

(19)



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(11)

EP 0 715 964 B2

(12)

NEW EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the opposition decision:
30.10.2002 Bulletin 2002/44

(51) Int Cl.7: **B41M 5/26**, B41M 5/40

(45) Mention of the grant of the patent:
09.09.1998 Bulletin 1998/37

(21) Application number: **95109213.9**

(22) Date of filing: **14.06.1995**

(54) **Thermosensitive recording medium**

Wärmeempfindliches Aufzeichnungsmedium

Élément d'enregistrement thermosensible

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **09.12.1994 JP 33185294**
14.12.1994 US 355974

(43) Date of publication of application:
12.06.1996 Bulletin 1996/24

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(56) References cited:
EP-A- 0 247 816 EP-A- 0 273 752
EP-A- 0 492 628 CH-A- 659 975
JP-A- 5 104 859 JP-A- 63 315 290

• **DATABASE WPI, no. 94-188 568, DERWENT**
PUBLICATIONS LTD., London; & JP-A-06 127
140 (FUJI PHOTO FILM CO., LTD)

EP 0 715 964 B2

Description**1. Field of the Invention**

[0001] The present invention relates to a thermosensitive recording medium which uses a color development reaction occurring between an electron donative coloration compound and an electron acceptor compound. (The electron donative coloration compound may be simply referred to as a color coupler, hereinafter. The electron acceptor compound may be referred to as a developer, hereinafter.) In particular, the present invention relates to the thermosensitive recording medium which is useful as a film sheet for image forming in an overhead projector (which will be abbreviated to an OHP, hereinafter), as a film sheet for image forming in a CAD (computer aided designing, and as a film for a video printer.

2. Prior Art

[0002] The thermosensitive recording medium which uses the color development reaction occurring between the color coupler and the developer has been well-known.

[0003] Recently, it has been demanded to use the thermosensitive recording medium for the OHP or as a diazo mother print or as a design drawing.

[0004] Japanese Patent Application No.61-121875 and Japanese Laid-Open Application No.1-99873 propose transparent thermosensitive recording media, it being possible that a thermal head directly prints on the transparent thermosensitive recording media. However, a problem is present in manufacturing the transparent thermosensitive recording media. Specifically, in order to obtain the transparent thermosensitive recording media, the color coupler is micro-capsulated, while the developer is dissolved in organic solvent which is slightly soluble or insoluble in water. As a result of performing emulsion dispersion of the thus-micro-capsulated color coupler and the thus-dissolved developer, emulsion dispersion substance is obtained and an application liquid consisting of emulsion dispersion substance is thus obtained. The thus-obtained application liquid is applied or coated on a transparent carrier and thus the transparent thermosensitive recording medium is obtained. Thus, the manufacturing process is considerably complicate. Further, another problem of the transparent thermosensitive recording media is that the transparency of the transparent thermosensitive recording media is insufficient. Further, as another problem, it is not sufficiently possible to print on the transparent thermosensitive recording media through a heat transfer printer which is used for a personal word processor for popular use.

[0005] An object of the present invention is to solve the above-mentioned problems present in the prior art and thus to provide the thermosensitive recording media, which use the reaction occurring between the color coupler and the developer and which has improved thermosensitivity, an improved color development image forming property, and, in particular, improved transparency.

[0006] According to the present invention, an irreversible thermosensitive recording medium as defined in claim 1 is provided, which medium has a thermosensitive recording layer on a carrier body. The thermosensitive recording layer has main ingredients consisting of the electron donative coloration compound and the electron acceptor compound together with binder resin. The thermosensitive recording medium includes 500 through 5,000 ppm of organic solvent. The organic solvent has a dielectric constant of 2.0 through 25.0 at 20°C, and has vapor pressure of 1333 to 26660 Pa (10 through 200 mmHg) at 20°C.

[0007] That is, the present inventors have diligently conducted research for solving the above-mentioned problems. As a result, they have found that it is preferable that:

[0008] The irreversible thermosensitive recording medium has the thermosensitive recording layer on the carrier body, a main ingredient of the carrier body being resin. The thermosensitive recording layer has main ingredients consisting of the electron donative coloration compound and the electron acceptor compound together with binder resin. The thermosensitive recording medium includes 500 through 5,000 ppm of organic solvent. The organic solvent has dielectric constant of 2.0 through 25.0 at 20°C, and has vapor pressure of 1333 to 26660 Pa (10 through 200 mmHg) at 20°C. By using the above-described thermosensitive recording medium, remarkable features can be obtained as described below. It is possible to control the optical density of a fresh recording medium to be low and also, if the carrier body is transparent, transparency of the recording medium is improved. If it is demanded to further reduce the optical density of the fresh recording medium and/or to further improve the transparency thereof, it is effective to carry out aging of the recording medium under a temperature lower than a color development temperature thereof. Further, it is also found that manufacturing of the recording media is easy. Thus, the present invention has been completed.

[0009] A major amount of the organic solvent included in the thermosensitive recording medium according to the present invention is present in the thermosensitive recording layer. However, it is possible that a protective layer of the recording medium has an amount of the organic solvent present therein. However, making the organic solvent be

included in the thermosensitive layer is effective for controlling the optical density of a fresh recording medium to be low. Further, since the carrier body is a carrier which is insoluble in the organic solvent, little amount of the organic solvent is present in the carrier body. Therefore, a content of the organic solvent included in the recording medium accordingly tells a content of the organic solvent which is included in the thermosensitive layer and protective layer but is not included in the carrier body.

