Heat sensitive copying papers using a spiro compound having the Formula A

\[
\begin{align*}
R_1 & \quad R_2 \\
\quad & \quad A
\end{align*}
\]

wherein \( R_1 \) and \( R_2 \) each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aminokyl group and a phenyl group, and a solid organic sulfonic acid having the Formula B

\[
R - \text{SO}_2 \text{H} \quad (B)
\]

wherein \( R \) is selected from the group consisting of an amino group, an N-substituted aminoalkyl group having from 2 to 18 carbon atoms, an unsubstituted aminoalkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxy group having from 10 to 20 carbon atoms, a carboxylic acid substituted alkyl group, a dialkyl group having from 6 to 18 carbon atoms, and an aromatic ring, and a thermofusible material having a melting point ranging from 50 to 180°C are disclosed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a heat sensitive copying sheet.

(2) Description of the prior art

Many heat sensitive copying sheets are well known. However, above all, one having a layer comprising two colorless solid compounds contacting with each other to cause the reaction of color development and a thermofusible material on a support is general. The coloration mechanism of this heat sensitive copying sheet is as follows:

When this sheet is superposed on an original drawing and heated or irradiated with an infra-red ray, the image of the character on the original drawing is preferentially raised in temperature and the thermofusible material of the part fuses the two colorless compounds. Then the two fused compounds react to develop color. One of the two colorless compounds includes crystal violet lactones and benzoo indolino spirocompounds, and another includes, for example, clays, such as acid clay, zeolite, kaolin, attapulgite, and the like; mineral acids, such as hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid, and the like; organic acids, such as benzoic acid, p-chlorobenzoic acid, gallic acid, phthalic acid, salicylic acid, oxalic acid, maleic acid, citric acid, stearic acid, and the like; and phenols, such as p-butylphenol, p-phenylphenol, \( \alpha \)-naphthol, catechol, resorcinol, and the like.

However, these heat sensitive copying sheets suffer from the disadvantages that a color development fog is formed before heating, the preservation of the developed color image, such as the light resistance, resistance to water, and the like, is poor, and the sheets are not developed in color the instant they are heated, and the like, because the two compounds are coated on the support in contact with each other. As a result, an excellent heat sensitive copying sheet has been desired.

Therefore, an object of the present invention is to provide a heat sensitive copying sheet in which such color development fog is not formed before heating and develops color instantly on heating. The developed color image is excellent in light resistance and resistance to water.

SUMMARY OF THE INVENTION

The present inventors have found that the above object is attained by combining a spiro compound and an organic sulfonic acid.

More specifically, the heat sensitive copying sheet of this invention is one having a spiro compound, represented by Formula A

\[
\begin{align*}
R_1 & \quad R_2 \\
\quad & \quad A
\end{align*}
\]

wherein \( R_1 \) and \( R_2 \) each is a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group, or a phenyl group, a solid organic sulfonic acid, represented by the Formula B

\[
R - \text{SO}_2 \text{H} \quad (B)
\]

wherein \( R \) is an amino group, an N-substituted aminoalkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxy group having from 10 to 20 carbon atoms, an aromatic ring, and a heat fusible material, having a melting point of from 50 to 180°C, and is colorless at ordinary temperatures of less than 50°C on a support.

DETAILED DESCRIPTION OF THE INVENTION

The general process for preparing the heat sensitive copying sheet of the present invention is as described below.

A nearly colorless spiro compound, an organic sulfonic acid and a thermofusible material, as described above, are sufficiently mixed in a solution or suspension of a binder in an organic solvent or water, and coated on a support such as paper, natural or synthetic resin films, and the like, and dried. The above liquid mixture can be combed into the support. Also, on mixing, an opacifying agent can be added and mixed therein. The heat sensitive copying sheet of the present invention is not limited to this technique. For example, the above-mentioned spiro compound and the thermofusible material can be mixed in the binder solution, and alternatively the organic sulfonic acid and the thermofusible material can be mixed in the binder solution, and then both solutions can be mixed and coated on a support, or the former solution may be coated on the support and then the latter solution may be coated thereon.

