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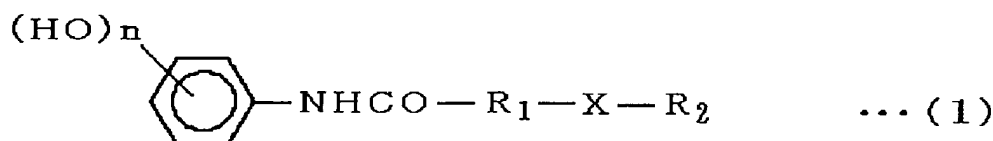
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(74) Representative: **Barz, Peter****Patentanwalt****Kaiserplatz 2****80803 München (DE)**(54) **REVERSIBLE THERMAL RECORDING MEDIUM**

(57) The present invention is a selective invention concerned with an improved reversible thermosensitive recording medium in which erasure failure at low temperature and low humidity and the color development failure at high temperature and high humidity due to the repetitive erasure and printing in an environment of actual use have been improved; stable quality can be provided; and high speed erasure can also be realized. An object of the present invention is to provide a reversible thermosensitive recording medium in which humidity does not affect color optical density and erasing optical density; high contrast is excellent; the occurrence of dents to the recording medium and the density change due to the repetitive use are less; durability is excellent; wherein it is also possible to perform erasure by a thermal head; and high speed erasure is excellent.

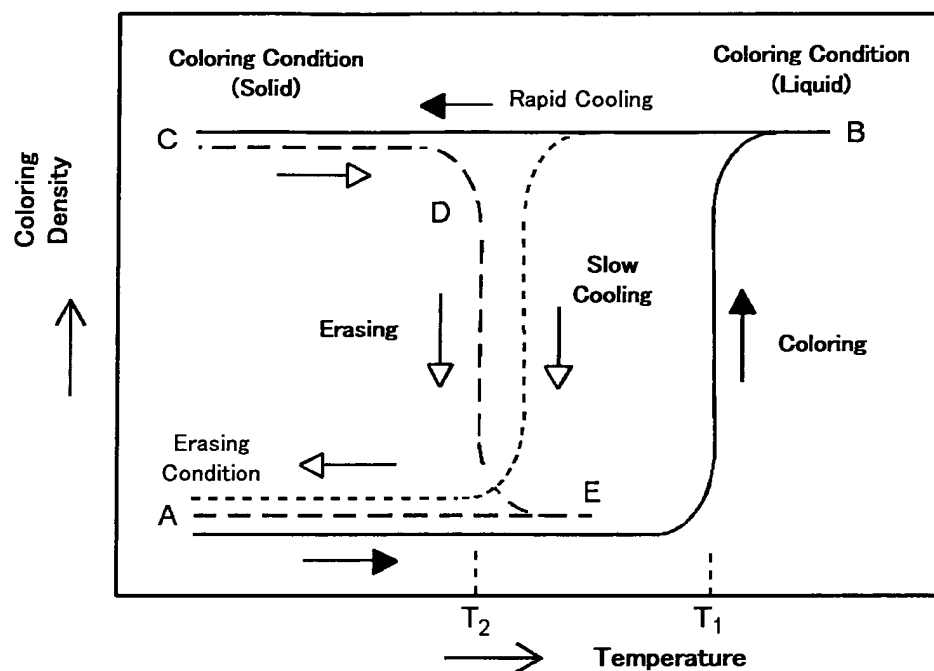
A reversible thermosensitive recording medium of the invention comprises: a reversible thermosensitive recording layer which comprises a reversible thermosensitive composition on a support, wherein the reversible thermosensitive composition comprises an electron-donating coloring compound and an electron-accepting compound and is capable of forming a relatively coloring state depending on the difference of heating temperatures and/or the difference of cooling rates after heating, and wherein the electron-accepting compound is a phenol compound expressed by the general formula (1) below, and when the reversible thermosensitive recording medium is printed in an environment of $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at relative humidity from 70% to 90%, a color optical density is 0.80 or more and an erasing optical density is 0.15 or less;



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where, in the formula (1), 'n' represents an integer of 1 to 3 and 'X' represents a divalent group containing either N atoms or O atoms, 'R₁' represents an aliphatic hydrocarbon group having 2 or more carbon atoms, which may have a substituents, and 'R₂' represents an aliphatic hydrocarbon group having 1 to 14 carbon atoms.

FIG.1



Description

Technical Field

[0001] The present invention relates to a reversible thermosensitive recording medium in which coloring images may be formed and erased reversibly based on color-developing reactions between electron-donating coloring compounds and electron-accepting compounds contained of a reversible thermosensitive coloring composition by controlling applied thermal energies.

Background Art

[0002] Thermosensitive recording media which utilize reactions between electron-donating coloring compounds (hereinafter, sometimes referred as "coloring agent" or "leuco dye") and electron-accepting compounds (hereinafter, sometimes referred as "color developer" .) have been well-known, and have been broadly utilized as output papers of facsimiles, word processors and scientific instrumentation apparatuses, with an advance of office automation, and nowadays in magnetic thermosensitive cards such as a pre-paid card and point card. From an environmental issue, these conventional recording media in practical use are under pressure to review their use and are required to be recycled, and to be used in less amount; however, recorded images cannot be erased because of irreversible coloring, and thus cannot be used repeatedly. In addition, new information is written only to non-recorded portion, and therefore the total areas capable of being recorded are limited. Thus, under the current situation, the amount of information to be recorded is reduced or a new card is issued when area to be recorded is fully occupied. Against the backdrop of waste problem or problem of deforestation, development of reversible thermosensitive recording medium which is rewritable many times had been desired.

[0003] From theses demands, various kinds of reversible thermosensitive recording media have been proposed. For example, there has been disclosed a reversible thermosensitive recording medium which is a kind of those using polymer, in which physical change, i.e., transparent and white opaque is utilized (see Patent Literatures 1 and 2). Alternatively, there has been disclosed a reversible thermosensitive recording medium which is a kind of those using a dye, in which chemical change is newly utilized. Specifically, for example, gallic acid is used in combination with phloroglucinol as a color developer (see, for example, Patent Literature 3). Such compounds as phenolphthalein and thymolphthalein are used as a color developer (see, for example, Patent Literature 4). Homogeneous mixed solution composed of coloring agent, color developer, and carboxylic acid ester are contained in a recording layer (see, for example, Patent Literatures 5, 6, and 7). Ascorbic acid derivatives are used as a color developer (see, for example, Patent Literature 8). Salts of bis (hydroxyphenyl) acetic acid or gallic acid and higher aliphatic amine are used as a color developer (see, for example, Patent Literatures 9 and 10).

[0004] Further, in Patent Literature 11, the present inventors have proposed a reversible thermosensitive coloring composition and thermosensitive recording medium using this composition for a recording layer. In the reversible thermosensitive coloring composition, an organic phosphorus compound, fatty carbonyl acid compound, or phenol compound each containing a long-chain aliphatic hydrocarbon group as a color developer is combined with a leuco dye as a coloring agent, thereby allowing coloring and erasing easily depending on the heating and cooling condition. The coloring state and erasing state can be stably maintained at normal temperature and in addition, developing and erasing can be repeated. And then, Patent Literatures 12 and 13 disclose use of a phenol compound containing a long-chain fatty hydrocarbon group which compound has a specific structure.

[0005] However, in actual use, even though used in a broad range of environments, extending from low temperature and low humidity to high temperature and high humidity, there is the problem that erasure failure can easily occur at low temperature and low humidity and color development failure may occur at high temperature and high humidity, so there are not always satisfactory results.

[0006] Further, in Patent Literature 14, it is described that the addition of a specific inorganic pigment to an intermediate layer or a protective layer results in excellent moisture-proof shelf life. However, the reality is that any improvement of erasure failure at low temperature and low humidity and color development failure at high temperature and high humidity due to repetitive erasure and printing in an environment of actual use has yet to be accomplished.

[0007] In addition, in recent years, high speed and miniaturization of printers have been in demand, and even with reversible thermosensitive recording materials, the modification from a type in which erasure is performed by a ceramic heater to another type in which erasure is performed by a thermal head has become obvious, and high speed erasure is desired.

Patent Literature 1

[0008] Japanese Patent Application Laid-Open No. 63-107584

Patent Literature 2

[0009] Japanese Patent Application Laid-Open No. 04-78573

5 Patent Literature 3

[0010] Japanese Patent Application Laid-Open No. 60-193691

Patent Literature 4

10 **[0011]** Japanese Patent Application Laid-Open No. 61-237684

Patent Literature 5

15 **[0012]** Japanese Patent Application Laid-Open No. 62-138556

Patent Literature 6

20 **[0013]** Japanese Patent Application Laid-Open No. 62-138568

Patent Literature 7

[0014] Japanese Patent Application Laid-Open No. 62-140881

25 Patent Literature 8

[0015] Japanese Patent Application Laid-Open No. 63-173684

Patent Literature 9

30 **[0016]** Japanese Patent Application Laid-Open No. 02-188293

Patent Literature 10

35 **[0017]** Japanese Patent Application Laid-Open No. 02-188294

Patent Literature 11

40 **[0018]** Japanese Patent Application Laid-Open No. 05-124360

Patent Literature 12

[0019] Japanese Patent Application Laid-Open No. 06-210954

45 Patent Literature 13

[0020] Japanese Patent Application Laid-Open No. 10-95175

Patent Literature 14

50 **[0021]** Japanese Patent Application Laid-Open No. 10-100541

[0022] The present invention is a selective invention concerned with an improved reversible thermosensitive recording medium in which erasure failure at low temperature and low humidity and the color development failure at high temperature and high humidity due to the repetitive erasure and printing in an environment of actual use, which have conventionally been problems, have been improved; stable quality can be provided; and high speed erasure can also be realized.