[0010] A considerably large portion of cause which results in the optical density of a fresh thermosensitive recording medium according to the present invention to be high depends on the organic solvent included in the thermosensitive layer and protective layer. If the content of the organic solvent is lower than the above-mentioned 500 ppm, the optical density of a fresh recording medium is relatively high so that no significant effect can be obtained even if the above-mentioned aging is performed thereon. Further, if the content of the organic solvent exceeds the above-mentioned 5,000 ppm, it is possible to control the optical density of a fresh recording medium to be low. However, in such a state as that the organic solvent exceeds the above-mentioned 5,000 ppm, an image, which has been obtained as a result of color development image forming on the recording medium, can not be well preserved. Therefore, the content of the organic solvent is limited within an extent between 500 through 5,000 ppm.

[0011] Further, in view of appearance of effect, the present invention uses the organic solvent having dielectric constant of 2.0 through 25.0 at 20°C, and having vapor pressure of 1333 to 26660 Pa (10 through 200 mmHg) at 20°C, as will be mentioned later.

[0012] The thermosensitive recording medium will now be described in detail. It is noted that the above-described effect obtained from the organic solvent remarkably appears in particular if the thermosensitive recording medium is an irreversible transparent thermosensitive recording medium which is obtained as a result of stacking of recording layer and protective layer on a transparent one of the carrier body. The above-mentioned irreversible transparent thermosensitive recording medium will now be described.

[0013] The color coupler used in the present invention is dye precursor which is colorless or light color in itself and is not specifically limited. Well-known compounds which can be used for the color coupler are, for example: triphenyl-methane phthalide compounds, fluoran compounds, phenothiazine compounds, leuco auramine compounds, rhodamine lactam compounds, spiro pyran compounds, indolino phthalide compounds.

[0014] The fluoran compounds are specially preferable to be used as the color coupler used in the present invention. Specific examples are listed below:

3,6-dimethoxy fluoran,
 3-cyclohexylamino-6-chloro fluoran,
 3-dimethylamino-5,7-dimethyl fluoran,
 3-diethylamino-5,7-dimethyl fluoran,
 3-dimethylamino-7-chloro-fluoran,
 3-diethylamino-7-chloro-fluoran,
 3-dimethylamino-7-methyl fluoran,
 3-diethylamino-7-methyl fluoran,
 3-diethylamino-6-methyl-7-chlor fluoran,
 3-diethylamino-6-methyl-7-bromo-fluoran,
 3-di-n-butylamino-6-methyl-7-bromo-fluoran,
 3-diethylamino-6-methyl-8-methyl fluoran,
 3-di-n-butylamino-6-methyl-8-methyl fluoran,
 3-diethylamino-7,8-benzo fluoran,
 3-di-n-butylamino-7,8-benzo fluoran,
 3-(N-n-butyl-N-methylamino)-7,8-benzo fluoran,
 3-(N-n-butyl-N-ethylamino)-7,8-benzo fluoran,
 3-(N-iso-butyl-N-ethylamino)-7,8-benzo fluoran,
 3-di-iso-butylamino-7,8-benzo fluoran,
 3-(N-iso-amyl-N-ethylamino)-7,8-benzo fluoran,
 3,6-bis (diphenylamino) fluoran,
 3,6-bis (N-biphenyl-N-phenylamino) fluoran,
 3-diethylamino-7-anilino fluoran,
 3-di-n-butylamino-7-anilino fluoran,
 3-(N-n-hexyl-N-ethylamino)-7-anilino fluoran,
 3-diethylamino-7-dibenzylamino fluoran,
 3-diethylamino-5-methyl-7-dibenzylamino fluoran,
 3-diethylamino-7-piperidino fluoran,

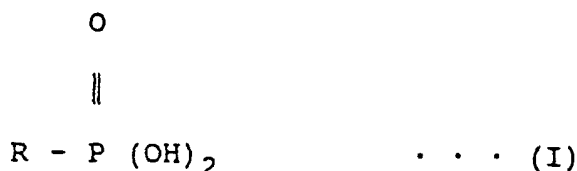
and so forth.

[0015] Further, other specific examples are listed below:

3-diethylamino-(O-chloro-anilino) fluoran,
 3-di-n-butylamino-7-(O-chloro-anilino) fluoran,
 3-dimethylamino-6-methyl-7-anilino fluoran,
 3-diethylamino-6-methyl-7-anilino fluoran,
 3-di-n-butylamino-6-methyl-7-anilino fluoran,
 3-(N-n-propyl-N-methylamino)-6-methyl-7-anilino fluoran,
 3-(N-iso-propyl-N-methylamino)-6-methyl-7-anilino fluoran,
 3-(N-n-butyl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-(N-iso-butyl-N-methylamino)-6-methyl-7-anilino fluoran,
 3-(N-n-amyl-N-methylamino)-6-methyl-7-anilino fluoran,
 3-(N-iso-amyl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-(N-cyclohexyl-N-methyl)-6-methyl-7-anilino fluoran,
 3-(N-n-amyl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-(N-2-ethoxy propyl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-pyrrolidino-6-methyl-7-anilino fluoran,
 3-(N-tetrahydrofurfuryl-N-ethylamino)-6-methyl-7-anilino fluoran,
 3-diethylamino-7-(m-trifluoro methylanilino) fluoran,
 3-diethylamino-6-methyl-7-(2', 4', -diethylanilino) fluoran,
 3-diethylamino-6-chloro-7-anilino fluoran,
 3-diethylamino-5-methyl-7-(α -phenyl ethylamino) fluoran,
 3-(N-p-tolyl-N-ethylamino)-7-(α -phenyl ethylamino) fluoran,

and so forth.

