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(71) Applicant: **NIPPON PAPER INDUSTRIES CO., LTD.**
Kita-ku, Tokyo 114 (JP)

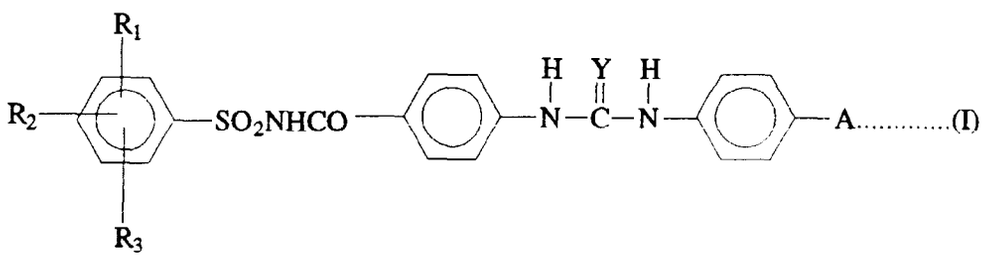
(72) Inventor: **Minami, Toshiaki,**
Nippon Paper Ind. Co., Ltd.
Shinjuku-ku, Tokyo 162 (JP)

(74) Representative: **Woods, Geoffrey Corlett**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

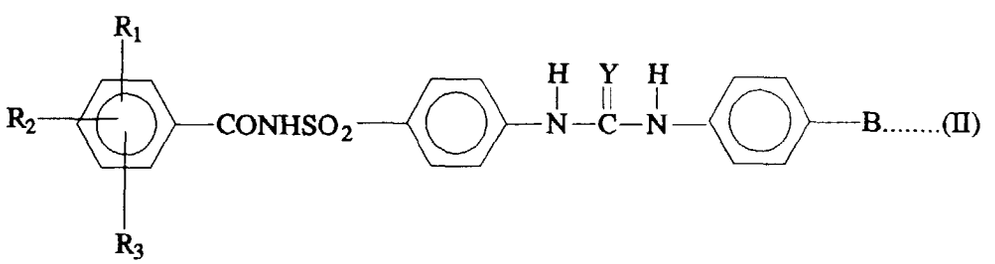
(54) A thermal sensitive recording sheet

(57) A thermally sensitive recording sheet which comprises on a substrate, a thermally sensitive colour developing layer comprising:

(a) a colourless or pale coloured basic leuco dye;
(b) an organic colour developer of formula (I):



wherein A is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, each of R_1, R_2 and R_3, which may be the same or different, is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, or R_1 and R_2 form, together with the carbon atoms to which they are attached, an aromatic ring, and Y is sulfur or oxygen;
or an organic colour developer of formula (II):



wherein B is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, each of R_1, R_2 and R_3, which may be the same or different, is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, or R_1 and R_2 form, together with the carbon

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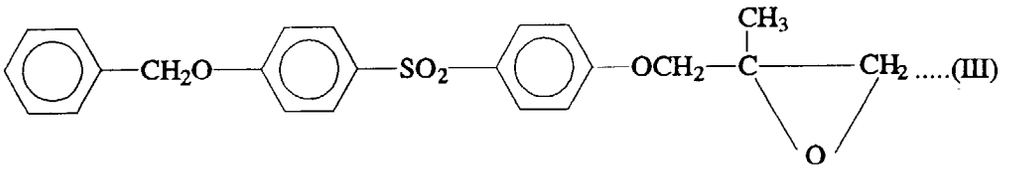
atoms to which they are attached, an aromatic ring, and Y is sulfur or oxygen; and
(c) 0.01-2 parts, based on 1 part of colour developer of formula (I) or (II), of a stabiliser which is a diphenylsulfone derivative of formula (III):



Description

This invention relates to a thermal sensitive recording sheet which has an excellent image stability.

In general, a thermal recording sheet can be obtained be obtained by following procedure ; A colourless or pale coloured basic leuco dye and a colour developer such as a phenolic compound are separately ground to fine particles, then mixed together and dispersed. By adding a binder, a filler, a sensitizer, a slip agent, and other additives to the said mixture, a coating colour can be obtained. The obtained coating colour is coated on a substrate such as paper, synthetic paper, none-woven cloth, film or plastic, thus a thermal sensitive recording sheet is prepared, which develops colour by a momentary chemical reaction caused by heating with a thermal pen, a thermal head, a hot stamp, laser light or the like.

These thermal recording sheets can be applied in a wide variety of fields such as measuring recorders, terminal printers for computers, facsimiles, automatic ticket venders, ATM (Automatic Teller Machine of bank), HT (Handy Terminal), bar code labels or the like. However, according to the recent advance for manifold application and high performance of these recording apparatus, a required quality improvement for the thermal sensitive recording sheet are becoming higher. For instance, accompanied with high speed recording, it is required to the thermal sensitive recording sheet to possess features of a high density and clear colour image by lower thermal energy, and on the other hand, it is required also to possess an excellent feature for preservation such as light resistance, weather resistance and oil resistance.