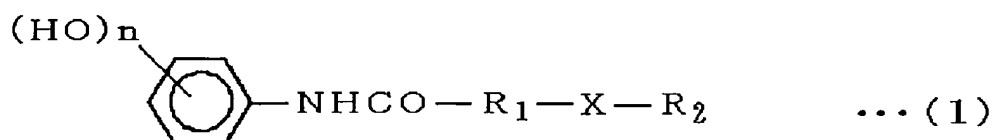
55 **[0023]** Therefore, an object of the present invention is to provide a reversible thermosensitive recording medium in which humidity does not affect color optical density and erasing optical density; high contrast is excellent; the occurrence

of dents to the recording medium and the density change due to the repetitive use are less; durability is excellent; wherein it is also possible to perform erasure by a thermal head; and high speed erasure is excellent.

Disclosure of the Invention

[0024] The present inventors considered that in reversible color developing and erasing phenomenon of the composition which comprises the coloring agent and color developer, balance between ability of the color developer having a long-chain aliphatic group to develop the coloring agent and the cohesive property between molecules, is important. As a result of investigating compounds with a variety of structures, they have found that the above-mentioned problems can be solved by using phenol compound having a specific structure as the color developer, further by including a compound with a specific functional group as an erasure promoter.

[0025] In other words, the above-mentioned problems are resolved by a reversible thermosensitive recording medium according to the present invention, which comprises a reversible thermosensitive recording layer containing a reversible thermosensitive composition on a support, wherein the reversible thermosensitive composition comprises a an electron-donating coloring compound and an electron-accepting compound and is capable of forming a relatively coloring state depending on the difference of heating temperatures and/or the difference of cooling rates after heating, and wherein the electron-accepting compound is a phenol compound expressed by the general formula (1) below, and when the reversible thermosensitive recording medium is printed in an environment of $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at relative humidity from 70% to 90%, a color optical density is 0.80 or more and an erasing optical density is 0.15 or less;



where, in the formula (1), 'n' represents an integer of 1 to 3 and 'X' represents a divalent group containing either N atoms or O atoms, 'R₁' represents an aliphatic hydrocarbon group having 2 or more carbon atoms, which may have a substituents, and 'R₂' represents an aliphatic hydrocarbon group having 1 to 14 carbon atoms.

[0026] Preferably, 'R₁' is an aliphatic hydrocarbon group having 10 to 16 carbon atoms and 'R₂' is aliphatic hydrocarbon group having 8 to 14 carbon atoms in the general formula (1).

[0027] Preferably, 'X' in the general formula (1) is a urea group.

[0028] Preferably, the reversible thermosensitive recording layer contains a resin being in the cross-linking state.

[0029] Preferably, the resin contained in the reversible thermosensitive recording layer has 70 (KOHmg/g) or more of hydroxyl value.

[0030] Preferably, the resin contained in the reversible thermosensitive recording layer is acrylic polyol resin.

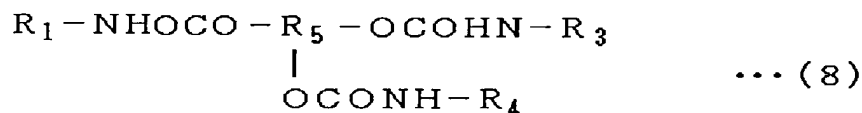
[0031] Preferably, the gel fraction of the resin is 30 % or more.

[0032] Preferably, the medium comprises a compound having a secondary amide group as an erasure promoter.

[0033] Preferably, the medium additionally comprises another erasure promoter having at least one of -NHCO— group and —OCONH— group in a molecule.

[0034] Preferably, the erasure promoter containing at least one of - NHCO— group and —OCONH— group in a molecule is any one of the compounds expressed by general formulae (2) to (8);





where, in the formulae, R_1 , R_2 , and R_4 represent linear alkyl group, branched alkyl group or unsaturated alkyl group having 7 to 22 carbon atoms, R_3 represents a divalent functional group having 1 to 10 carbon atoms and R_5 represents a trivalent functional group having 4 to 10 carbon atoms.

[0035] Preferably, a protective layer for protecting the thermosensitive recording layer is provided on the reversible thermosensitive recording layer, and the protective layer contains a resin in the cross-linking state.

[0036] In another aspect of the present invention, a member which comprises an information-memorizing part and a reversible displaying part may be provided, and the reversible thermosensitive recording mediums described above constitutes the reversible displaying part.

[0037] Preferably, the member comprising the information-memorizing part and the reversible displaying part is any one of a card, a disc, a disc cartridge and a tape cassette.

[0038] In another aspect of the present invention, a reversible thermosensitive recording label may be provided, the reversible thermosensitive recording medium described above constitutes the label, and the label comprises an adhesive layer or a tacky layer, which is provided on a surface of the support opposite the reversible thermosensitive recording layer.

[0039] Preferably, the reversible thermosensitive recording label described above is used for the reversible displaying part of the members described above.

[0040] In still another aspect of the present invention, an image processing method for forming and/or erasing an image on/from a reversible thermosensitive recording layer by heating the reversible thermosensitive recording layer may be provided, and at least one of the reversible thermosensitive recording mediums described above, the reversible thermosensitive recording label described above, or the members described above is used.

[0041] Preferably, the image is formed on the reversible thermosensitive recording layer using a thermal head.

[0042] Preferably, the image is erased using a thermal head or a ceramic heater.

[0043] In still another aspect of the present invention, an image processing apparatus which comprises an image forming and/or erasing unit may be provided, and at least one of the reversible thermosensitive recording medium described above, the reversible thermosensitive recording label described above, and the members comprising the information-memorizing part and the reversible displaying part described above is mounted in the image processing apparatus.

[0044] Preferably, the image forming unit is a thermal head.

[0045] Preferably, the image erasing unit is at least one of a thermal head and a ceramic heater.

Brief Description of Drawings

[0046]

FIG. 1 schematically shows the color developing and erasing property in an example of the reversible thermosensitive coloring composition according to the invention.

FIG. 2 is a diagram exemplifying a configuration, in which a reversible thermosensitive recording label is affixed to an MD disc cartridge.

FIG. 3 is a diagram exemplifying a configuration, in which a reversible thermosensitive recording label is affixed to a CD-RW.

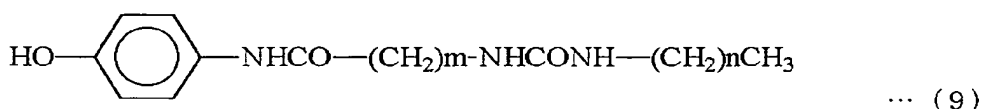
FIG. 4 is a diagram exemplifying a configuration, in which a reversible thermosensitive recording label is employed on a video cassette as a display label.

FIG. 5 schematically exemplifies an image-processing apparatus according to the invention.

Best Mode for Carrying Out the Invention

[0047] With a conventional reversible thermosensitive recording medium using a color developer, when erasure or printing is performed in an environment at high temperature and high humidity, there is a problem that the color optical density decreases. The reversible thermosensitive recording medium is capable of forming the relatively coloring state and the relatively erasing state depending on the heating temperature and/or the cooling rate after heating, and in the case that the cooling rate is rapid, the coloring state can be formed, and in the case that the cooling rate is gradual, the erasing state can be formed. Therefore, the image formation in a high temperature environment easily shifts to the gradual cooling condition, so the color optical density easily decreases. Further, in the environment at high temperature and high humidity, excess water molecules migrate to within the reversible thermosensitive recording medium and establish a hydrogen bond with the color developer, causing the inhibition of the ring opening of leuco dye, and the color optical density additionally decreases. Therefore, with the conventional reversible thermosensitive recording medium, even though 0.8 or more of color optical density and 0.15 or less of erasing optical density can be obtained at normal temperature and normal humidity, the color optical density becomes less than 0.8 in an environment of high temperature and high humidity, so a stable color development image cannot be obtained.

[0048] As a result of studying, the present inventors have found that by using the color developer expressed by the above-mentioned general formula (1) or more preferably using the compound expressed by a general formula (9), the above-mentioned problems can be solved;



where 'm' in the formula indicates a number from 10 to 16, and 'n' indicates a number from 7 to 13.

[0049] In other words, even if repetitive erasure and printing from/into the reversible thermosensitive recording medium using the color developer expressed by the general formula (1) or more preferably using the compound expressed by the general formula (9) in an environment of a temperature of 35°C or around 35°C and at a relative humidity of from 70% to 90%, a reversible thermosensitive recording medium in which there is no difference in the color optical density when erasure and printing are performed in an environment of normal temperature and normal humidity; at which no erasure failure will also occur; and in which the contrast is excellent, can be obtained. In other words, the reversible thermosensitive recording medium of the present invention has at least performance with 0.80 or more of color optical density and 0.15 or less of erasure of optical density when printing is performed in an environment at 35°C ± 2°C and at relative humidity of from 70% to 90%.

[0050] The compound expressed by the general formula (9) contains urea groups in the structure, and because of its hydrogen-bonding capacity, the compound has interaction with water molecules. Further, the color developer expressed by the general formula (9) demonstrates a reversible function by generating a state change between the coloring state and the erasing state depending on the thermal effect, and it is believed that the state change at this time is contributed by the molecular association capacity utilizing the hydrogen-bonding capacity of the urea groups. Therefore, in an environment in which the relative humidity is high; in other words, in an environment in which many water molecules exist, in the color developer, both the hydrogen bond between the urea groups contained in the color developer and the other hydrogen bond to the water molecules occur, it can be considered that this is a cause for the loss of balance between the coloring state and the erasing state so as to cause color development failure.

[0051] Therefore, in the color developer expressed by the general formula (9), the diminishment of the interaction with the water molecules is required for excellent color development in an environment of high relative humidity. The inventors have studied the status of the interaction with the water molecules by variously changing the magnitude of 'm' and 'n' in the general formula (9), and have found that, in the case where 'm' is smaller than 10, interaction with the water molecules is great, but if 'm' is over 10, the interaction with the water molecules becomes smaller. In addition, the inventors have found that in the case that 'n' is greater than 13, interaction with the water molecules is great, but if 'n' is 13 or less, the interaction with the water molecules becomes smaller. In other words, the color developer expressed by the general formula (9) enables the adjustment of the effect of the water molecules by the adjustment of 'm' and 'n'. As a result, it is possible to obtain the reversible thermosensitive recording medium that even if repetitive erasure and printing are performed in an environment with a temperature of 35°C and at relative humidity of from 70% to 90%, there is no difference in the color optical density when erasure and printing are performed in an environment of normal temperature and normal humidity; no erasure failure will occur; and the contrast is excellent. This is a phenomenon not discovered from the conventional knowledge but a phenomenon discovered by the present inventors for

the first time.