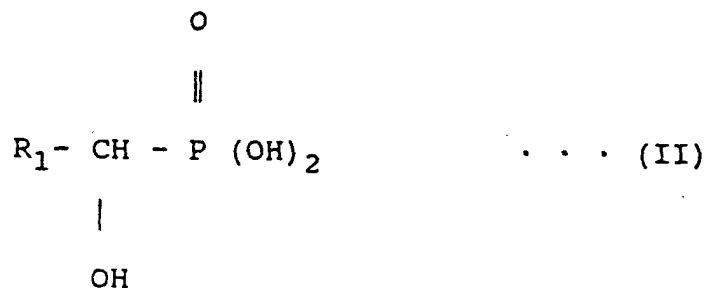
[0016] Organic phosphorus compounds are used as the developer for color developing of the above-mentioned color coupler in the present invention. In particular, phosphonic acid expressed by the following general chemical formula (I) or (II) is used:



(In the above formula, the sign 'R' is referred alkyl group having 16 through 24 carbons.)

[0017] Compounds in specific examples of the above-mentioned phosphonic acid are listed below:

[0018] Hexadecyl phosphonic acid, octadecyl phosphonic acid, icosyl phosphonic acid, docosyl phosphonic acid, tetracosyl phosphonic acid, and so forth.



(In the above formula, the sign 'R₁' is referred alkyl group having 13 through 23 carbons.)

[0019] Compounds in specific examples of the above-mentioned phosphonic acid are listed below:

α -hydroxy tetradecyl phosphonic acid, α -hydroxy hexadecyl phosphonic acid, α -hydroxy octadecyl phosphonic acid, α -hydroxy icosyl phosphonic acid, α -hydroxy docosyl phosphonic acid, α -hydroxy tetracosyl phosphonic acid, and so forth.

[0020] In the present invention, the developer is used, which developer consists of a single compound or consisting of mixture of a plural types of compounds. Similarly, the color coupler is used, which color coupler may consist of a single compound or mixture of a plural types of compounds.

[0021] A substance having an index of refraction of an extent between 1.45 through 1.60 in normal temperature and having a hydroxyl group in its molecule is used as the binder resin used in the thermosensitive recording layer. Specific examples of such binder resin are listed below: poly(vinyl butyral), poly(vinyl acetal), epoxy resin, ethyl cellulose, cellulose acetate, hydroxy propyl cellulose, ethyl hydroxy cellulose, and so forth.

[0022] In the present invention, in order to improve a coating property or a recording property, for example, dispersing agent, high-molecular cationic electrically conductive agent, color development image stabilizing agent, or the like may be included in the thermosensitive recording layer.

[0023] Further, in order to improve a light resistance property of the thermosensitive recording medium according to the present invention, light stabilization agent may be included in the thermosensitive recording layer. Ultraviolet ray absorbing agent, oxidation inhibitor, quencher of singlet oxygen, quencher of superoxido anion may be used as the above-mentioned light stabilization agent used in the present invention.

[0024] The carrier body of the thermosensitive recording medium according to the present invention is a carrier body mainly formed of a synthetic paper sheet, a metallic foil, and/or synthetic resin. Usually a transparent or opaque carrier body is used as the carrier body, the transparent or opaque carrier body consisting of one of a polyester film such as that of poly(ethylene terephthalate), poly(butylene terephthalate), or the like, a cellulose derivative film such as that of cellulose triacetate, or the like, a polyolefine film such as that of polypropylene, polyethylene, or the like, and a polystyrene film. Further, instead, the transparent or opaque carrier body is obtained as a result of pasting some of the above-listed films with one another.

[0025] A thermosensitive recording medium, which does not have the protective layer therein, of the thermosensitive recording medium according to the present invention will now be described. In the thermosensitive recording layer of the thermosensitive recording medium, the developer is dispersed in the binder resin. However, the dispersion is not uniform in a surface portion and an internal portion of the layer. Further, voids are present in the recording layer and thus air present in the voids has an index of refraction different from an index of refraction of the recording layer itself and the refraction index difference causes light scattering. As a result, the recording layer is opaque. Such voids may be formed, for example, as a result of the organic solvent present in the recording layer being transformed into gas and then removed therefrom, or as a result of a space being defined between adjacent developer particles. However, by uniformly coating *resin* on the above-mentioned opaque recording layer and drying (curing) it, the voids present in and unevenness present on the recording layer are eliminated and thus the surface thereof is smoothed. As a result, the light scattering is reduced and thus transparent recording medium can be obtained. The above-mentioned resin has an index of refraction of 1.45 through 1.60 in normal temperature, the extent of which index is the same as that of the index of the binder resin. Thus, the protective layer is formed. The thus-formed protective layer not only contributes for making the recording medium be transparent but also has great effect to improve a chemical resistant property, a water proof property, a friction resistant property, a light proof property and a head matching property. The good head matching property means a state of a surface of the recording medium such as that a thermal head can smoothly slides on the surface of the recording medium. Further, the good head matching property means a state of the surface of the recording medium such that no sticking occurs, that is, the thermal head running on the surface of the recording medium does not cause the protective layer to be shaped nor cause the protective layer to crack. Thus, the protective layer is an essential element to obtain the transparent thermosensitive recording medium having a superior property.