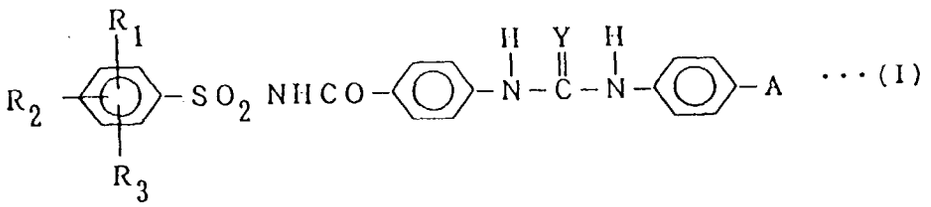
As a conventional example of the thermal sensitive recording sheet, for instance, thermal sensitive recording materials such as disclosed in Japanese Patent publication 4160/68 or in Japanese Patent publication 14039/70 can be mentioned. However, since the responding speed of these conventional thermal sensitive recording materials is slow, a sufficient colour developing density can not be expected when the recording speed is high.

As a method to improve above mentioned defect, developments of high sensitive dye such as a leuco dye which uses 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilinofluorane (Japanese Patent Laid-open publication 109120/74) or 3-dibuthylamino-6-methyl-7-anilinofluorane (Japanese Patent Laid-open publication 190891/84) have been proposed. Further, methods attempting to obtain a high speed recording and a high sensitivity are proposed by using a substance which has a good colour developing ability such as 1,7-bis(4-hydroxyphenylthio)-3,5-dioxahepthane (Japanese Patent Laid-open publication 106456/84), 1. 5-bis (4-hydroxyphenylthio) -3-oxaheptane (Japanese Patent Laid-open publication 116262/84), 4-hydroky-4'-isopropoxy diphenylsulfone (Japanese Patent Laid-open publication 106456/84) as a colour developer have been disclosed.

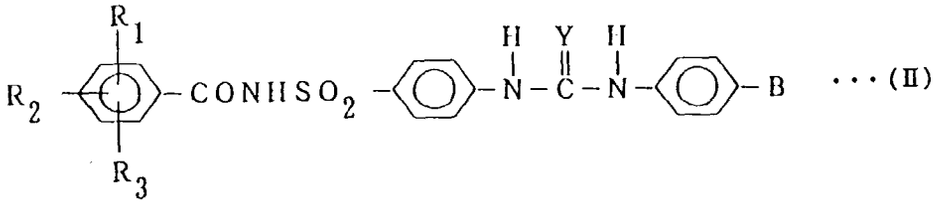
Meanwhile, the inventor of this invention has already proposed a thermal sensitive recording sheet which uses a newly developed derivative of urea (thiourea) as a colour developer. Said thermal sensitive recording sheet can sufficiently be used for a high energy printing, but in a case of lower energy printing or a high speed printing, an enough colour developing density can not be obtained, furthermore, a stability of recorded image against the plasticizer included in polyvinylchloride film is not sufficient. So it is thought to be impossible to put said thermal sensitive recording sheet to a practical use.

The object of the present invention is to provide a thermal sensitive recording sheet which has an excellent image stability.

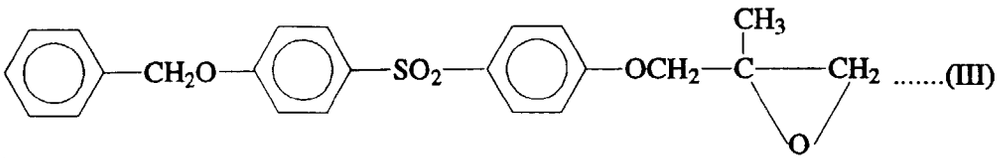
The inventor has conduced intensive studies to develop a thermal sensitive recording sheet which has an excellent image stability, and consequently accomplished the present invention. That is, the above mentioned object can be solved by including a derivative of urea (thiourea) indicated by general formula (I) or (II) in a thermal sensitive colour developing layer as an organic colour developer, and also including 0.01-2 parts of a derivative of diphenylsulfone indicated by general formula (III) based on 1 part of colour developer indicated by general formula (I) or (II) as a stabilizer.



(in this formula, "A" indicates a hydrogen atom, an alkyl group of C_1-C_4, an alkoxy group of C_1-C_4, a hydroxy group or a nitro group, "R_1" "R_2" and "R_3" indicates a hydrogen atom, an alkyl group of C_1-C_4, an alkoxy group of C_1-C_4, a hydroxy group or a nitro group. "R_1" and "R_2" can be mutually combined and form an aromatic ring. Further, "Y" indicates a sulfur or an oxygen atom.)



(in this formula, "B" indicates a hydrogen atom, an alkyl group of C_1-C_4, an alkoxy group of C_1-C_4, a hydroxy group or a nitro group, "R_1" "R_2" and "R_3" indicates a hydrogen atom, an alkyl group of C_1-C_4, an alkoxy group of C_1-C_4, a hydroxy group or a nitro group. "R_1" and "R_2" can be mutually combined and form an aromatic ring. Further, "Y" indicates a sulfur or an oxygen atom.)



A C_1-C_4 alkyl group is, for example, methyl, ethyl, i-propyl, n-propyl, t-butyl, s-butyl or n-butyl. A C_1-C_4 alkoxy group is, for example, methoxy, ethoxy, i-propoxy, n-propoxy, t-butoxy, s-butoxy or n-butoxy. When R_1 and R_2 form, together with the carbon atoms to which they are attached, an aromatic ring that aromatic ring is, for example, a benzene ring which forms a naphthalene ring system with the benzene ring to which it is attached.