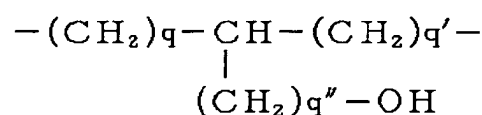
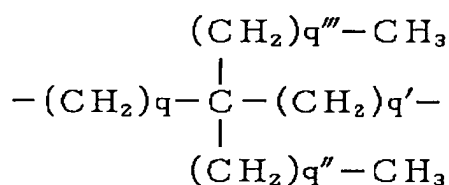
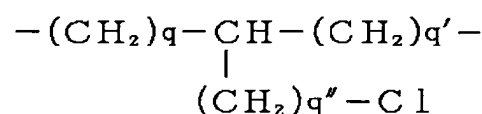
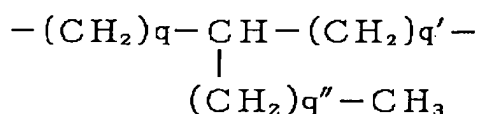
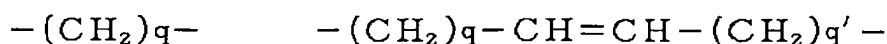
[0052] In the meantime, another phenomenon has been confirmed where, in the case that 'm' is over 16 and in the case that 'n' is smaller than 7, it is possible to maintain small interaction with the water molecules, but the erasure characteristics are remarkably deteriorated; therefore, a preferable range of 'm' is from 10 to 16, and the preferable range of 'n' is from 7 to 13.

[0053] Furthermore, the detailed mechanism of this phenomenon has not been completely explained. However, it is obvious that the moisture absorption characteristic of the color developer compound affects the phenomenon.

[0054] The reversible thermosensitive color developing composition of the present invention is characterized by using a phenol compound expressed by the above-mentioned general formula (1) as an electron-accepting compound. In the above-mentioned general formula (1), the aliphatic hydrocarbon group can be a linear chain or branching, and it can also have an unsaturated bond. The substituents attached to the hydrocarbon group include the hydroxyl group, the halogen atom and the alkoxy group. If the sum of the number of carbons in R₁ and R₂ is 7 or less, the stability of color development and the erasability are deteriorated, so it is preferable that the number of carbon atoms be 8 or more, and more preferably that it be 11 or more.

[0055] Preferable examples of R₁ are shown in the following Table 1.

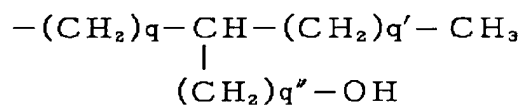
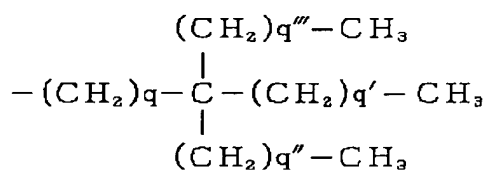
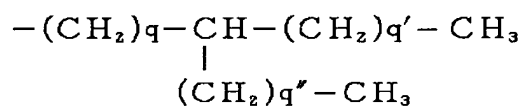
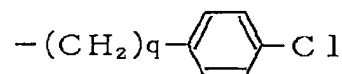
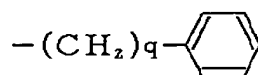
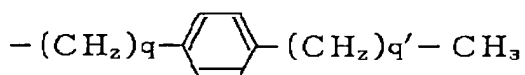
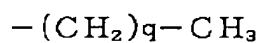
Table 1



[0056] Among them, $-(CH_2)_q-$ is especially preferred. In formulae, each of q, q', q'', and q''' represents integer which fulfill the carbon number of the above-mentioned R₁ or R₂.

[0057] Preferable examples of R₂ are shown in the following Table 2.

Table 2



[0058] Among them, $-(\text{CH}_2)_q-\text{CH}_3$ is especially preferred. In formulae, each of q , q' , q'' , and q''' is the same as described above.

[0059] 'X' indicates a divalent group containing either N atoms or O atoms, preferably a divalent group having at least one or more group shown in the following Table 3. Examples of such divalent group are shown in Table 4. Among them, a divalent group shown in Table 5 is preferred.

Table 3

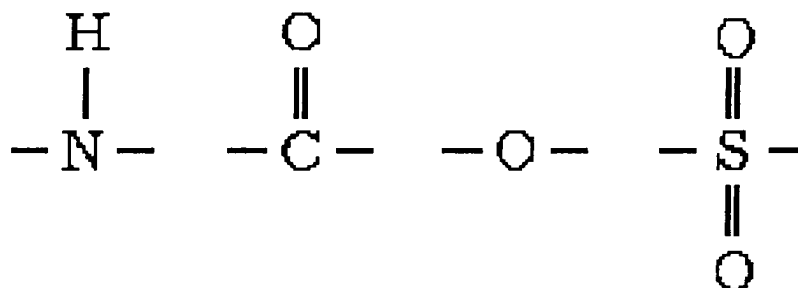


Table 4

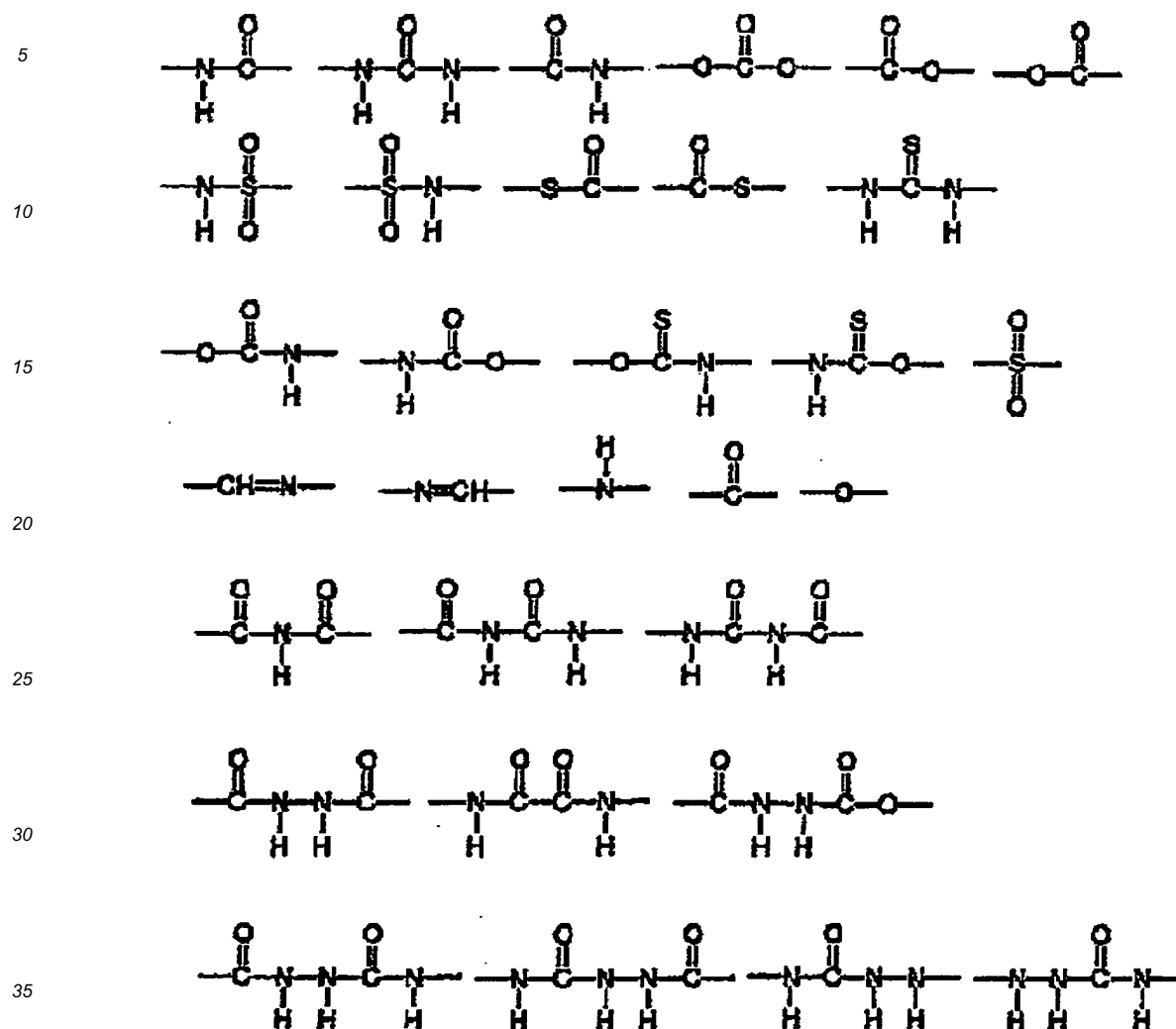
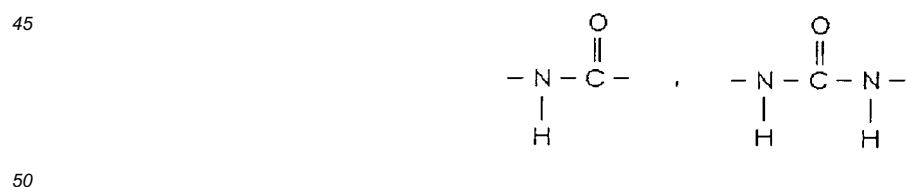


Table 5



[0060] More specific examples of phenol compound are shown below. In Table 6, examples of the compounds are represented by general formulae. Specific examples of the compounds represented by the general formulae in Table 6 are shown in Tables 7 and 8. Examples of compound represented by another general formula in Table 6 may be similarly shown. However, the phenol compound used in the present invention is not limited to these compounds.