[0026] In the protective layer in the present invention, the following elements are included: a coat mainly formed of watersoluble resin and hydrophobic resin, a coat mainly formed of ultraviolet ray setting resin or electron ray setting resin, and so forth. By forming such a protective layer, it is possible to obtain the recording medium which does not create substantial problems even after coming into contact with organic solvent, plasticizer, oil, sweat, water or the like. Further, by making organic or inorganic filler and lubricant be included in the protective layer, it is possible to eliminate problems of sticking which may occur as a result of a thermal head or the like coming into contact with the recording medium. Therefore, it is possible to obtain the thermosensitive recording medium having improved reliability and an improved head matching property.

[0027] Matters other than those regarding the *transparent* thermosensitive recording medium will now be described.

[0028] The color coupler used in the present invention is not specifically limited and may consist of one which was described in the description of the transparent thermosensitive recording medium. Compounds which may be used as

the developer are, other than the organic phosphorus compounds described above, phenyl compounds which are relatively unlikely to be dissolved in the organic solvent. Specific examples thereof are derivatives of bis(hydroxyphenyl) acetic acid and derivatives of gallic acid. Substance to be used as the binder resin used in the thermosensitive recording medium may consist of resin which is dissolved in the organic solvent and becomes a film when it is coated and dried.

Specific examples thereof are: poly(vinyl chloride) resin, ethylene - vinyl acetate copolymer, polystyrene, poly(vinyl acetate) resin, vinyl chloride- acetate copolymer, saturated polyester resin, polyurethan acryl resin, polycarbonate resin, and so forth. Other specific examples are those which were described in the description of the transparent thermosensitive recording medium.

[0029] In the present invention, it is possible to add additives which were described in the description of the transparent thermosensitive recording medium, if it is necessary.

[0030] The carrier body used in the present invention may consist of not only the transparent carrier body described above but also a synthesis paper sheet using a resin film, a white polyester film having inorganic substance added thereto, a foamed white polyester film or the like.

[0031] The protective layer in the present invention may also use the resins and additives described in the description of the transparent thermosensitive recording medium.

[0032] The organic solvent for dissolving the binder resin has dielectric constant of 2.0 through 25.0 at 20°C, and has vapour pressure of 1333 to 26660 Pa (10 through 200 mmHg) at 20°C. Specific examples of the organic solvent are listed below: kinds of ether such as dibutyl ether, isopropyl ether, dioxane, tetrahydrofuran, or the like, kinds of ketone such as acetone, diethyl ketone, methyl ethyl ketone, methyl isobutyl ketone, methyl propyl ketone or the like, kinds of ester such as ethyl acetate, isopropyl acetate, n-propyl acetate, n-butyl acetate, or the like, kinds of aromatic hydrocarbon such as benzene, toluene, xylene, or the like. In practice, one of them alone is used as the organic solvent for dissolving the binder resin, or combination of some of them is used for the same purpose.

[0033] No specific limitation is present in a method for coating of the protective layer and an amount of the coating. However, in view of desirable performance of the protective layer and in an economic view point, an extent of coating thickness mentioned below is considered. That is, if the extent of coating thickness is such that the protective layer formed on the recording medium as a result of coating has a thickness in an extent between 0.1 µm and 20 µm, preferably a thickness in an extent between 0.5 µm and 10 µm, the desirable performance of the protective layer can be sufficiently exhibited and thus the desirable performance of the recording medium can be ensured.

[0034] A method of forming an image on the thermosensitive recording medium according to the present invention will now be described. The method depends on particular purposes of using the image formed on the recording media. The thermosensitive recording medium according to the present invention can be used for any image forming method of those such as a method using a heat pen, a method using a thermal head, a method using laser heating, a method using a thermal etching technique using light and so forth. However, the image forming method, for which the thermosensitive recording medium according to the present invention can be used, is not specifically limited to the above-mentioned methods. However, in practice, it is preferable that the thermosensitive recording medium according to the present invention is useful for being used in the image forming method using the thermal head and that using the thermal etching technique using light (white light including visible light and infrared light).

[0035] Other objects and further features of the present invention will become more apparent from the following detailed description when read in conjunction with the accompanying drawings.

[0036] FIG.1 shows evaluation results obtained from samples in embodiments according to the present invention and comparison examples.

[0037] The present invention will now be described in further detail using embodiments thereof. It is noted that each of units 'part' and '%' is that of weight basis.

[0038] A first embodiment according to the present invention will now be described.

[0039] Substance having the following composition will be dispersed through a portable ball mill and thus an average particle diameter of octadecyl phosphonic acid reaches approximately 0.4 µm:

3-dimethylamino-6-methyl-7-anilino fluoran	10 parts,
octadecyl phosphonic acid	30 parts,
poly(vinyl butyral) (Denka butyral #3000-2, manufactured by Denki Kagaku Kogyo Company)	15 parts,
and toluene/methyl ethyl ketone (1/1) mixture liquid	285 parts.

[0040] A coating liquid of the recording layer is thus prepared. The thus-prepared coating liquid of the recording layer is coated on a foamed white polyethylene film of 100 µm using a wire bar so as to result in a coated film thickness of approximately 6.0 µm, and the thus-coated liquid is dried. Thus, the thermosensitive recording medium is produced. While drying, the conditions in which the above-mentioned coated liquid is dried to provide the recording layer are adjusted so that a content of the organic solvent in the recording layer is approximately 1,000 ppm.