In the present invention, a derivative of urea (thiourea) indicated by general formula (I) or (II) indicates stronger acidity than a phenolic compound which is a well-known colour developer, and performs very strong colour developing ability to a basic leuco dye. The ground of said fact is explained as follows. That, is in a molecule of a derivative of urea (thiourea) used in this invention, since two electron extractive groups e.g. a sulfonyl group, a carbonyl group or a thiocarbonyl group exist so as to put one benzene ring between, an electron density surrounding a nitrogen atom is remarkably fallen down and consequently results a strong colour developing ability to a basic leuco dye.

Further, in this invention, since the molecule of stabilizer indicated by general formula (III) possesses a sulfone group, when it is fused by heat together with the organic colour developer indicated by general formula (I) or (II), it makes an electron density surrounding a nitrogen atom fall down more, and consequently effects to improve the preservable stability of a recording image.

As the substantial examples of a derivative of urea (thiourea) used in this invention, following compounds are mentioned, however, it is not intended to be limited to them. This derivatives of urea (thiourea) can be used alone or by mixing with others.

N-(benzenesulfonyl)-*p*-(phenylureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(phenylureylene)benzamide
N-(4-ethylphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-*n*-propylphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-iso-propylphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(t-butylphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-ethoxyphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(2-hydroxyphenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(4-nitrophenylsulfonyl)-*p*-(phenylureylene)benzamide
N-(benzenesulfonyl)-*p*-(4-tolylureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(4-tolylureylene)benzamide
N-(4-ethlphenylsulfonyl)-*p*-(4-tolylureylene)benzamide
N-(4-iso-propylphenylsulfonyl)-*p*-(4-tolylureylene)benzamide
N-(*n*-butylphenylsulfonyl)-*p*-(4-tolylureylene)benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(4-tolylureylene)benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(4-tolyoureylene)benzamide
N-(2-hydroxyphenylsulfonyl)-*p*-(4-tolyoureylene)benzamide

N-(4-nitrophenylsulfonyl)-*p*-(4-tolylureylene)benzamide
N-(benzenesulfonyl)-*p*-(2-naphthylureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(2-naphthylureylene)benzamide
N-(4-iso-propylphenylsulfonyl)-*p*-(2-naphthylureylene) benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(2-naphthylureylene)benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(2-naphthylureylene)benzamide
N-(4-nitrophenylsulfonyl)-*p*-(2-naphthylureylene)benzamide
N-(benzenesulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-ethylphenylsulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-n-propylphenylsulfonyl)-*p*-(phenylthioureylene) benzamide
N-(4-iso-propylphenylsulfonyl)-*p*-(phenylthioureylene) benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-ethoxyphenylsulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(phenylthioureylene)benzamide
N-(2-hydroxyphenylsulfonyl)-*p*-(phenylthioureylene)benzamide
N-(4-nitrophenylsulfonyl)-*p*-(phenylthioureylent)benzamide
N-(benzenesulfonyl)-*p*-(4-tolylthioureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(4-tolylthioureylene)benzamide
N-(4-*n*-propylphenylsulfonyl)-*p*-(4-tolylthioureylene) benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(4-methylphenylthioureylene) benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(4-tolylthioureylene) benzamide
N-(2-hydroxyphenylsulfonyl)-*p*-(4-methylphenylthioureylene) benzamide
N-(4-nitrophenylsulfonyl)-*p*-(4-methylphenylthioureylene) benzamide
N-(benzenesulfonyl)-*p*-(2-naphthylthioureylene)benzamide
N-(4-toluenesulfonyl)-*p*-(2-naphthylthioureylene)benzamide
N-(4-methoxyphenylsulfonyl)-*p*-(2-naphthylthioureylene) benzamide
N-(4-hydroxyphenylsulfonyl)-*p*-(2-naphthylthioureylene) benzamide
N-(2-hydroxyphenylsulfonyl)-*p*-(2-naphthylthioureylene) benzamide
N-(4-nitrophenylsulfonyl)-*p*-(2-naphthylthioureylene) benzamide
N-(phenyl)-N'-(*p*-benzoylaminosulfonyl)phenylurea
N-(phenyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(2-hydroxybenzoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(4-methoxybenzoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(4-ethoxybenzoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(4-n-propoxybenzoylaminosulfonyl)} phenylurea
N-(phenyl)-N'-{*p*-(4-iso-propoxybenzoylaminosulfonyl)} phenylurea
N-(phenyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)}phenylurea
N-(4-toluyl)-N'-(*p*-benzoylaminosulfonyl)phenylurea
N-(4-toluyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylurea
N-(4-toluyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylurea
N-(3-toluyl)-N'-(*p*-benzoylaminosulfonyl)phenylurea
N-(3-toluyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylurea
N-(3-toluyl)-N'-{*p*-(3-toluoylaninosulfonyl)}phenylurea
N-(3-toluyl)-N'-{*p*-(2-toluoylaminosulfonyl)}phenylurea
N-(3-toluyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylurea
N-(4-toluyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)} phenylurea
N-(4-toluyl)-N'-{*p*-(2-hydroxybenzoylaminosulfonyl)} phenylurea
N-(4-toluyl)-N'-{*p*-(4-methoxybenzoylaminosulfonyl)} phenylurea
N-(4-toluyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)}phenylurea
N-(phenyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylthiourea
N-(phenyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylthiourea
N-(phenyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)} phenylthiourea
N-(phenyl)-N'-{*p*-(4-methoxybenzoylaminosulfonyl)} phenylthiourea
N-(phenyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)} phenylthiourea
N-(4-toluyl)-N'-(*p*-benzoylaminosulfonyl)phenylthiourea