Table 6

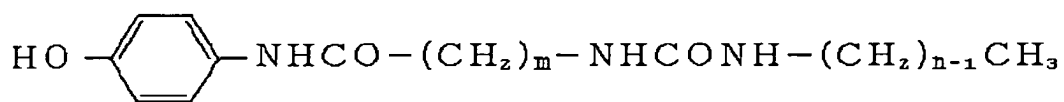
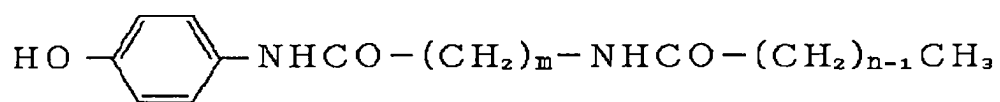


Table 7

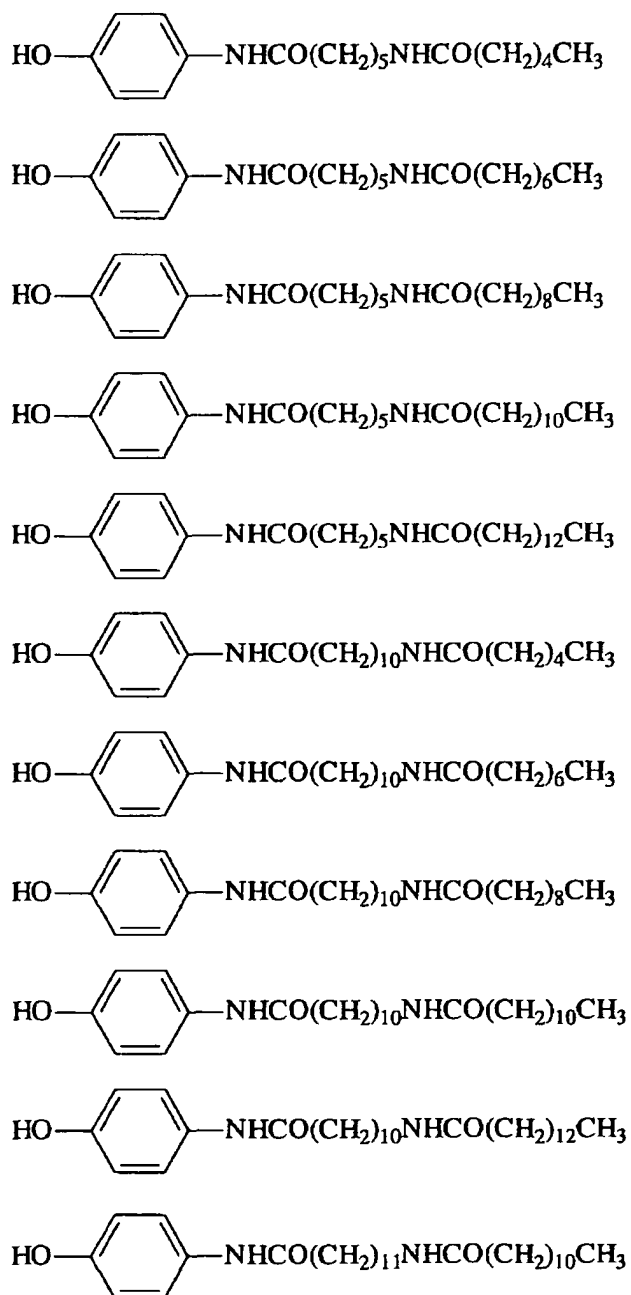


Table 8-1

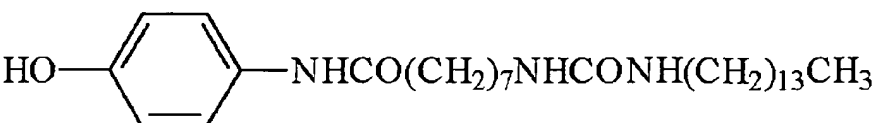
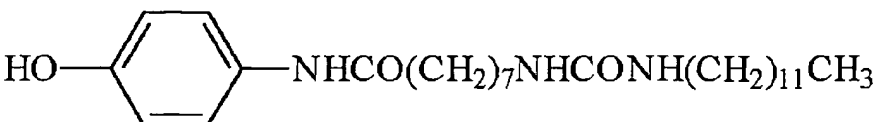
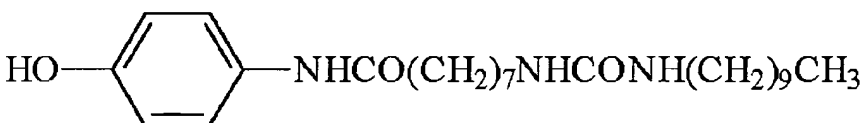
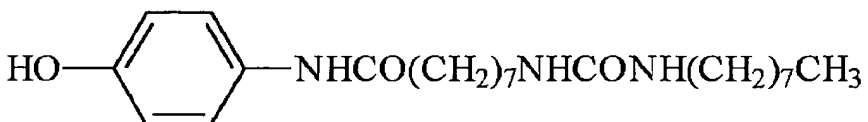
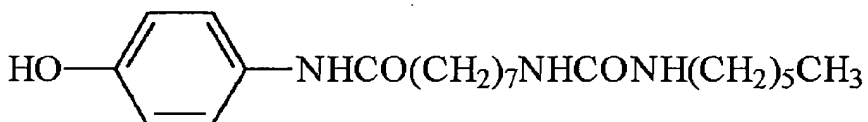
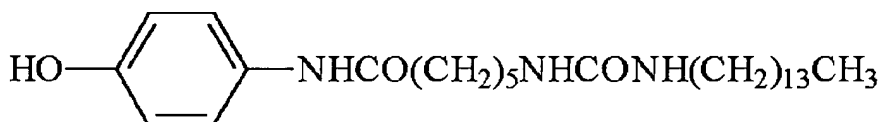
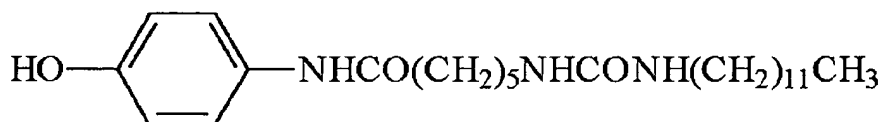
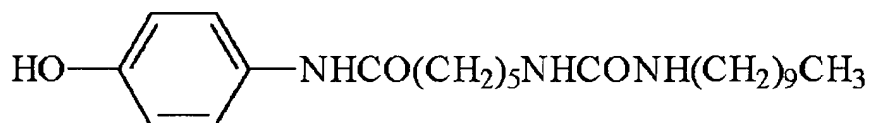
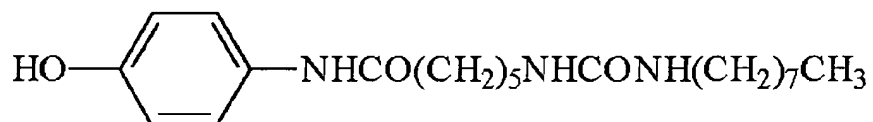
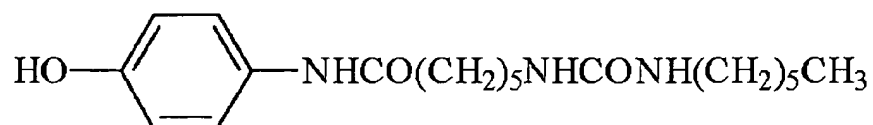
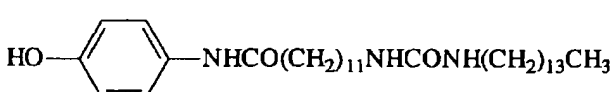
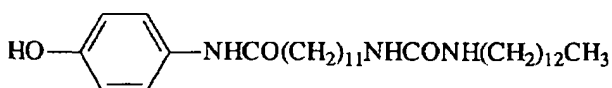
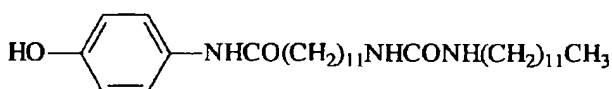
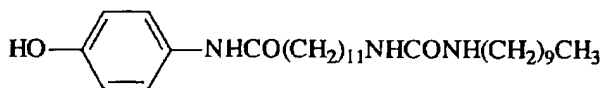
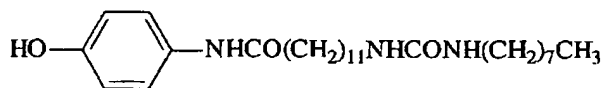
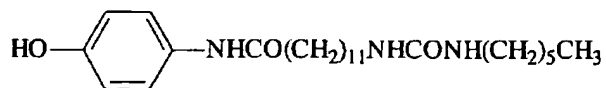
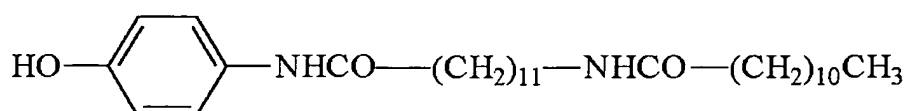
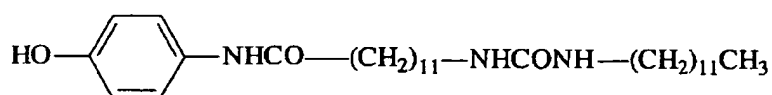
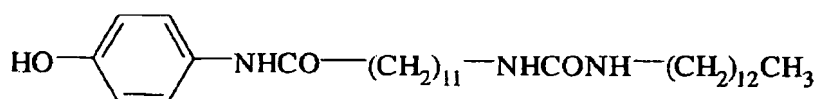
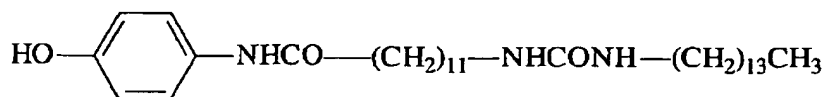
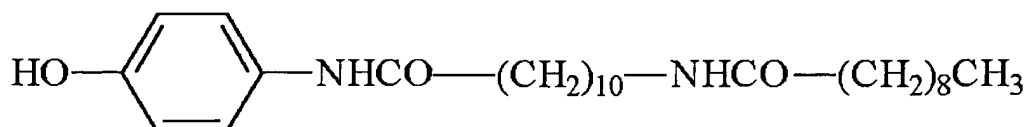


Table 8-2



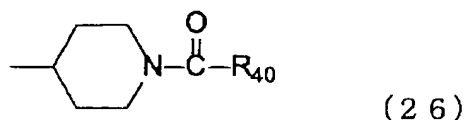
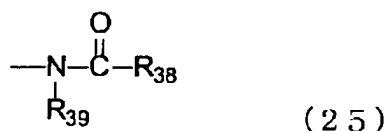
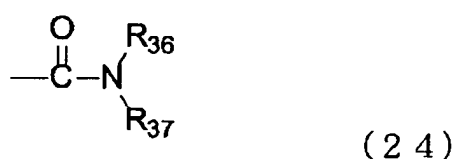
[0061] Among the compounds shown in Tables 7 and 8, the compounds in which 'm' is from 5 to 11 and 'n-1' is from 8 to 13 are preferred, if showing it according to the general formulae in Table 6. Especially preferable compounds are shown below.