[0041] A second embodiment according to the present invention will now be described.

[0042] Substance having the following composition will be dispersed through a portable ball mill and thus an average particle diameter of bis(P-hydroxyphenyl) methyl ester acetate reaches approximately 1.2 μm :

3-di-n-butylamino-6-methyl-7-anilino fluoran	10 parts,
bis(P-hydroxyphenyl) methyl ester acetate	30 parts,
poly(vinyl acetate)	25 parts,
and xylene/methyl isobutyl ketone (7/3) mixture liquid	275 parts.

A coating liquid of the recording layer is thus prepared.

[0043] By uniformly dispersing substance having the following composition, a coating liquid of the protective layer is prepared:

butyl acetate solution having therein 75% urethane acrylate ultraviolet ray setting resin, which consists of 25% of the butyl acetate solution and 75% of urethane acrylate ultraviolet ray setting resin (Unidick C7-157 manufactured by Dainippon Ink Kagaku Company)	100 parts,
xylene solution having therein 52% silicon resin, which consists of 48% of xylene solution and 52% of silicone resin (Byk-344 manufactured by Big Chem Japan Company)	4.5 parts,
and ethyl acetate	50 parts.

[0044] Using the above-prepared coating liquids, the transparent thermosensitive recording medium is produced as described below. The coating liquid of the recording layer is coated on a transparent polyester film of 100 μm using a wire bar so as to result in a coated film thickness of approximately 7.5 μm , and the thus-coated liquid is dried. Thus, the thermosensitive recording layer is formed.

[0045] Further, upon the thus-formed thermosensitive recording layer, the coating liquid of the protective layer is coated using a wire bar and dried. After that, a thus-coated and dried film is cured using an 80 W/cm ultraviolet ray lamp. Thus, a coated film thickness of approximately 5 μm constituting the protective layer is formed on the thermosensitive recording layer. Thus, the transparent thermosensitive recording medium is produced. During the above-mentioned process, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 2,000 ppm.

[0046] A third embodiment according to the present invention will now be described.

[0047] Substance having the following composition will be dispersed through a portable ball mill and thus an average particle diameter of octadecyl phosphonic acid reaches approximately 0.3 μm (not including a particle having a diameter thereof equal to or larger than 1 μm):

3-diethylamino-6-methyl-7-anilino fluoran	10 parts,
octadecyl phosphonic acid	30 parts,
poly(vinyl butyral) (Denka butyral #3000-2, manufactured by Denki Kagaku Kogyo Company)	15 parts,
and toluene/methyl ethyl ketone (1/1) mixture liquid	285 parts.

A coating liquid of the recording layer is thus prepared.

[0048] By uniformly dispersing substance having the following composition, a coating liquid of the protective layer is prepared:

75% butyl acetate solution having therein urethane acrylate ultraviolet ray setting resin (Unidick C7-157 manufactured by Dainippon Ink Kagaku Company)	100 parts,
52% xylene solution having therein silicone resin (Byk-344 manufactured by Big Chem Japan Company)	4 parts,
and ethyl acetate	50 parts.

[0049] Using the above-prepared coating liquids, the transparent thermosensitive recording medium is produced as described below. The coating liquid of the recording layer is coated on a transparent polyester film of 100 μm using a wire bar so as to result in a coated film thickness of approximately 6.0 μm , and the thus-coated liquid is dried. Thus, the thermosensitive recording layer is formed.

[0050] Further, upon the thus-formed thermosensitive recording layer, the coating liquid of the protective layer is coated using a wire bar and dried by heating. After that, a thus-coated and dried film is cured using an 80 W/cm ultraviolet ray lamp. Thus, a coated film thickness of approximately 5 μm constituting the protective layer is formed on the thermosensitive recording layer. Thus, the transparent thermosensitive recording medium is produced. During the above-described production process, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 2,200 ppm.

[0051] A fourth embodiment of the present invention will now be described.

[0052] The transparent thermosensitive recording medium in the above-described third embodiment is then preserved in a thermostat for 12 hours under 40°C. Thus, the transparent thermosensitive recording medium in the fourth embodiment is obtained.

[0053] A fifth embodiment of the present invention will now be described.

[0054] According to a method similar to one described in the description of the above-described third embodiment, the coating liquids are prepared and the recording medium is produced. However, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are differently adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 4,300 ppm. Thus, the transparent thermosensitive recording medium in the fifth embodiment is produced.

[0055] A sixth embodiment of the present invention will now be described.

[0056] The transparent thermosensitive recording medium in the above-described fifth embodiment is then preserved in a thermostat for 12 hours under 40°C. Thus, the transparent thermosensitive recording medium in the sixth embodiment is obtained.

[0057] A first comparison example will now be described.

[0058] According to a method similar to one described in the description of the above-described first embodiment, the coating liquid is prepared and the recording medium is produced. However, the conditions in which the above-mentioned coated liquid is dried to provide the recording layer are differently adjusted so that a content of the organic solvent in the recording layer is approximately 350 ppm. Thus, the thermosensitive recording medium in the first comparison example is produced.

[0059] A second comparison example will now be described.

[0060] According to a method similar to one described in the description of the above-described second embodiment, the coating liquids are prepared and the recording medium is produced. However, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are differently adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 450 ppm. Thus, the transparent thermosensitive recording medium in the second comparison example is produced.