N-(4-toluyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylthiourea
N-(4-toluyl)-N'-{*p*-(3-toluoylaminosulfonyl)}phenylthiourea
N-(4-toluyl)-N'-{*p*-(2-naphthoylaminosulfonyl)} phenylthiourea
N-(3-toluyl)-N'-(*p*-benzoylaminosulfonyl)phenylthiourea
N-(3-toluyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylthiourea
N-(3-toluyl)-N'-{*p*-(3-toluoylaminosulfonyl)}phenylthiourea
N-(3-toluyl)-N'-{*p*-(2-naphthoylaminosulfonyl)} phenylthiourea
N-(4-toluyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)} phenylthiourea
N-(4-toluyl)-N'-{*p*-(4-methoxybenzoylaminosulfonyl)} phenylthiourea
N-(4-toluyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)} phenylthiourea

In this invention, as a stabilizer, a derivative of diphenylsulfone indicated by general formula (III) is used. In this invention, if the proportion of a stabilizer indicated by general formula (III) is smaller than 0.01 parts based on 1 part of an organic colour developer indicated by general formula (I) and (II), the stabilizing effect is not sufficient, and if it is bigger than 2 parts based on 1 part of an organic colour developer the enough stabilizing effect can not be expected. Therefore, the most desirable proportion of the stabilizer is 0.01-2 parts based on 1 part of the organic colour developer.

As the basic leuco dye used in this invention, triphnylmethane type, fluorane type, fluorene type and divinyl type are desirably used, however, it is not intended to be limited to them. The substantial examples of them are indicated below. These dyes can be used alone or by mixing with others.

<triphenylmethane-based leuco dye>

3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide [another name is crystal violet lactone]

<fluoran-based leuco dye(I)>

3-diethylamino-6-methyl-7-anilinofluoran
3-(N-ethyl-*p*-toluidino)-6-methyl-7-anilinofluoran
3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran
3-diethylamino-6-methyl-7-(*o,p*-dimethylanilino)fluoran
3-pyrrolidino-6-methyl-7-anilinofluoran
3-piperidino-6-methyl-7-anilinofluoran
3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluoran
3-diethylamino-7-(*m*-trifluoromethylanilino)fluoran
3-N-*n*-dibutylamino-6-methyl-7-anilinofluoran
3-N-*n*-dibutylamino-7-(*o*-chloroanilino)fluoran
3-(*n*-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran
3-dibutylamino-6-methyl-7-(*o,p*-dimethylanilino)fluoran
3-(*n*-methyl-N-propylamino)-6-methyl-7-anilinofluoran
3-diethylamino-6-chloro-7-anilinofluoran
3-dibutylamino-7-(*o*-chloroanilino)fluoran
3-diethylamino-7-(*o*-chloroanilino)fluoran
3-diethylamino-6-methyl-chlorofluoran
3-diethylamino-6-methyl-fluoran
3-cyclohexylamino-6-chlorofluoran
3-diethylamino-benzo[a]-fluoran
3-n-dipentylamino-6-methyl-7-anilinofluoran
2-(4-oxo-hexyl)-3-dimethylamino-6-methyl-7-anilinofluoran
2-(4-oxo-hexyl)-3-diethylamino-6-methyl-7-anilinofluoran
2-(4-oxo-hexyl)-3-dipropylamino-6-methyl-7-anilinofluoran

<fluorene-based leuco dye>

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

<fluoran-based leuco dye(II)>

2-methyl-6-*p*-(*p*-dimethylaminophenyl)aminoanilinofluoran
2-methoxy-6-*p*-(*p*-dimethylaminophenyl)aminoanilinofluoran
2-chloro-3-methyl-6-*p*-(*p*-phenylaminophenyl) aminoanilinofluoran
2-chloro-6-*p*-(*p*-dimethylaminophenyl)aminoanilinofluoran
2-nitro-6-*p*-(*p*-diethylaminophenyl)aminoanilinofluoran
2-amino-6-*p*-(*p*-diethylaminophenyl)aminoanilinofluoran
2-diethylamino-6-*p*-(*p*-diethylaminophenyl) aminoanilinofluoran
2-phenyl-6-methyl-6-*p*-(*p*-phenylaminophenyl) aminoanilinofluoran
2-benzyl-6-*p*-(*p*-phenylaminophenyl)aminoanilinofluoran
2-hydroxy-6-*p*-(*p*-phenylaminophenyl)aminoanilinofluoran
3-methyl-6-*p*-(*p*-dimethylaminophenyl)aminoanilinofluoran
3-diethylamino-6-*p*-(*p*-diethylaminophenyl) aminoanilinofluoran
3-diethylamino-6-*p*-(*p*-dibutylaminophenyl) aminoanilinofluoran

<divinyl-based leuco dye>

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

<others>

1,1-bis-[2',2',2",2"-tetrakis-(*p*-dimethylaminophenyl)ethenyl]-2,2-dinitrileethane
1,1-bis-[2',2',2",2"-tetrakis-(*p*-dimethylaminophenyl)ethenyl]-2-β-naphthoylethane
1,1-bis-[2',2',2",2"-tetrakis-(*p*-dimethylaminophenyl)ethenyl]-2,2-diacetylethane
bis-[2,2,2',2'-tetrakis-(*p*-dimethylaminophenyl)-ethenyl]methymalonatedimethyl ester

In the present invention, the conventional public known sensitizer can be used as far as it does not hurt the necessary effects of this invention. As the substantial example of the sensitizer, following compounds can be mentioned :

fatty acid amide such as amide stearate or amide palmitate
ethylene bisamide
montane-based wax
polyethylene wax
dibenzyl terephthalate
p-benzyloxybenzylbenzoate
di-*p*-tolylcarbonate
p-benzylbiphenyl
phenyl-a-naphthylcarbonate
1,4-diethoxynaphthalene
l-hydroxy-2-naphthoeic acid phenyl ester
1,2-di-(3-methylphenoxy)ethane
di(p-methylbenzyl)oxalate
β-benzyloxynaphthalene
4-biphenyl-p-tolyleter
o-xylylene-bis-(phenylether)
4-(*m*-methylphenoxymethyl)biphenyl

These sensitizers can be used alone or by mixing with others.