The amount of each component to be used for producing the heat sensitive copying sheet of the present invention is from 1 to 2 parts by weight of the spiro compound (the Formula A); from 1 to 6 parts by weight of the organic sulfonic acid (the Formula B); from 3 to 30 parts by weight of the thermofusible material; from 3 to 15 parts by weight of the binder; and from 20 to 300 parts by weight of solvent.
Examples of the spiro compounds represented by the above Formula A are shown in the following table:

<table>
<thead>
<tr>
<th>Color developing agent</th>
<th>R</th>
<th>R'</th>
<th>Melting point, °C</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.</td>
<td>C₂H₅</td>
<td>H</td>
<td>182</td>
<td>3-ethyl-2,2'-spirobi(benzof[i]chromene) Ber., 61, 666.</td>
</tr>
<tr>
<td>VIII.</td>
<td>CH₃</td>
<td>H</td>
<td>207</td>
<td>3-benzyl-2,2'-spirobi(benzof[i]chromene) Ber., 61, 666.</td>
</tr>
<tr>
<td>X.</td>
<td>H</td>
<td>H</td>
<td>260</td>
<td>3-phenyl-2,2'-spirobi(benzof[i]chromene) Ber., 61, 666.</td>
</tr>
</tbody>
</table>

These compounds are almost colorless crystals. These spiro compounds can be prepared by condensing 2-hydroxy-1-naphthoic aldehyde with the respective corresponding ketones as described in the literature references.

Next, the organic sulfonic acids represented by the Formula B can be exemplified as follows:

1. NH₄SO₃H
2. NH₂CH₂CH₂SO₃H
3. CH₂=CH₂
4. CH₂=CH₂
5. (CH₃)₂NCH₂CH₂SO₃H
6. C₆H₅SO₃H
7. C₆H₅SO₃H
8. C₆H₅SO₃H
9. C₆H₅SO₃H
10. C₆H₅SO₃H
11. C₆H₅SO₃H
12. C₆H₅SO₃H
13. C₆H₅SO₃H
14. C₆H₅SO₃H
15. C₆H₅SO₃H
16. C₆H₅SO₃H
17. C₆H₅SO₃H
18. C₆H₅SO₃H
These compounds are almost colorless solids. Suitable thermofusible materials are acetanilide, urea, diphenylamine, naphthalene, benzoin, α-naphthol, β-naphthol, para-butyl phenol, para-phenylphenol, 4,4'-cyclohexyldiene diphene diphenol, 4,4'-iso- propyldiene diphenol, phthalic anhydride, maleic anhydride, stearic acid, benzoic acid, α-naphthyl acetate acid, methyl para-hydroxybenzoate, diphenyl phthalate, triphenyl phosphate, para-hydroxydiphenyl ether, and the like.

These compounds are colorless or lightly colored solids at ordinary temperatures of lower than 50°C and have sharp melting points near the temperature suitable as the heating temperature for copying, that is, from 50 to 180°C, and dissolve the above spiro compounds (the Formula A) and the organic sulfinic acids (the Formula B) in the fused state. The above three components are not necessarily used on or in the same support, and one or two of said components can be used on two separate supports.

The binders to be used in the present invention are exemplified by styrene-butadiene copolymers, alkyd resins, polybutylmethacrylates, vinyl chloride-vinyl acetate copolymers, styrene maleic anhydride copolymers, synthetic rubbers, gum arabic, polyvinyl alcohol, hydroxystyryl-cellulose, and the like.

These binders bind the above spiro compounds (the Formula A) and the thermofusible materials and not easily discolored on heating. They can be used alone or in combination.

The solvents to be used in the present invention are exemplified by organic solvents such as benzene, toluene, hexane, xylene, ligroin, acetone, ethyl acetate, and the like; and water.

These solvents are used to dissolve the above binders or as dispersion emulsions, and are finally distilled off.

