalide,
3,3-bis(p-dimethylaminophenyl)-6-dimethylamino-phthalide,
3,3-bis(p-dimethylaminophenyl)-6-nitrophthalide,
3,3-bis(p-dimethylaminophenyl)-6-monomethylamino-phthalide,
3,3-bis(p-dimethylaminophenyl)-6-chlorophthalide,
3,3-bis(p-dimethylaminophenyl)-6-ethoxyphthalide,
3,3-bis(p-dimethylaminophenyl)-6-diethylamino-phthalide,
3-dimethylamino-6-methoxyfluoran,
7-acetamino-3-dimethylaminofluoran,
3-dimethylamino-5,7-dimethylfluoran,
3-diethylamino-5,7-dimethylfluoran,
3,6-bis-β-methoxyethoxyfluoran,
3,6-bis-β-cyanoethoxyfluoran,
9-p-nitroanilino-3,6-bis(diethylamino)-9-xanthenyl-6-benzoic acid lactam, and
9-nitroamino-3,6-bis(dimethylamino)-9-thioxanthenyl-6-benzoic acid lactam.

11. The heat-sensitive two color recording paper of claim 9 wherein said phenolic substance is selected from the group consisting of
4-tert-butylphenol,
4-phenylphenol,
4-hydroxydiphenoxide,
α-naphthol,
methyl-4-hydroxybenzoate,
β-naphthol,
4-hydroxyacetophenone,
4-tert-octyl catechol,
2,2'-dihydroxydiphenyl,
2,2'-methylenebis(4-chlorophenol),
4,4'-isopropylidene diphenol,
4,4'-isopropylidenebis(2-chlorophenol),
4,4'-isopropylidenebis(2,6-dibromophenol),
4,4'-isopropylidenebis(2,6-dichlorophenol),
4,4'-isopropylidenebis(2-methylphenol),
4,4'-sec-isobutylidene diphenol,
4,4'-cyclohexylidene diphenol,
2,2'-thiobis(4,6-dichlorophenol),
hydroquinone,
pyrogallol,
phloroglucine, and
phloroglucinolcarboxylic acid.

12. The heat-sensitive two color recording paper of claim 9 wherein said organic acid is selected from the group consisting of
p-hydroxybenzoic acid,
m-hydroxybenzoic acid,
o-hydroxybenzoic acid,
boric acid,
tartaric acid,
oxalic acid,
maleic acid,
citric acid,
succinic acid,
gallic acid,
1-hydroxy-2-naphthenic acid, and
2-hydroxy-p-toluyl acid.

13. The heat-sensitive two color recording paper of claim 9 wherein said thermofusible polyether is selected from the group consisting of
polyethylene glycol,
polyethylene oleyl ether,
sorbitan monostearate,
polyoxyethylene sorbitan mono-oleate,
polyethylene glycol monostearate,
polypropylene glycol,
polyoxyethylene alkylamide,
polyoxyethylene alkylamine,
polyoxyethylene alkylallyl ether, and
polyoxymethylene.

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