As a binder to be used in this invention, full saponificated polyvinylalcohol having 200-1900 polymerization degree, partially saponificated polyvinylalcohol, denatured polyvinylalcohol such as carboxy denatured polyvinylalcohol, amide denatured polyvinylalcohol, sulfonic acid denatured polyvinylalcohol and buthylal denatured polyvinylalcohol, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, copolymer of styrene-maleic anhydryde, copolymer of styrene-buthadien, derivatives of cellulose such as ethyl-cellulose or acetyl-cellulose, polyvinylchrolide, polyvinylacetate, polyacrylicamide, polyacrilate, polyvinylbuthylal, polystyrene and copolymer of these polymers, polyamide resin, silicon

resin, petroleum resin, terpene resin, ketone resin, cumarone resin can be mentioned. These kinds of macromolecule compound can be used by dissolving in water or in solvents such as alcohol, ketone, ester of hydrocarbon, and also can be used by dispersing it by emulsion or paste state in water or other solvent. These methods can be used in combination with, if necessary.

As a filler to be used in this invention, following inorganic or organic filler such as silica, calcium carbonate, kaoline, calcined kaoline, diatomaceous earth, talk, titanium oxide, aluminium hydroxide, urea-formalin resin or hollow plastic pigment can be mentioned.

Further, parting agents such as metallic salt of fatty acid, lubricant such as wax, ultra violet lay absorder such as benzophenone group or triazole group, waterproof agent such as glyoxal, dispersing agents and deformer can be used in this invention.

EXAMPLES

The present invention will be more clearly understood with reference to the following Examples.

The thermal sensitive recording sheet of this invention can be obtained by following procedure, that is ; prepare the coating colour of thermal sensitive colour developing layer by grinding and dispersing a basic leuco dye, a derivative of urea (thiourea) indicated by aforementioned general formula (I) or (II) as an organic colour developer and a derivative of diphenylsulfone indicated by aforementioned general formula (III) as a stabilizer together with a binder, and adding a filler and other additives according to the necessity, then coating the obtained coating colour on the substrate and drying it up. A proportion of a derivative of diphenylsulfone indicated by aforementioned general formula (III) to be added to one part of an organic developer indicated by general formula (I) or (II) is 0.01-2 parts.

The type and the amount of an organic developer, a basic leuco dye and other additives are decided according to the required features and to the recording property, and generally the preferable amount of these compounds are follows, however, are not intended to be limited. That is, 0.01-2 parts of stabilizer indicated by general formula (III), 0.1-2 parts of basic leuco dye and 0.5-4 parts of filler based on 1 part of organic developer indicated by general formula (I) or (II). The preferable amount of binder is 5-25 % to the total amount of solid.

By coating the coating colour having above mentioned composition on a voluntarily selected supporter such as a paper, a non woven cloth, a film or a plastic, an objected thermal sensitive recording sheet can be obtained. Further, for the purpose of improve the preservability, an overcoat layer of a macromolecule including a filler can be prepared on the thermal sensitive colour developing layer. And, furthermore, for the purpose to improve both preservability and sensitivity, an undercoat layer including an organic or an inorganic filler can be prepared under the thermo sensitive colour developing layer.

These organic developer, basic leuco dye, sensitizer and other additives to be added as necessary are ground to the fine particles smaller than one micron size level by means of a pulverizer such as a ball mill, an attritor or a sand grinder, or by means of an adequate emulsifying apparatus, and binder and other additives are added in accordance with the necessity, thus the coating colour is prepared.

The present invention is further illustrated by following Examples and Comparative Examples. In the illustration, the term of "parts" means "parts by weight".

EXAMPLE 1 (experiment No. 1-32)

Solution A (dispersion of dye)	
3-N-n-dibuthylamino-6-methyl-7-anilinofluoran	2.0 parts
10% polyvinylalcohol aqueous solution	4.6 parts
water	2.5 parts
Solution B (dispersion of colour developer)	
colour developer (refer to table 1 and 2)	6.0 parts
10% polyvinylalcohol aqueous solution	18.8 parts
water	11.2 parts
Solution C (dispersion of stabilizer)	
stabilizer 4-benziloxy-4'-(2,3-epoxy-2-methylpropoxy) diphenyl sulfone	4.0 parts
10% polyvinylalcohol aqueous solution	12.5 parts
water	7.5 parts

These three kinds of dispersion are separately ground to average diameter of 1μm by means of a sand grinder. Then the resulting dispersion are mixed together in the proportion below so as to prepare the coating colour.

Solution A (dispersion dye)	9.1 parts
Solution B (dispersion of colour developer)	36.0 parts
Solution C (dispersion of stabilizer)	24.0 parts
Kaoline clay (50% dispersion)	12.0 parts

The prepared coating colours are applied to one side of 50g/m^2 sheet paper so as obtain a coating weight of 5.0g /m^2 amount, dried up and the sheet is processed by a super calender to surface smoothness of 400-500 second. Thus the thermal sensitive recording paper can be obtained.