In general, with organic sulfinic acids having an amino group in the Formula B, an organic solvent or water may be optionally used. With organic sulfinic acids not having an amino group or one's easily soluble in an organic solvent, water is preferable. With organic sulfinic acids easily soluble in water, use of water is allowed. This appears to result from the lack of solubility of the coupler represented by the Formula A in water.

Pacifying agents which can be used in the present invention are exemplified by titanium oxide, zinc oxide, barium sulfate, calcium sulfate, starch and the like.

The heat sensitive copying sheet of this invention has the advantages that a color development fog is not formed during the preparation and during the period after drying and before heating even though the compounds of the Formulas A and B are in contact with each other, that, even if the sheet is exposed before copying color development, it is good in stability during the lapse of time with-
ground for 2 hours. The solution was coated on a film and dried at 40° C. to obtain a heat sensitive copying sheet. The sheet was superposed on an original drawing and heated by means of a heat sensitive copying machine (trademark: Risofax; manufactured by Riso Kagaku Co., Ltd.) to obtain a blue image which was similarly excellent as in Example 1 in light resistance and resistance to water.

Example 3.—30 g of coupler No. III, 300 g of urea, 600 g of acetone were mixed and ground in a ball mill for 2 days. On the other hand, 30 g of organic sulfonic acid No. 8, 300 g of urea, 200 g of polybutyl-methacrylate, and 600 g of ethyl acetate were mixed and ground in a ball mill. The ground materials were mixed and then treated in a ball mill for 5 hours. The resulting mixture, thus treated, was coated on a support and dried to obtain a heat sensitive copying sheet. The sheet was heated in the same manner as in Example 1 to obtain a blue image. The light resistance and resistance to water of the image were similarly excellent as in Example 1.

Example 4.—10 g of coupler No. IV, 20 g of organic sulfonic acid No. 36, 200 g of stearic acid, 70 g of styrenemaleic anhydride copolymer and 2000 g of xylene were treated in the same manner as in Example 1 to obtain a heat sensitive copying sheet. The sheet was heated in the same manner as in Example 1 to obtain a blue image. In case of the omission of the organic sulfonic acid, the color was not developed.

Example 5.—10 g of coupler No. V, 30 g of organic sulfonic acid No. 49, 100 g of p-phenylenediamine, 40 g of chlorinated rubber, and 3000 g of benzene were treated in the same manner as in Example 1 to obtain a heat sensitive copying sheet which was then heated to obtain a blue image. In case of the omission of the organic sulfonic acid, the color was not developed at all.

Example 6.—10 g of ground coupler No. VI, and 100 g of acetanilide were dispersed in a solution of 30 g of polyvinyl alcohol and 500 g of water. On the other hand, 10 g of ground organic sulfonic acid No. 29 and 50 g of acetanilide were dispersed in a solution of 15 g of polyvinyl alcohol and 300 g of water. Both dispersions were mixed and were treated in a ball mill for 5 hours, and then were coated on a paper and dried to obtain a heat sensitive copying sheet which was then heated to obtain a blue image. In case of substituting salicylic acid for organic sulfonic acid No. 29 (sulfoisalicylic acid), the color was not developed.

Example 7.—Example 1 was repeated using coupler Nos. VII, VIII, IX and X, respectively, to obtain a blue image.

Example 8.—10 g of coupler No. X, 15 g of organic sulfonic acid No. 18, 140 g of benzoeic acid, 50 g of a vinyl chloride-vinyl acetate copolymer and 1500 g of tolune were mixed and ground in a ball mill for 2 days, and were coated on a paper and dried to obtain a heat sensitive copying sheet. The sheet was superposed on an original drawing and heated by means of a heat sensitive copying machine to obtain a blue image corresponding to the characters on the original drawing. Also, the sheet was treated in the same manner as described above, in the absence of substituting 50 g of hydroxyethylcellulose and 1500 g of water for vinyl chloride-vinyl acetate copolymer and toluene to obtain the same result.