10 **[0062]** The reversible thermosensitive recording mediums in the case of using the compound provided as the above-mentioned especially preferable compounds as a color developer all demonstrate 1.00 or more of color optical density and 0.14 or less of the erasing optical density when printing in a high temperature and high humidity environment (at 35°C and 85% RH), which performance is substantially the same as that printed at normal temperature and normal humidity. Hence, it demonstrates extremely excellent performance, unseen in the prior art.

15 **[0063]** As the erasure promoter used in the present invention, using a secondary amide group as expressed by the following general formula results in excellent erasure characteristic.



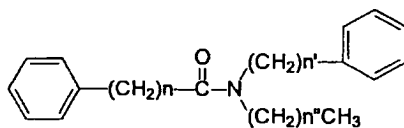
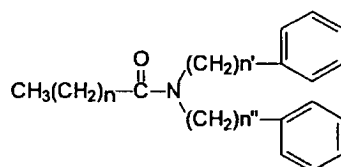
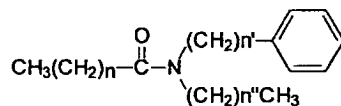
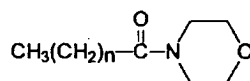
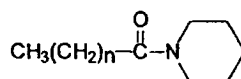
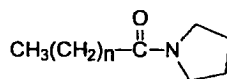
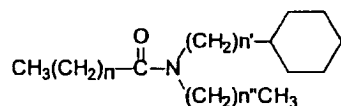
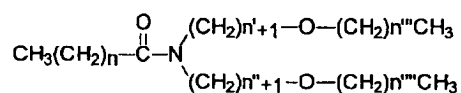
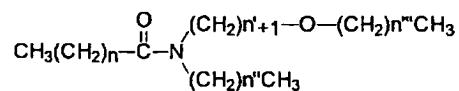
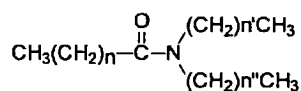
45 **[0064]** In the formulae, R_{36} to R_{40} indicate a saturated or unsaturated hydrocarbon group that may have a substituent, and R_{36} and R_{37} can form a ring, and the ring to be formed can be via a nitrogen atom, an oxygen atom or a sulfur atom. In addition, as an example of a hydrocarbon group preferably used for R_{36} to R_{40} , and that can have a substituent, it can be only a normal chain or branching, and it can be via -O-, -S-, -CO- or —COO— group. Further, it can have an aromatic ring or an aliphatic ring.

[0065] Preferable examples of the erasure promoter used in the present invention are provided in Table 9 as shown below. However, the erasure promoter compound used in the present invention is not limited to these compounds.

50

55

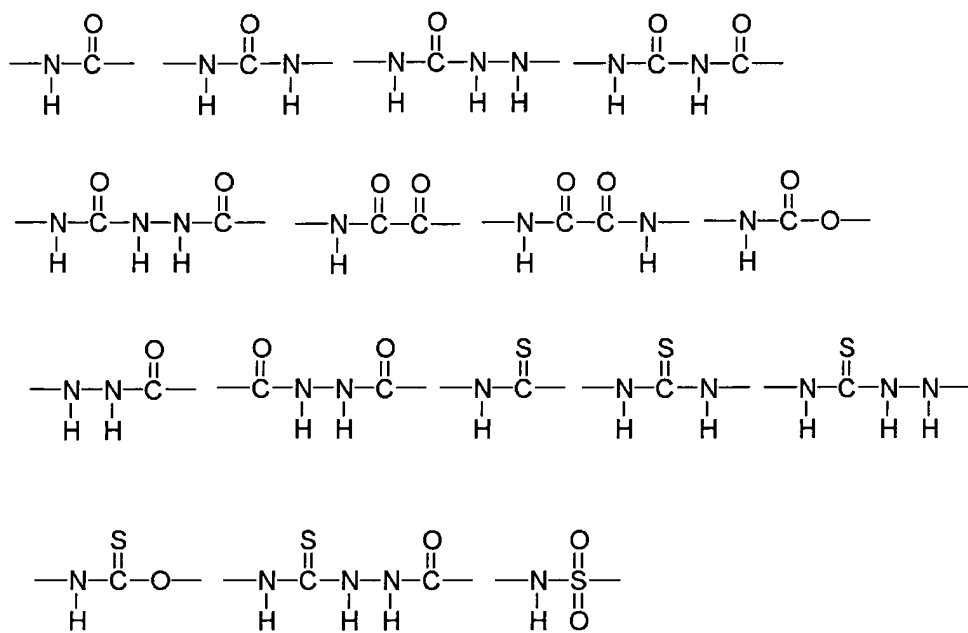
Table 9



[0066] In Table 9, n, n', n'', n''', n'''' indicate an integer of 0 to 21. However, all need not be 5 or less.

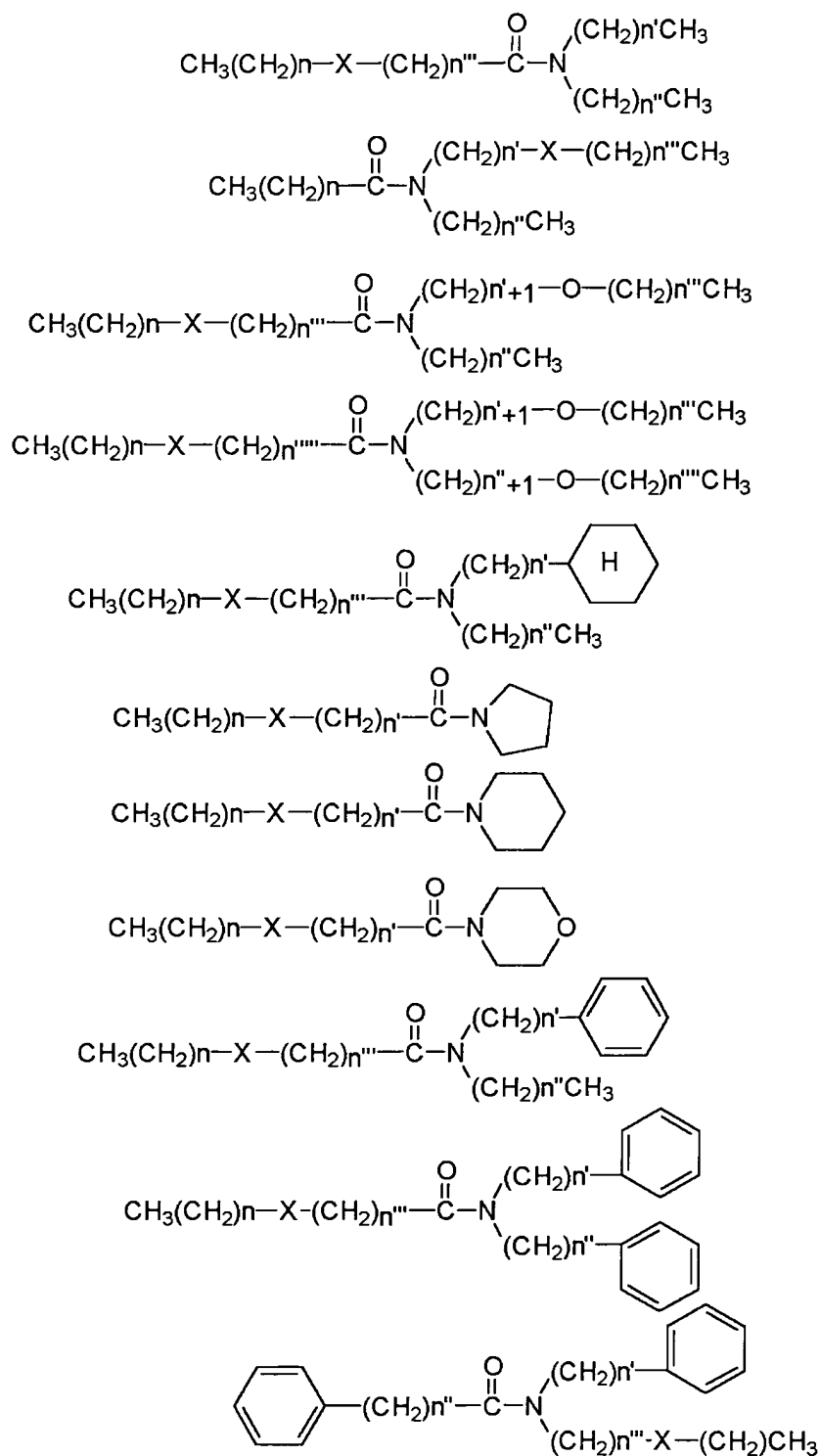
[0067] Further, the erasure promoter used in the present invention may have one or more associative group as show in Table 10.