COMPARATIVE EXAMPLE 1 (experiment No.33-37)

Solution A (dispersion of dye)	
3-N-n-dibuthylamino-6-methyl-7-anilinofluoran	2.0 parts
10% polyvinylalcohol aqueous solution	4.6 parts
water	2.5 parts
Solution D (dispersion of colour developer)	
colour developer (refer to table 5)	6.0 parts
10% polyvinylalcohol aqueous solution	18.8 parts
water	11.2 parts

These two kinds of dispersion are separately ground to average diameter of 1μm by means of a sand grinder. Then the resulting dispersion are mixed together in the proportion below so as to prepare the coating colour.

Solution A (dispersion dye)	9.1 parts
Solution D (dispersion of colour developer)	36.0 parts
Kaoline clay (50% dispersion)	12.0 parts

The prepared coating colours are applied to one side of 50g/m^2 sheet paper so as obtain a coating weight of 5.0g /m^2 amount, dried up and the sheet is processed by a super calender to surface smoothness of 400-500 second. Thus the thermal sensitive recording paper can be obtained.

COMPARATIVE EXAMPLE 2 (experiment No.38-42)

Solution A (dispersion of dye)	
3-N-n-dibuthylamino-6-methyl-7-anilinofluoran	2.0 parts
10% polyvinylalcohol aqueous solution	4.6 parts
water	2.5 parts
Solution E (dispersion of colour developer)	
colour developer (refer to table 5)	6.0 parts
10% polyvinylalcohol aqueous solution	18.8 parts
water	11.2 parts

(continued)

Solution A (dispersion of dye)	
Solution C (dispersion of stabilizer)	
stabilizer 4-benziloxy-4'-(2,3-epoxy-2-methylpropoxy) diphenyl sulfone	4.0 parts
10% polyvinylalcohol aqueous solution	12.5 parts
water	7.5 parts

These three kinds of dispersion are separately ground to average diameter of 1μm by means of a sand grinder. Then the resulting dispersion are mixed together in the proportion below so as to prepare the coating colour.

Solution A (dispersion dye)	9.1 parts
Solution E (dispersion of colour developer)	36.0 parts
Solution C (dispersion of stabilizer)	24.0 parts
Kaoline clay (50% dispersion)	12.0 parts

The prepared coating colours are applied to one side of 50g/m^2 sheet paper so as obtain a coating weight of 5.0g /m^2 amount, dried up and the sheet is processed by a super calender to surface smoothness of 400-500 second. Thus the thermal sensitive recording paper can be obtained.

Quality evaluation tests mentioned below are carried out on thermal sensitive recording papers prepared in above mentioned Examples and Comparative Examples. The obtained results are summarized in table 3, 4 and 6. In the tables, stabilizer (III) indicates compound of 4-benziloxy-4'-(2,3-epoxy-2-methylpropoxy)diphenylsulfone.

Remark (1) resistance against plasticizer ; are carried out using TH-PMD (thermal sensitive recording paper testing apparatus, to which thermal head [Kyosera Ltd.] is installed) made by Ohkura Denki Ltd., by 0.38mj/dot impressive energy. Image density of the recorded portion of each specimen is measured by a Macbeth densitometer (RD-914, an amber filter is used), and the obtained results are regarded as the image density of untreated specimen. Wrapping film of polyvinylchloride (High Wrap KMA ; product of Mitsui Toatsu Ltd.) is wound around a paper tube to form a single layer, recorded sheet of the thermal sensitive recording paper is stuck on it, then the wrapping film of polyvinylchloride is wound over the sheet to form a quarto layer. This specimen is left for 4 hours in the chamber of 40°C, then the Macbeth density of image portion is measured and the obtained results are regarded as the image density after treated.

Table 1

The Results of Quality Evaluation Tests			
Test No.		colour developer	stabilizer
Ex.1	1	N-(benzenesulfonyl)-*p*-(phenylureylene)benzamide	(III)
	2	N-(4-toluenesulfonyl)-*p*-(phenylureylene)benzamide	(III)
	3	N-(benzenesulfonyl)-*p*-(phenylthioureylene)benzamide	(III)
	4	N-(4-toluenesulfonyl)-*p*-(phenylthioureylene)benzamide	(III)
	5	N-(4-methoxyphenylsulfonyl)-*p*-(phenylureylene)benzamide	(III)
	6	N-(2-hydroxyphenylsulfonyl)-*p*-(phenylureylene)benzamide	(III)
	7	N-(4-toluenesulfonyl)-*p*-(4-tolylureylene)benzamide	(III)
	8	N-(*n*-butylphenylsulfonyl)-*p*-(4-tolylureylene)benzamide	(III)
	9	N-(2-hydroxyphenylsulfonyl)-*p*-(4-tolylureylene)benzamide	(III)
	10	N-(4-toluenesulfonyl)-*p*-(2-naphthylureylene)benzamide	(III)
	11	N-(4-hydroxyphenylsulfonyl)-*p*-(2-naphthylureylene)benzamide	(III)
	12	N-(4-toluenesulfonyl)-*p*-(phenylureylene)benzamide	(III)
	13	N-(4-iso-propylphenylsulfonyl)-*p*-(phenylthioureylene)benzamide	(III)
	14	N-(4-hydroxyphenylsulfonyl)-*p*-(phenylthioureylene)benzamide	(III)
	15	N-(benzenesulfonyl)-*p*-(4-tolylthiourne)benzamide	(III)
	16	N-(4-methoxyphenylsulfonyl)-*p*-(4-methylphenylthioureylene)benzamide	(III)