[0061] A third comparison example will now be described.

[0062] According to a method similar to one described in the description of the above-described third embodiment, the coating liquids are prepared and the recording medium is produced. However, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are differently adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 480 ppm. Thus, the transparent thermosensitive recording medium in the third comparison example is produced.

[0063] A fourth comparison example will now be described.

[0064] The transparent thermosensitive recording medium in the above-described third comparison example is then preserved in a thermostat for 12 hours under 40°C. Thus, the transparent thermosensitive recording medium in the fourth comparison example is obtained.

[0065] A fifth comparison example will now be described.

[0066] According to a method similar to one described in the description of the above-described third embodiment, the coating liquids are prepared and the recording medium is produced. However, the conditions in which the above-mentioned coated liquids are dried to provide the recording layer and protective layer are differently adjusted so that a content of the organic solvent in the recording layer and protective layer is approximately 6,000 ppm. Thus, the transparent thermosensitive recording medium in the fifth comparison example is produced.

[0067] A sixth comparison example will now be described.

[0068] According to a method similar to one described in the description of the above-described third embodiment, the coating liquids are prepared and the recording medium is produced, except for the following matter: Instead of the use of the toluene/methyl ethyl keton (1/1) mixture liquid, toluene/ethanol (with a dielectric constant of 27.0 at 20°C and with a vapour pressure of 5866 Pa (44 mmHg) at 20°C) (1/1) mixture liquid is used. Thus, the thermosensitive recording medium in the sixth comparison example is produced.

[0069] A seventh comparison example will now be described.

[0070] According to a method similar to one described in the description of the above-described third embodiment, the coating liquids are prepared and the recording medium is produced, except for the following matter: Instead of the

use of the toluene/methyl ethyl keton (1/1) mixture liquid, n-hexane (with a dielectric constant of 1.85 at 20°C and with a vapour pressure of 20660 Pa (155 mmHg) at 20°C) / n-butanol (with a dielectric constant of 19.2 at 20°C and with a vapour pressure of 733 Pa (5.5 mmHg) at 20°C) (1/1) mixture liquid is used. Thus, the thermosensitive recording medium in the seventh comparison example is produced.

[0071] An evaluation test is performed on the thermosensitive recording medium in each of the above-described first, second, third, fourth, fifth, sixth embodiments according to the present invention, and first, second, third, fourth, and fifth comparison examples. The evaluation test is such that a printing device using a thermal head of 8 dots/mm prints an image on the thermosensitive recording medium. In the printing, energy is applied to the recording medium such that power of 0.7 W/dot is applied and the power is applied for each pulse span of 0.5 msec. Items of the evaluation test will now be described.

Color Development Color Tone:

[0072] A color development color tone appearing immediately after the printing is directly observed.

Transmission Density:

[0073] An image part (optical) density and a background part (optical) density are measured immediately after the printing using a transmission density meter, X-Rite 310TR (manufactured by XRITE COMPANY).

Transparency:

[0074]

1) A transparency of the transparent thermosensitive recording medium is measured using a Ricoh Reflection-type OHP 312R. The measuring is made by actually projecting the printed image through the OHP and the illuminance (lux) obtained as a result of the projection is measured. In order to compare the results of the above-describing measurement performed on actual samples of the thermosensitive recording media, we performed the same measuring on a transparent PET (poly(ethylene terephthalate)) film (1000 µm). The measurement result of the transparent PET film is an illuminance of 500 luxes.

2) The transparency of the transparent thermosensitive recording medium is evaluated using a spectral transmittance thereof. A spectrophotometer UV-3100 manufactured by Shimazu Corporation is used for measuring the spectral transmittance with a spectral wavelength of 570 nm.

Preservation Property:

[0075]

1) Heat resistance property: The thermosensitive recording medium is preserved for 24 hours under 40°C in dry condition. Then, the densities of the image part and background part are measured and thus evaluated.

[0076] The results of the above-described items of the evaluation test performed on the thermosensitive recording media in the embodiments according to the present invention and those in the comparison examples are shown in FIG. 1.

[0077] Note 1) Since the carrier body is not transparent one in each of the first embodiment according to the present invention and the first comparison example, a Macbeth illuminometer, RD-914 was used to measure the densities of the image parts obtained as a result of the color development.

[0078] Note 2) The content of the solvent included in the recording layer or that included in the recording layer and protective layer of the thermosensitive recording medium of each of the samples used in the above-mentioned evaluation test was measured by using a pyrolysis gas chromatograph (GC-17A manufactured by Shimazu Corporation)

[0079] According to the present invention, a fixed content of the organic solvent is included in the recording layer and protective layer of the thermosensitive recording medium. As a result, it is possible to reduce an optical density of fresh one of the thermosensitive recording medium. Further, it is possible to remarkably improve contrast between the image part obtained as a result of the color development and the background part consisting of a remaining part of the fresh recording medium.

[0080] Further, the present invention is not limited to the above-described embodiments, and variations and modifications may be made without departing from the scope of the present invention, which is defined in the claims.

Claims

1. An irreversible thermosensitive recording medium comprising a carrier body and a thermosensitive recording layer provided on said carrier body;

said thermosensitive recording medium being **characterized in that**:

said thermosensitive recording layer is mainly composed of electron donative coloration compound, and electron acceptor compound, together with binder resin; and

said thermosensitive recording medium includes 500 through 5,000 ppm of organic solvent,

said organic solvent having a dielectric constant of 2.0 through 25.0 at 20°C, and having a vapor pressure of 1333 to 26660 Pa (10 through 200 mmHg) at 20°C.