Table 10



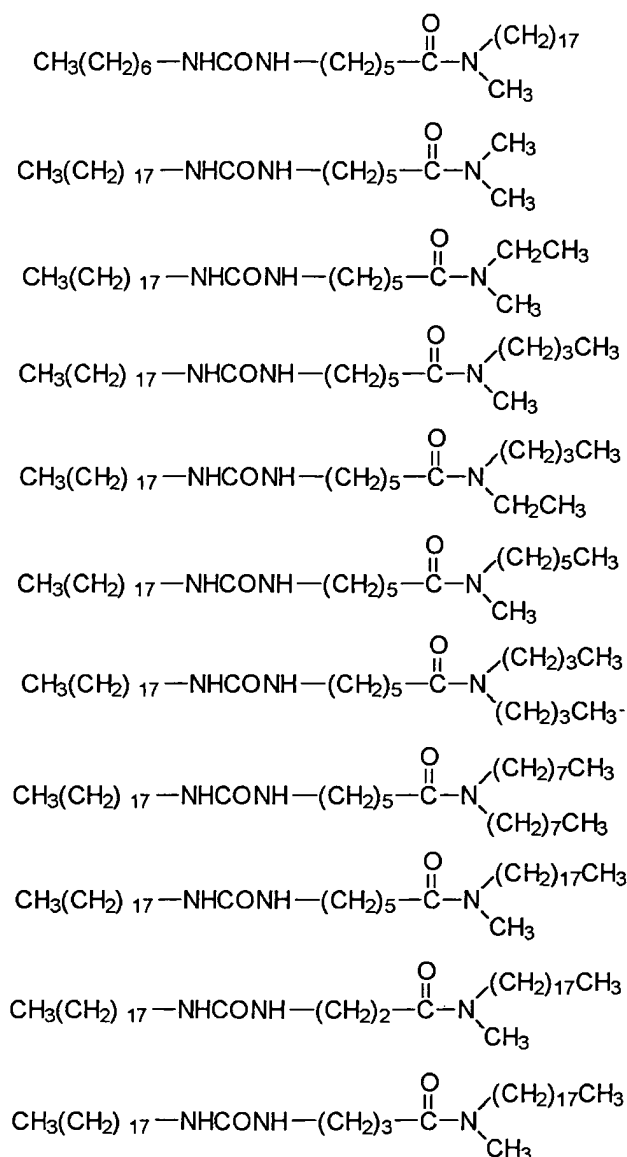
[0068] Preferable examples of the erasure promoter used in the present invention are provided in Table 11. However, the erasure promoter used in the present invention is not limited to these compounds. In Table 11, 'X' indicates the above-mentioned associative group. n, n', n'', n''', n'''' indicate an integer of 0 to 21, however, all need not be 5 or less.

Table 11



[0069] Specific examples of the erasure promoter are shown in Table 12. However, the erasure promoter used in the present invention is not limited to these compounds.

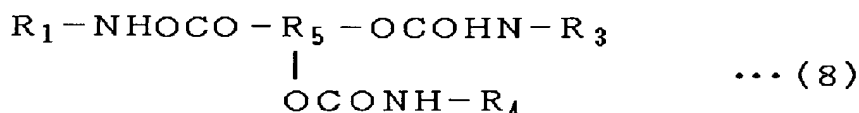
Table 12



[0070] In addition, it has been found to be possible to induce an intermolecular interaction between an erasure promoting compound and a color developer and to remarkably accelerate the erasure rate in the process of forming the erasing state by simultaneously using the color developer with the above-mentioned characteristics and a compound having at least one or more -NHCO- group and -OCONH- group in a molecule as an erasure promoter.

[0071] As the erasure promoter having one or more of the —NHCO— group and the —OCONH— group in a molecule used in the present invention, compounds expressed by the below-mentioned general formulae (2) to (8) are preferable;

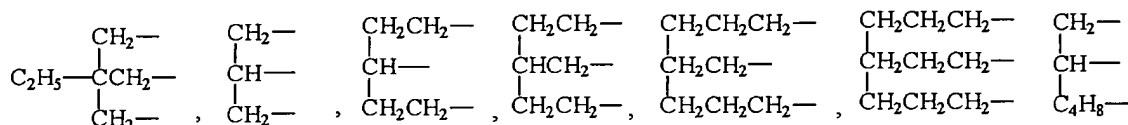




where, in formulae, R_1 , R_2 , and R_4 represent linear alkyl group, branched alkyl group or unsaturated alkyl group having 7 to 22 carbon atoms. R_3 represents a divalent functional group having 1 to 10 carbon atoms. R_5 represents a trivalent functional group having 4 to 10 carbon atoms.

[0072] Preferable examples of R_1 , R_2 , and R_4 include heptyl, octyl, nonyl, decyl, undecyl, dodecyl, stearyl, behenyl, and oleyl groups. Preferable examples of R_3 include methylene, ethylene, propylene, butylene, heptamethylene, hexamethylene, octamethylene, $-\text{C}_3\text{H}_6\text{OC}_3\text{H}_6-$, $-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4-$, and $-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4-$ groups. Preferable examples of R_5 are provided in Table 13 as shown below.

Table 13



[0073] The concrete examples of the compounds expressed by the general formulae (2) to (8) preferably include the following compounds;

[0074] $\text{C}_{11}\text{H}_{23}\text{CONHC}_{12}\text{H}_{25}$, $\text{C}_{15}\text{H}_{31}\text{CONHC}_{16}\text{H}_{33}$, $\text{C}_{17}\text{H}_{35}\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{17}\text{H}_{35}\text{CONHC}_{18}\text{H}_{35}$, $\text{C}_{21}\text{H}_{41}\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{15}\text{H}_{31}\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{17}\text{H}_{35}\text{CONHCH}_2\text{HNOCC}_{17}\text{H}_{35}$, $\text{C}_{11}\text{H}_{23}\text{CONHCH}_2\text{HNOCC}_{11}\text{H}_{23}$, $\text{C}_7\text{H}_{15}\text{CONHC}_2\text{H}_4\text{HNOCC}_{17}\text{H}_{35}$, $\text{C}_9\text{H}_{19}\text{CONHC}_2\text{H}_4\text{HNOCC}_9\text{H}_{19}$, $\text{C}_{11}\text{H}_{23}\text{CONHC}_2\text{H}_4\text{HNOCC}_{11}\text{H}_{23}$, $\text{C}_{17}\text{H}_{35}\text{CONHC}_2\text{H}_4\text{HNOCC}_{17}\text{H}_{35}$, $(\text{CH}_3)_2\text{CHC}_{14}\text{H}_{35}\text{CONHC}_2\text{H}_4\text{HNOCC}_{14}\text{H}_{35}(\text{CH}_3)_2$, $\text{C}_{21}\text{H}_{43}\text{CONHC}_2\text{H}_4\text{HNOCC}_{21}\text{H}_{43}$, $\text{C}_{17}\text{H}_{35}\text{CONHC}_6\text{H}_{12}\text{HNOCC}_{17}\text{H}_{35}$, $\text{C}_{21}\text{H}_{43}\text{CONHC}_6\text{H}_{12}\text{HNOCC}_{21}\text{H}_{43}$, $\text{C}_{17}\text{H}_{33}\text{CONHCH}_2\text{HNOCC}_{17}\text{H}_{33}$, $\text{C}_{17}\text{H}_{33}\text{CONHC}_2\text{H}_4\text{HNOCC}_{17}\text{H}_{33}$, $\text{C}_{21}\text{H}_{41}\text{CONHC}_2\text{H}_4\text{HNOCC}_{21}\text{H}_{41}$, $\text{C}_{17}\text{H}_{33}\text{CONHC}_6\text{H}_{12}\text{HNOCC}_{17}\text{H}_{33}$, $\text{C}_8\text{H}_{17}\text{NHCOC}_2\text{H}_4\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{10}\text{H}_{21}\text{NHCOC}_2\text{H}_4\text{CONHC}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}\text{NHCOC}_2\text{H}_4\text{CONHC}_{12}\text{H}_{25}$, $\text{C}_{18}\text{H}_{37}\text{NHCOC}_2\text{H}_4\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{21}\text{H}_{43}\text{NHOCC}_2\text{H}_4\text{CONHC}_{21}\text{H}_{43}$, $\text{C}_{18}\text{H}_{37}\text{NHOCC}_6\text{H}_{12}\text{CONHC}_{18}\text{H}_{37}$, $\text{C}_{18}\text{H}_{35}\text{NHCOC}_4\text{H}_8\text{CONHC}_{18}\text{H}_{35}$, $\text{C}_{18}\text{H}_{35}\text{NHCOC}_8\text{H}_{16}\text{CONHC}_{18}\text{H}_{35}$, $\text{C}_{12}\text{H}_{25}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{13}\text{H}_{27}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{16}\text{H}_{33}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{18}\text{H}_{37}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{21}\text{H}_{43}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{12}\text{H}_{25}\text{OCONHC}_{16}\text{H}_{33}$, $\text{C}_{13}\text{H}_{27}\text{OCONHC}_{16}\text{H}_{33}$, $\text{C}_{16}\text{H}_{33}\text{OCONHC}_{16}\text{H}_{33}$, $\text{C}_{18}\text{H}_{37}\text{OCO-NHC}_{16}\text{H}_{33}$, $\text{C}_{21}\text{H}_{43}\text{OCONHC}_{16}\text{H}_{33}$, $\text{C}_{12}\text{H}_{25}\text{OCONHC}_{14}\text{H}_{29}$, $\text{C}_{13}\text{H}_{27}\text{OCONHC}_{14}\text{H}_{29}$, $\text{C}_{16}\text{H}_{33}\text{OCONHC}_{14}\text{H}_{29}$, $\text{C}_{18}\text{H}_{37}\text{OCONHC}_{14}\text{H}_{29}$, $\text{C}_{22}\text{H}_{45}\text{OCONHC}_{14}\text{H}_{29}$, $\text{C}_{12}\text{H}_{25}\text{OCONHC}_{12}\text{H}_{37}$, $\text{C}_{13}\text{H}_{27}\text{OCONHC}_{12}\text{H}_{37}$, $\text{C}_{16}\text{H}_{33}\text{OCONHC}_{12}\text{H}_{37}$, $\text{C}_{18}\text{H}_{37}\text{OCONHC}_{12}\text{H}_{37}$, $\text{C}_{21}\text{H}_{43}\text{OCONHC}_{12}\text{H}_{37}$, $\text{C}_{22}\text{H}_{45}\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{18}\text{H}_{37}\text{NHCOOC}_2\text{H}_4\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{18}\text{H}_{37}\text{NHCOOC}_3\text{H}_6\text{OCONHC}_{18}\text{H}_{37}$, $\text{C}_{18}\text{H}_{37}\text{NHCOOC}_4\text{H}_8\text{OCONHC}_{18}\text{H}_{37}$, 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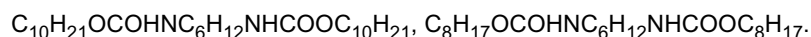
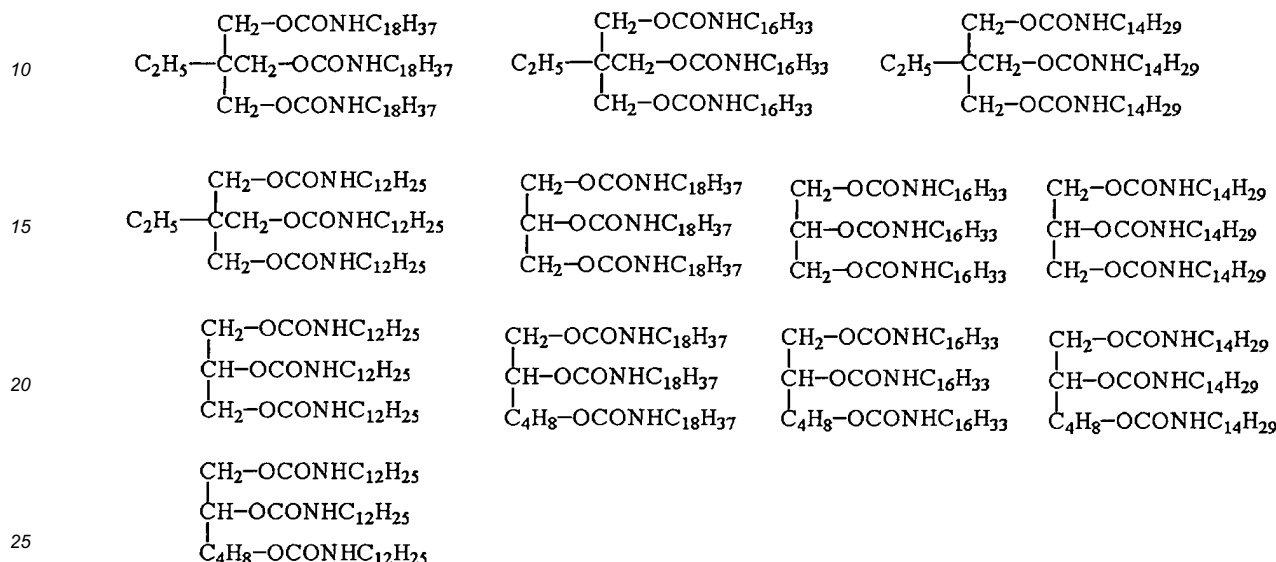