In every case, when an organic sulfonic acid was not used, a colored image could not be obtained.

Example 9.—The color development of the respective combination of couplers Nos. I to X and organic sulfonic acids Nos. 1 to 60 in the same manner as in Examples 1 to 8 was blue. However, in using the coupler No. 1, the color developed was blue violet, and in using the coupler No. VII, the color obtained first was blue by increasing the amount of an organic sulfonic acid to be used by about 30% by weight.

What is claimed is:

1. A heat sensitive copying sheet comprising a support having coated thereon a layer comprising (a) a spiro compound having the Formula A

   \[ R_1 - O - \]

   \[ \overset{A}{\text{O}} - R_2 \]

   wherein \( R_1 \) and \( R_2 \) each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, (b) a solid organic sulfonic acid having the Formula B,

   \[ R - SO_3H \]

   wherein \( R \) is selected from the group consisting of an amino group, an N-substituted amino alkyl group having from 2 to 18 carbon atoms, an unsubstituted amino alkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxyl group having from 10 to 20 carbon atoms, an alkyl group having from 6 to 18 carbon atoms, an alkyl group, and an aromatic ring, and (c) a thermofusible material having a melting point ranging from 50 to 180° C., from 1 to 2 parts by weight of the spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

2. The heat sensitive copying sheet as claimed in claim 1 wherein said spiro compound is selected from the group consisting of 2,2'-spirobi(benzof[f]chromene), 3-methyl-2,2'-spirobi(benzof[f]chromene), 3-isopropyl-2,2'-spirobi(benzof[f]chromene), 3-amy-2,2'-spirobi(benzof[f]chromene), 3-octyl-2,2'-spirobi(benzof[f]chromene), 3,3'-dimethyl-2,2'-spirobi(benzof[f]chromene), 3,3'-dicarboxe-oxy-2,2'-spirobi(benzof[f]chromene), 3-benzyl-2,2'-spirobi(benzof[f]chromene), 3-phenylethyl-2,2'-spirobi(benzof[f]chromene), or 3-phenyl-2,2'-spirobi(benzof[f]chromene).

3. The heat sensitive copying sheet as claimed in claim 1 wherein said thermofusible material is selected from the group consisting of acetanilide, urea, diphenylamine, diphenyl, naphtalene, benzoin, \( \alpha \)-naphtol, \( \beta \)-naphtol, \( p \)-butsylphenol, \( p \)-phenylenediamine, \( 4,4' \)-cyclohexylidindiphenol, phthalic anhydride, maleic anhydride, stearic acid, benzoic acid, \( \alpha \)-naphtyl acetic acid, methyl p-hydroxybenzoate, diphenyl phthalate, triphenyl phosphate or p-hydroxydiphenyl ester.

4. A heat sensitive copying sheet comprising a support having coated thereon a layer comprising (a) a spiro compound having the Formula A

   \[ R_1 - O - \]

   \[ \overset{A}{\text{O}} - R_2 \]

   wherein \( R_1 \) and \( R_2 \) each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, (b) a solid organic sulfonic acid having the Formula B,

   \[ R - SO_3H \]

   wherein \( R \) is selected from the group consisting of an amino group, an N-substituted amino alkyl group having from 2 to 18 carbon atoms, an unsubstituted amino alkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxyl group having from 10 to 20 carbon atoms, an alkyl group having from 6 to 18 carbon atoms, an alkyl group, and an aromatic ring, and (c) a thermofusible material having a melting point ranging from 50 to 180° C., which is substantially colorless at a temperature lower than 50° C., and (d) a binder, from 1 to 2 parts by weight of the
spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

5. The heat sensitive copying paper as claimed in claim 4 wherein said binder is selected from the group consisting of styrrene-butadiene copolymers, alkyl resins, polybutyl methacrylates, vinyl chloride-vinyl acetate copolymers, styrene-maleic anhydride copolymers, synthetic rubbers, gum arabic, polyvinyl alcohol and hydroxethyl cellulose.