2. The thermosensitive recording medium according to claim 1, **characterized in that** said thermosensitive recording medium further comprises a protective layer provided on said thermosensitive recording layer.

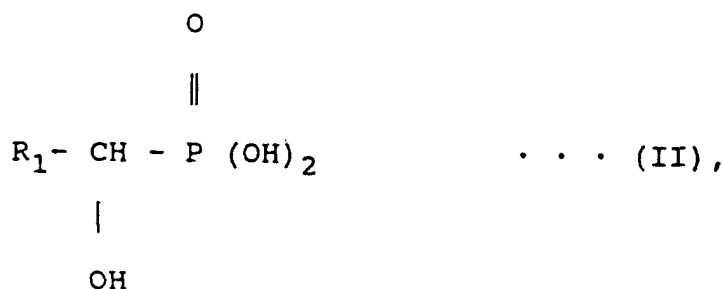
3. The thermosensitive recording medium according to claim 2, **characterized in that** said organic solvent is included in said thermosensitive layer and said protective layer.

4. The thermosensitive recording medium according to claims 1- 3, **characterized in that**:

said electron acceptor compound comprises an organic phosphorus compound expressed by a general formula (I):



said R being an alkyl group having 16 through 24 carbons, or a general formula (II):



said R₁ being an alkyl group having 13 through 23 carbons.

5. The thermosensitive recording medium according to claims 1 - 4, **characterized in that** said carrier body is insoluble in said organic solvent.

6. The thermosensitive recording medium according to claims 1 - 5, **characterized in that** said carrier body comprises a transparent resin film having an index of refraction of between 1.45 and 1.60 at normal temperature.

7. The thermosensitive recording medium according to claims 1 - 6, **characterized in that** said binder resin of said thermosensitive recording layer is a transparent resin having an index of refraction of between 1.45 and 1.60 at normal temperature, and having in its molecule a hydroxyl group or a carboxyl group.

8. The thermosensitive recording medium according to claims 2 - 7, **characterized in that** said protective layer comprises a resin as a main ingredient thereof, said resin having an index of refraction of between 1.45 and 1.60 at normal temperature.

Patentansprüche

1. Irreversibles wärmeempfindliches Aufzeichnungsmaterial, umfassend einen Trägerkörper und eine auf dem Trägerkörper vorgesehene wärmeempfindliche Aufzeichnungsschicht;
wobei das wärmeempfindliche Aufzeichnungsmaterial **dadurch gekennzeichnet ist, dass:**

die wärmeempfindliche Aufzeichnungsschicht hauptsächlich aus Elektronen abgebender Farbgebungs-Verbindung und Elektronenakzeptor-Verbindung zusammen mit Bindemittel-Harz zusammengesetzt ist; und das wärmeempfindliche Aufzeichnungsmaterial 500 bis 5000 ppm organisches Lösungsmittel einschließt,

wobei das organische Lösungsmittel eine Dielektrizitätskonstante von 2,0 bis 25,0 bei 20°C aufweist und einen Dampfdruck bei 20°C von 1333 bis 26660 Pa (10 bis 200 mmHg) aufweist.

2. Wärmeempfindliches Aufzeichnungsmaterial nach Anspruch 1, **dadurch gekennzeichnet, dass** das wärmeempfindliche Aufzeichnungsmaterial weiter eine auf der wärmeempfindlichen Aufzeichnungsschicht vorgesehene Schutzschicht umfasst.

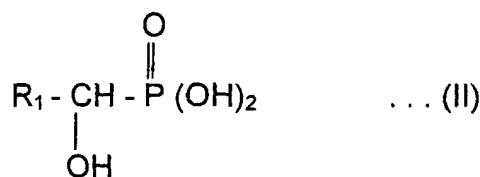
3. Wärmeempfindliches Aufzeichnungsmaterial nach Anspruch 2, **dadurch gekennzeichnet, dass** das organische Lösungsmittel in der wärmeempfindlichen Schicht und der Schutzschicht eingeschlossen ist.

4. Wärmeempfindliches Aufzeichnungsmaterial nach den Ansprüchen 1 - 3, **dadurch gekennzeichnet, dass:**

die Elektronenakzeptor-Verbindung eine organische Phosphor-Verbindung umfasst, die ausgedrückt wird durch eine allgemeine Formel (I):



wobei R eine Alkylgruppe mit 16 bis 24 Kohlenstoffatomen darstellt, oder eine allgemeine Formel (II):



wobei R₁ eine Alkylgruppe mit 13 bis 23 Kohlenstoffatomen darstellt.

5. Wärmeempfindliches Aufzeichnungsmaterial nach den Ansprüchen 1 - 4, **dadurch gekennzeichnet, dass** der Trägerkörper in dem organischen Lösungsmittel unlöslich ist.

6. Wärmeempfindliches Aufzeichnungsmaterial nach den Ansprüchen 1 - 5, **dadurch gekennzeichnet, dass** der Trägerkörper eine transparente Harzfolie mit einem Brechungsindex bei Normaltemperatur zwischen 1,45 und 1,60 umfasst.