Table 14



[0075] The reversible thermosensitive recording medium of the present invention will be described in more detail below.

[0076] Examples of the binder resin used for forming the reversible thermosensitive recording layer include polyvinyl chloride resins, polyvinyl acetate resins, vinylchloride-vinylacetate copolymers, ethylcellulose resins, polystyrene resins, styrene copolymers, phenoxy resins, polyester resins, aromatic polyester resins, polyurethane resins, polycarbonate resins, polyester acrylate resins, polyester methacrylate, acrylic acid copolymers, maleic acid copolymers, polyvinylalcohol resins, modified polyvinylalcohol resins, hydroxyethylcellulose resins, carboxymethylcellulose resins, and starch.

[0077] These binder resins serve to prevent the deviation of the respective materials in the composition due to heating for the recording erasures thereby to maintain the uniformly dispersed condition. Accordingly, the binder resin is preferred to be highly heat-resistant. For example, the binder resin may be crosslinked by means of heating, ultra-violet irradiation, electron beam and the like.

[0078] Specific examples of the resin in crosslinking state to be used in the present invention include resins having a group reactive with a crosslinker, such as acrylpolyol resins, polyesterpolyol resins, polyurethanepolyol resins, phenoxy resins, polyvinylbutyral resins, celluloseacetate propionate resins, and celluloseacetate butyrate resins, and also the other copolymer resins between a monomer having a group reactive with a crosslinker and another monomer. However, the resin used in the present invention is not limited to these compounds.

[0079] In addition, in the present invention, it is preferable that resin with 70 (KOH mg/g) or more of hydroxyl value be contained (used at beginning), and as the resin with 70 (KOH mg/g) or more of hydroxyl value, acrylic polyol resin, polyester polyol resin or polyurethane polyol resin can be used, and because the color development stability is especially excellent and the erasability is excellent, the acrylic polyol resin is preferably used. The hydroxyl value is 70 (KOH mg/g) or more, and more preferably 90 (KOH mg/g) or more. Since the magnitude of the hydroxyl value affects crosslinking density, it affects the resistance to chemicals and the properties of a coating. The present inventors have found that when the hydroxyl value is 70 (KOH mg/g) or more, the durability, surface hardness of the coating and cracking resistance are improved. Whether or not a resin with 70 (KOH mg/g) or more of hydroxyl value is used in the reversible thermosensitive recording material can be checked by analyzing the quantity of remaining hydroxyl group or the quantity of ether linkage.

[0080] The property of the acrylpolyol resin is different depending on its structure. Examples of the monomer having hydroxyl group include hydroxyethylacrylate (HEA), hydroxypropylacrylate (HPA), 2-hydroxyethylmethacrylate (HEMA), 2-hydroxypropylmethacrylate (HPMA), 2-hydroxybutylmonoacrylate (2-HBA), and 1,4-hydroxybutylmonoacrylate (1-HBA). Particularly, 2-hydroxyethylmethacrylate is preferably used, in light of superior cracking resistance and du-

rability of the coating in the case of using a monomer having primary hydroxyl group.

[0081] The curing agent used in the present invention may be selected from conventional isocyanate compounds, amine compounds, phenol compounds, epoxy compounds and the like. Among these compounds, isocyanate compound is preferably used. The isocyanate compound used in this embodiment may be selected from various derivatives of isocyanate monomer such as urethane-modified, allophanate-modified, isocyanurate-modified, buret-modified, and carbodiimide-modified compounds, and blocked isocyanate compounds. Examples of the isocyanate monomer, which may yield the above-noted modified compounds, include tolylenediisocyanate (TDI), 4,4'-diphenylmethanediisocyanate (MDI), xylylenediisocyanate (XDI), naphthylenediisocyanate (NDI), paraphenylenediisocyanate (PPDI), tetramethylxylylenediisocyanate (TMXDI), hexamethylenediisocyanate (HDI), dicyclohexylmethanediisocyanate (HMDI), isophoronediiisocyanate (IPDI), lysinediiisocyanate (LDI), isopropylidenebis(4-cyclohexylisocyanate) (IPC), cyclohexyldiisocyanate (CHDI), and tolidinediiisocyanate (TODI). However, the curing agent used in the present invention is not limited to these compounds.

[0082] As the crosslinking promoter, a catalyst may be employed which is utilized in general for such reaction. Examples of the crosslinking promoter include tertiary amines such as 1,4-diaza-bicyclo(2,2,2)octane, and metal compounds such as organic tin compounds. Further, all of the introduced curing agent may not necessarily react for the crosslinking. That is, the curing agent may be remained in unreacted condition. Such crosslinking reaction may progress with time; therefore, the presence of unreacted curing agent does not indicate that the crosslinking reaction has not progress at all, nor suggests that the crosslinked resins do not exist, even if the unreacted curing agent is detected. Further, an immersion test of polymer into a solvent with a high solubility may be employed for distinguishing whether or not the polymer of the invention is in crosslinked condition. That is, the non-crosslinked polymer cannot remain in the solute since such polymer dissolves into the solvent, an analysis may be properly carried out for examining the existence of the polymer in the solute. When the polymer is not detected in the solute, the polymer is recognized to be in a non-crosslinked condition, and the polymer may be distinguished from the crosslinked polymer. In this specification, "gel fraction" is employed.

[0083] The above-noted "gel fraction" means the percentage of the gel yielded in a condition that the resin solute comes to lose the independent mobility in the solvent due to the interaction for flocking into a solidified gel. Preferably, the gel fraction of the resin is 30 % or more, more preferably 50 % or more, still more preferably 70 % or more, and 80 % or more is particularly preferred. Lower gel fraction represents lower repeating durability; therefore in order to enhance the gel fraction, a curable resin, which is curable by means of heating, exposure to UV irradiation or electron beam and the like, may be incorporated into the resin, alternatively the resin itself may be crosslinked by such means.

[0084] The gel fraction may be determined as follows: a piece of coating is peeled from the support to weigh the initial mass. Then the coating is nipped between wire nets of #400 mesh and immersed into a solvent, in which the pre-crosslinking resin being soluble, for 24 hours. The coating is dried under vacuum, then the mass after the drying is measured.

[0085] The gel fraction may be calculated by the following equation.

$$\text{Gel Fraction (\%)} = (\text{mass after drying (g)}) / \text{initial mass (g)} \times 100$$

[0086] In the calculation of the gel fraction by the equation, the mass of the organic substances, having a lower molecular mass, but of the resin ingredients in the thermosensitive layer is to be eliminated. When the mass of the organic substances having a lower molecular mass is not definite, the gel fraction may be obtained by an observation of the resin cross-section by means of TEM or SEM and by measuring the area ratio of the resin and organic substances having a lower molecular mass; and from the area ratio and the respective specific gravity, the mass of the organic substances having a lower molecular mass may be obtained.

[0087] Further, when the reversible thermosensitive recording layer is provided on the support on which the other layers such as a protective layer are laminated, or when another layer is provided between the support and the thermosensitive layer, the gel fraction may be similarly determined such that the layer thicknesses of the reversible thermosensitive recording layer and the other layer are measured through the observation using TEM or SEM, the depth corresponding to the thicknesses of the other layers are shaved off, thereby the reversible thermosensitive recording layer is exposed and peeled off, then the above-noted way may be applied similarly.