Table 2

The Results of Quality Evaluation Tests			
	Test No.	colour developer	stabilizer
Ex.1	17	N-(phenyl-N'-(*p*-benzoylaminosulfonyl)phenylurea	(III)
	18	N-(phenyl)-N'-{*p*-(benzoylaminosulfonyl)}	(III)
	19	N-(phenyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)}phenylurea	(III)
	20	N-(phenyl)-N'-{*p*-(4-ethoxybenzoylaminosulfonyl)}phenylurea	(III)
	21	N-(phenyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)}phenylurea	(III)
	22	N-(4-toluyl)-N'-{*p*-(2-naphthoilaminosulfonyl)}phenylurea	(III)
	23	N-(3-toluyl)-N'-{*p*-(3-toluoylaminosulfonyl)}phenylurea	(III)
	24	N-(4-toluyl)-N'{*p*-(4-hydroxybenzoylaminosulfonyl)}phenylurea	(III)
	25	N-(4-toluyl)-N'-{*p*-(4-nitrobenzoylaminosulfonyl)}phenylurea	(III)
	26	N-(phenyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylthiourea	(III)
	27	N-(phenyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylthiourea	(III)
	28	N-(phenyl)-N'-{*p*-(4-hydroxybenzoylaminosulfonyl)}phenylthiourea	(III)
	29	N-(phenyl)-N'-{*p*-(4-methoxybenzoylaminosulfonyl)}phenylthiourea	(III)
	30	N-(4-toluyl)-N'-{*p*-(2-naphthoylaminosulfonyl)}phenylthiourea	(III)
	31	N-(3-toluyl)-N'-(*p*-benzoylaminosulfonyl)phenylthiourea	(III)
	32	N-(3-toluyl)-N'-{*p*-(4-toluoylaminosulfonyl)}phenylthiourea	(III)

Table 3

The Results of Quality Evaluation Tests			
	Test No.	resistance against plasticizer (1)	
		untreated	treated
Example-1	1	1.19	0.81
	2	1.19	0.76
	3	1.18	0.72
	4	1.25	0.73
	5	1.19	0.76
	6	1.26	0.73
	7	1.18	0.76
	8	1.22	0.74
	9	1.17	0.79
	10	1.24	0.74
	11	1.19	0.72
	12	1.22	0.71
	13	1.19	0.75
	14	1.25	0.81
	15	1.23	0.79
	16	1.21	0.78

Table 4

The Results of Quality Evaluation Tests			
	Test No.	resistance against plasticizer (1)	
		untreated	treated
Example-2	17	1.21	0.81
	18	1.22	0.75
	19	1.23	0.78
	20	1.19	0.84
	21	1.18	0.75
	22	1.20	0.76
	23	1.21	0.71
	24	1.19	0.72
	25	1.23	0.77
	26	1.24	0.74
	27	1.20	0.73
	28	1.18	0.76
	29	1.24	0.74
	30	1.23	0.79
	31	1.20	0.77
	32	1.18	0.75

Table 5

The Results of Quality Evaluation Tests			
	Test No.	colour developer	stabilizer
Com. Ex.1	33	N-(benzenesulfonyl)-*p*-(phenylthioureylene)benzamide	none
	34	N-(4-toluenesulfonyl)-*p*-phenylthioureylene)benzamide	none
	35	N-(benzenesulfonyl)-*p*-(phenylureylene)benzamide	none
	36	N-(4-toluenesulfonyl)-*p*-phenylthioureylene)benzamide	none
	37	N-(4-methoxyphenylsulfonyl)-*p*-(phenylureylene)benzamide	none
Com. Ex.2	38	4,4'-dihydroxydiphenylsulfone	(III)
	39	4-hydroxy-4'-isopropoxydiphenylsulfone	(III)
	40	4-hydroxy-4'-*n*-butoxydiphenylsulfone	(III)
	41	4,4'-isopropylidenediphenol	(III)
	42	4-hydroxy-4'-*n*-propoxydiphenylsulfone	(III)

Table 6

The Results of Quality Evaluation Tests			
	Test No.	resistance against plasticizer (1)	
		untreated	treated
Com. Ex.1	33	1.18	0.26
	34	1.19	0.28
	35	1.17	0.27
	36	1.18	0.29
	37	1.16	0.28
Com. Ex.2	38	1.21	0.23
	39	1.23	0.22
	40	1.24	0.23
	41	1.22	0.22
	42	1.25	0.20