7. Wärmeempfindliches Aufzeichnungsmaterial nach den Ansprüchen 1 - 6, **dadurch gekennzeichnet, dass** das Bindemittel-Harz der wärmeempfindlichen Aufzeichnungsschicht ein transparentes Harz mit einem Brechungsindex bei Normaltemperatur zwischen 1,45 und 1,60, das in seinem Molekül eine Hydroxylgruppe oder eine Car-

boxylgruppe aufweist, ist.

8. Wärmeempfindliches Aufzeichnungsmaterial nach den Ansprüchen 2 - 7, **dadurch gekennzeichnet, dass** die Schutzschicht ein Harz als Hauptkomponente derselben umfasst, wobei das Harz einen Brechungsindex bei Normaltemperatur zwischen 1,45 und 1,60 aufweist.

Revendications

1. Matériau d'enregistrement thermosensible irréversible comprenant un support et une couche d'enregistrement thermosensible formée sur ledit support ;
ledit matériau d'enregistrement thermosensible étant **caractérisé en ce que** :

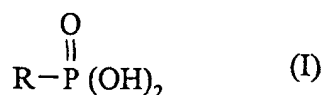
ladite couche d'enregistrement thermosensible est composée principalement d'un composé colorant donneur d'électrons et d'un composé accepteur d'électrons, associés à une résine de liaison ; et
ledit matériau d'enregistrement thermosensible comprend de 500 à 5000 ppm de solvant organique,
ledit solvant organique ayant une constante diélectrique comprise entre 2,0 et 25,0 à 20°C et ayant une pression de vapeur comprise entre 1333 et 26660 Pa (entre 10 et 200 mm de Hg) à 20°C.

2. Matériau d'enregistrement thermosensible selon la revendication 1, **caractérisé en ce que** ledit matériau d'enregistrement thermosensible comprend en outre une couche protectrice formée sur ladite couche d'enregistrement thermosensible.

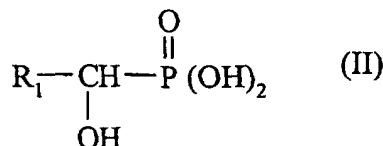
3. Matériau d'enregistrement thermosensible selon la revendication 2, **caractérisé en ce que** ledit solvant organique est incorporé dans ladite couche thermosensible et dans ladite couche protectrice.

4. Matériau d'enregistrement thermosensible selon les revendications 1 à 3, **caractérisé en ce que** :

ledit composé accepteur d'électrons comprend un composé organique du phosphore représenté par la formule générale (I) :



dans laquelle R est un groupe alkyle ayant de 16 à 24 atomes de carbone,
ou la formule générale (II) :



dans laquelle R₁ est un groupe alkyle ayant de 13 à 23 atomes de carbone.

5. Matériau d'enregistrement thermosensible selon les revendications 1 à 4, **caractérisé en ce que** ledit support est insoluble dans ledit solvant organique.

6. Matériau d'enregistrement thermosensible selon les revendications 1 à 5, **caractérisé en ce que** ledit support comprend un film en résine transparente ayant un indice de réfraction compris entre 1,45 et 1,60 à température normale.

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7. Matériau d'enregistrement thermosensible selon les revendications 1 à 6, **caractérisé en ce que** ladite résine de liaison de ladite couche d'enregistrement thermosensible est une résine transparente ayant un indice de réfraction compris entre 1,45 et 1,60 à température normale et comportant dans sa molécule un groupe hydroxy ou un groupe carboxy.

8. Matériau d'enregistrement thermosensible selon les revendications 2 à 7, **caractérisé en ce que** ladite couche protectrice comprend une résine en tant qu'ingrédient principal, ladite résine ayant un indice de réfraction compris entre 1,45 et 1,60 à température normale.

FIG. 1

EVALUATION ITEM SAMPLE	COLOR DEVELOPMENT COLOR TUNE	TRANSMISSION DENSITY		TRANSPARENCY		PRESERVATION PROPERTY	
		BACK- GROUND PART	IMAGE PART	OHP ILLUMINANCE (LUX)	SPECTRAL TRANSMITTANCE (%)	BACK- GROUND PART	IMAGE PART
FIRST EMBODIMENT OF INVENTION (NOTE 1)	BLACK	0.16	1.85	—	—	0.15	1.86
SECOND EMBODIMENT OF INVENTION	BLACK	0.22	1.21	303	53	0.21	1.01
THIRD EMBODIMENT OF INVENTION	BLACK	0.07	1.55	450	80	0.06	1.55
FOURTH EMBODIMENT OF INVENTION	BLACK	0.06	1.56	453	81	0.06	1.56
FIFTH EMBODIMENT OF INVENTION	BLACK	0.06	1.53	450	81	0.05	1.48
SIXTH EMBODIMENT OF INVENTION	BLACK	0.05	1.54	473	82	0.05	1.50
FIRST COMPARISON EXAMPLE (NOTE 1)	BLACK	0.18	1.86	—	—	0.18	1.86
SECOND COMPARISON EXAMPLE	BLACK	0.25	1.23	280	61	0.25	1.03
THIRD COMPARISON EXAMPLE	BLACK	0.10	1.55	420	78	0.095	1.55
FOURTH COMPARISON EXAMPLE	BLACK	0.095	1.57	425	78	0.095	1.56
FIFTH COMPARISON EXAMPLE	BLACK	0.05	1.49	472	82	0.05	1.21
SIXTH COMPARISON EXAMPLE	BLACK	0.51	1.58	250	50	0.52	1.56
SEVENTH COMPARISON EXAMPLE	BLACK	0.13	0.98	43	10	0.13	0.93