6. A heat sensitive copying sheet comprising a support having coated thereon (a) a spiro compound having the Formula A

wherein R₁ and R₂ each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, (b) a solid organic sulfonic acid having the Formula B

R—SO₂H

(B)

wherein R is selected from the group consisting of an amino group, an N-substituted amino alkyl group having from 2 to 18 carbon atoms, an unsubstituted amino alkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxy group having from 10 to 20 carbon atoms, a carboxylic acid substituted alkyl group, said alkyl group having from 6 to 18 carbon atoms, an aralkyl group, or an aromatic ring, and (c) a thermostable material having a melting point ranging from 50 to 180°C, from 1 to 2 parts by weight of the spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

7. Heat sensitive copying sheets comprising a combination of two supports, one support having coated thereon a layer comprising (a) a spiro compound having the Formula A

wherein R₁ and R₂ each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, and (b) as a coupler, a solid organic sulfonic acid having the Formula B

R—SO₂H

(B)

wherein R is selected from the group consisting of an amino group, an N-substituted amino alkyl group having from 2 to 18 carbon atoms, an unsubstituted amino alkyl group having from 2 to 18 carbon atoms, an alkyl group having from 10 to 20 carbon atoms, an alkoxy group having from 10 to 20 carbon atoms, a carboxylic acid substituted alkyl group, said alkyl group having from 6 to 18 carbon atoms, an aralkyl group, or an aromatic ring, and (b) a thermostable material having a melting point ranging from 50 to 180°C, from 1 to 2 parts by weight of the spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

8. Heat sensitive copying sheets comprising a combination of two supports, one support having coated thereon a layer comprising (a) a spiro compound having the Formula A,

wherein R₁ and R₂ each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, and (b) a thermostable material having a melting point ranging from 50 to 180°C, from 1 to 2 parts by weight of the spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

9. Heat sensitive copying sheets comprising a combination of two supports, one surface having coated thereon a layer comprising a spiro compound having the Formula A,

wherein R₁ and R₂ each is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a carboxylic acid ester, an aralkyl group and a phenyl group, and (b) a thermostable material having a melting point ranging from 50 to 180°C, from 1 to 2 parts by weight of the spiro compound being present for every 1 to 6 parts by weight of the solid organic sulfonic acid.

10. The heat sensitive copying sheet of claim 1 wherein the thermostable material is substantially colorless at a temperature lower than 50°C, and is present in an amount of from 3 to 30 weight parts.

11. The heat sensitive copying sheet of claim 4 wherein said thermostable material is present in an amount from 3 to 30 weight parts and said binder is present in an amount of from 3 to 15 weight parts.

12. The heat sensitive copying sheet of claim 6 wherein said thermostable material is substantially colorless at a temperature lower than 50°C, and is present in an amount of from 3 to 30 weight parts.

13. Heat sensitive copying sheets as claimed in claim 7 wherein the thermostable material is substantially colorless at temperatures lower than 50°C, and is present in an amount of from 3 to 30 weight parts.

14. Heat sensitive copying sheets as claimed in claim 8 wherein the thermostable material is substantially colorless at temperatures lower than 50°C, and is present in an amount of from 3 to 30 weight parts.

15. Heat sensitive copying sheets as claimed in claim 9 wherein the thermostable material is substantially colorless at temperatures lower than 50°C, and is present in an amount of from 3 to 30 weight parts.

16. The heat sensitive copying sheet as claimed in claim 1 wherein the layer further comprises from 3 to 15 weight parts of a binder.
13. The heat sensitive copying sheet as claimed in claim 6 wherein the material coated thereon further contains from 3 to 15 weight parts of a binder.

References Cited
UNITED STATES PATENTS
3,293,060 12/1966 Harbort 117—36.9

14
OTHER REFERENCES

MURRAY KATZ, Primary Examiner
U.S. Cl. X.R.
117—155 UA; 260—345.2