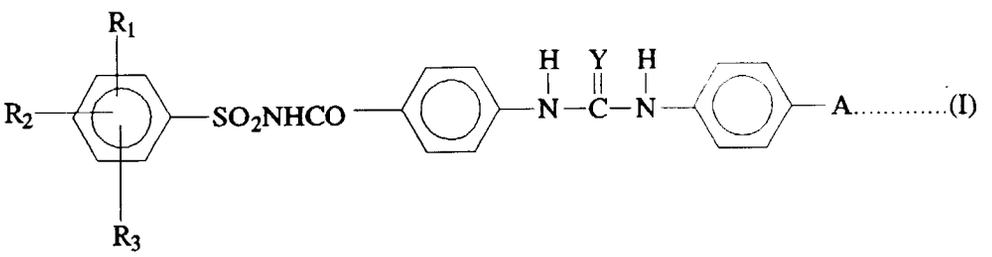
As clearly understood from the test results shown in table 3, 4 and 6, the specimens of thermal sensitive recording sheets prepared by Examples 1 of this invention which use the colour developer indicated by general formula (I) and (II) and the stabilizer indicated by general formula (III) have a remarkable superior image stability to a plasticizer. On the contrary, the effects of image stability to a plasticizer of the specimens prepared by Comparative Example 1 which do not use the stabilizer indicated by general formula (III) and the specimens prepared by Comparative Example 2 which use a typical well-known phenolic colour developer (for instance, bisphenol A) in combination with the stabilizer indicated by general formula (III) are inferior, and the image density after treated is low. Therefore, it is clearly understood that an excellent effect can be expected only in a case using the compound of general formula (I) or (II) together with the compound of general formula (III).

In the present invention, by using a derivative of urea (thiourea) indicated by aforementioned general formula (I) or (II) as a colour developer, and by using a derivative of diphenylsulfone indicated by aforementioned general formula (III) as a stabilizer, an excellent sharp recording image which has good preserving stability can be obtained even in a high speed and high density recording condition.

Claims

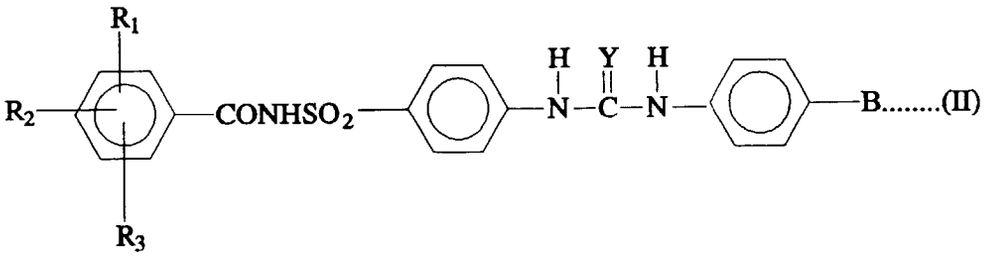
1. A thermally sensitive recording sheet which comprises, on a substrate, a thermally sensitive colour developing layer comprising:

(a) a colourless or pale coloured basic leuco dye;
(b) an organic colour developer of formula (I):

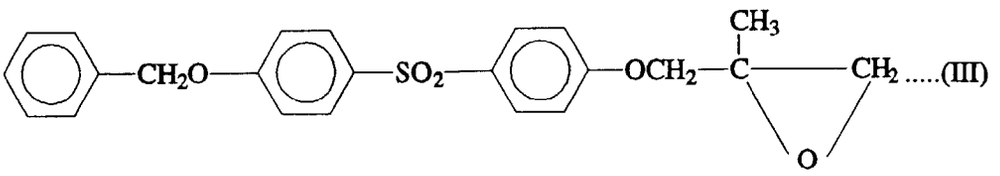


wherein A is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, each of R_1, R_2 and R_3, which may be the same or different, is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, or R_1 and R_2 form, together with

the carbon atoms to which they are attached, an aromatic ring, and Y is sulfur or oxygen; or an organic colour developer of formula (II):



wherein B is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, each of R_1, R_2 and R_3, which may be the same or different, is hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, hydroxy or nitro, or R_1 and R_2 form, together with the carbon atoms to which they are attached, an aromatic ring, and Y is sulfur or oxygen; and
(c) 0.01-2 parts, based on 1 part of colour developer of formula (I) or (II), of a stabiliser which is a diphenylsulfone derivative of formula (III):



2. A recording sheet according to claim 1 wherein, in the organic colour developer of formula (I) or (II), A or B, respectively, is hydrogen, methyl, ethyl, n-propyl, i-propyl, t-butyl, methoxy, ethoxy, n-propoxy, i-propoxy, hydroxy or nitro.

3. A recording sheet according to claim 1 or 2 wherein, in the organic colour developer of formula (I) or (II), each of R_1, R_2 and R_3, which may be the same or different, is hydrogen, methyl, ethyl, n-propyl, i-propyl, t-butyl, methoxy, ethoxy, n-propoxy, i-propoxy, hydroxy or nitro.

4. A recording sheet according to any one of the preceding claims wherein the thermally sensitive colour developing layer further includes a sensitizer, binder, metallic salt, filler, lubricant, UV absorbent, waterproofing agent, dispersing agent, deformer, antioxidant or fluorescent dye.

5. A recording sheet according to any one of the preceding claims wherein the colourless or pale coloured basic leuco dye is selected from fluoran-based leuco dyes, triphenylmethane-based leuco dyes, fluorene-based leuco dyes and divinyl-based leuco dyes.

6. A recording sheet according to any one of the preceding claims which further includes, on the thermally sensitive colour developing layer, an overcoating layer which comprises macromolecules.

7. A recording sheet according to any one of the preceding claims which further includes, between the thermally sensitive colour developing layer and the substrate, an undercoating layer which comprises an organic or inorganic filler.

8. A recording sheet according to any one of the preceding claims wherein the substrate is paper, synthetic paper, plastic film, non-woven cloth or metallic foil, or comprises a combination thereof.

9. A recording sheet according to any one of the preceding claims wherein the thermally sensitive colour developing layer is present on the substrate in a coating weight of 5.0 g/m^2.