[0088] Further, when a protective layer formed of UV curable resin etc. exists on the reversible thermosensitive recording layer, the thickness equivalent to the protective layer as well as small depth of the reversible thermosensitive recording layer should be shaved so as to reduce the inclusion of the protective layer as little as possible and to prevent the influence on the obtainable gel fraction.

[0089] Examples of the leuco dyes used in the present invention are provided below. However, the leuco dyes used in the invention is not limited to these dyes. These may be used alone or in combination.
2-anilino-3-methyl-6-diethylaminofluoran,

- 2-anilino-3-methyl-6-di(n-butylamino)fluoran,
 2-anilino-3-methyl-6-(N-n-propyl-N-methylamino)fluoran,
 2-anilino-3-methyl-6-(N-isopropyl-N-methylamino)fluoran,
 2-anilino-3-methyl-6-(N-isobutyl-N-methylamino)fluoran,
 5 2-anilino-3-methyl-6-(N-n-amyl-N-methylamino)fluoran,
 2-anilino-3-methyl-6-(N-sec-butyl-N-methylamino)fluoran,
 2-anilino-3-methyl-6-(N-n-amyl-N-ethylamino)fluoran,
 2-anilino-3-methyl-6-(N-isoamyl-N-ethylamino)fluoran,
 2-anilino-3-methyl-6-(N-n-propyl-N-isopropylamino)fluoran,
 10 2-anilino-3-methyl-6-(N-cyclohexyl-N-methylamino)fluoran,
 2-anilino-3-methyl-6-(N-ethyl-p-toluidino)fluoran,
 2-anilino-3-methyl-6-(N-methyl-p-toluidino)fluoran,
 2-(m-trichloromethylanilino)-3-methyl-6-diethylaminofluoran,
 2-(m-trifluoromethylanilino)-3-methyl-6-diethylaminofluoran,
 15 2-(m-trichloromethylanilino)-3-methyl-6-(N-cyclohexyl-N-methylamino)fluoran ,
 2-(2,4-dimethylanilino)-3-methyl-6-diethylaminofluoran,
 2-(N-ethyl-p-toluidino)-3-methyl-6-(N-ethylanilino)fluoran,
 2-(N-ethyl-p-toluidino)-3-methyl-6-(N-propyl-p-toluidino)fluoran,
 2-anilino-6-(N-n-hexyl-N-ethylamino)fluoran,
 20 2-(o-chloroanilino)-6-diethylaminofluoran,
 2-(o-chloroanilino)-6-dibutylaminofluoran,
 2-(m-trifluoromethylanilino)-6-diethylaminofluoran,
 2,3-dimethyl-6-dimethylaminofluoran,
 3-methyl-6-(N-ethyl-p-toluidino)fluoran,
 25 2-chloro-6-diethylaminofluoran,
 2-bromo-6-diethylaminofluoran,
 2-chloro-6-dipropylaminofluoran,
 3-chloro-6-cyclohexylaminofluoran,
 3-bromo-6-cyclohexylaminofluoran,
 30 2-chloro-6-(N-ethyl-N-isoamylamino)fluoran,
 2-chloro-3-methyl-6-diethylaminofluoran,
 2-anilino-3-chloro-6-diethylaminofluoran,
 2-(o-chloroanilino)- 3-chloro-6-cyclohexylaminofluoran,
 2-(m-trifluoromethylanilino)-3-chloro-6-diethylaminofluoran,
 35 2-(2,3-dichloroanilino)-3-chloro-6-diethylaminofluoran,
 1,2-benzo-6-diethylaminofluoran,
 3-diethylamino-6-(m-trifluoromethylanilino)fluoran,
 3-(1-ethyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide,
 3-(1-ethyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-7-azaphthalide,
 40 3-(1-octyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide,
 3-(1-ethyl-2-methylindole-3-yl)-3-(2-methyl-4-diethylaminophenyl)-4-azaphthalide,
 3-(1-ethyl-2-methylindole-3-yl)-3-(2-methyl-4-diethylaminophenyl)-7-azaphthalide,
 3-(1-ethyl-2-methylindole-3-yl)-3-(4-diethylaminophenyl)-4-azaphthalide,
 3-(1-ethyl-2-methylindole-3-yl)-3-(4-N-n-amyl-N-methylaminophenyl)-4-azaphthalide,
 45 3-(1-methyl-2-methylindole-3-yl)-3-(2-hexyloxy-4-diethylaminophenyl)-4-azaphthalide,
 3,3-bis(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide, and
 3,3-bis(2-ethoxy-4-diethylaminophenyl)-7-azaphthalide.
- [0090]** The coloring agent used in the invention may include conventional leuco dyes other than the above-noted fluoran and azaphthalide compounds, which may be used alone or in combination. Examples of the coloring agent are shown below.
- 2-(p-acetylanilino)-6-(N-n-amyl-N-n-butylamino)fluoran,
 2-benzylamino-6-(N-ethyl-p-toluidino)fluoran,
 2-benzylamino-6-(N-methyl-2,4-dimethylanilino)fluoran,
 2-benzylamino-6-(N-ethyl-2,4-dimethylanilino)fluoran,
 55 2-dibenzylamino-6-(N-methyl-p-toluidino)fluoran,
 2-dibenzylamino-6-(N-ethyl-p-toluidino)fluoran,
 2-(di-p-methylbenzylamino)-6-(N-ethyl-p-toluidino)fluoran,
 2- (α-phenylethylamino) - 6- (N-ethyl-p -toluidino)fluoran,

2-methylamino-6-(N-methylanilino)fluoran,
 2-methylamino-6-(N-ethylanilino)fluoran,
 2-methylamino-6-(N-propylanilino)fluoran,
 2-ethylamino-6-(N-methyl-p-toluidino)fluoran,
 2-methylamino-6-(N-methyl-2,4-dimethylanilino)fluoran,
 2-ethylamino-6-(N-ethyl-2,4-dimethylanilino)fluoran,
 2-dimethylamino-6-(N-methylanilino)fluoran,
 2-dimethylamino-6-(N-ethylanilino)fluoran,
 2-diethylamino-6-(N-methyl-p-toluidino)fluoran,
 2-diethylamino-6-(N-ethyl-p-toluidino)fluoran,
 2-dipropylamino-6-(N-methylanilino)fluoran,
 2-dipropylamino-6-(N-ethylanilino)fluoran,
 2-amino-6-(N-methylanilino)fluoran,
 2-amino-6-(N-ethylanilino)fluoran,
 2-amino-6-(N-propylanilino)fluoran,
 2-amino-6-(N-methyl-p-toluidino)fluoran,
 2-amino-6-(N-ethyl-p-toluidino)fluoran,
 2-amino-6-(N-propyl-p-toluidino)fluoran,
 2-amino-6-(N-methyl-p-ethylanilino)fluoran,
 2-amino-6-(N-ethyl-p-ethylanilino)fluoran,
 2-amino-6-(N-propyl-p-ethylanilino)fluoran,
 2-amino-6-(N-methyl-2,4-dimethylanilino)fluoran,
 2-amino-6-(N-ethyl-2,4-dimethylanilino)fluoran,
 2-amino-6-(N-propyl-2,4-dimethylanilino)fluoran,
 2-amino-6-(N-methyl-p-chloroanilino)fluoran,
 2-amino-6-(N-ethyl-p-chloroanilino)fluoran,
 2-amino-6-(N-propyl-p-chloroanilino)fluoran,
 1,2-benzo-6-(N-ethyl-N-isoamylamino)fluoran,
 1,2-benzo-6-dibutylaminofluoran,
 1,2-benzo-6-(N-ethyl-N-cyclohexylamino)fluoran, and
 1,2-benzo-6-(N-ethyl-N-toluidino)fluoran may be exemplified.

[0091] For the reversible thermosensitive recording medium of the present invention, additives for the purpose of improving and controlling the coating characteristic and the color developing and erasing characteristics of a recording layer can be used, if necessary. These additives include, for example, a surfactant, a conductant agent, filler, an anti-oxidant, an optical stabilizer and a color developing stabilizer.

[0092] For the ratio of the coloring agent to the color developer, although the appropriate range is changed according to the combination of the compounds to be used, when the coloring agent is 1 according to the mole ratio, the color developer is within the range of 0.1 to 20, and preferably within the range of 0.2 to 10. Even if the color developer is lower or over this range, the density of coloring state decreases, becoming a problem. Further, it is preferable that the ratio of the erasure promoter be within the range of 0.1% by mass to 300% by mass relative to the color developer, and it is more preferable that the ratio be within the range of 3% by mass to 100% by mass. Further, the coloring agent and the color developer can be used by being internally contained in a microcapsule. Concerning the ratio of the color development element to the resin in the reversible thermosensitive recording layer, it is preferable that when the color development element is 1, that the resin be within the range of 0.1 to 10, and if the resin is contained in an amount lower than this range, the thermal strength of the reversible thermosensitive recording layer becomes insufficient, and if it is contained in excess of this range, there is the problem that the color optical density decreases.

[0093] Formation of the recording layer may use a coating solution which is prepared by evenly mixing-dispersing a mixture made of the developing agent, the coloring agent, the various additives, the curing agent, the resin in crosslinking state, and the coating solvent which are described above.

[0094] Specific examples of the solvent used for preparing the coating solution include water; alcohols such as methanol, ethanol, isopropanol, n-butanol, methyl isocarbinol; ketones such as acetone, 2-butanone, ethyl amyl ketone, diacetone alcohol, isophorone, cyclohexanone, and the like; amides such as N,N-dimethyl formamide, N,N-dimethyl acetamide, and the like; ethers such as diethyl ether, isopropyl ether, tetrahydrofuran, 1,4-dioxane, 3,4-dihydro-2H-pyran, and the like; glycol ethers such as 2-methoxy ethanol, 2-ethoxy ethanol, 2-butoxy ethanol, ethylene glycol dimethyl ether, and the like; glycol ether acetates such as 2-methoxy ethyl acetate, 2-ethoxy ethyl acetate, 2-butoxy ethyl acetate, and the like; esters such as methyl acetate, ethyl acetate, isobutyl acetate, amyl acetate, ethyl lactate, ethylene carbonate, and the like; aromatic hydrocarbons such as benzene, toluene, xylene, and the like; aliphatic hydrocarbons such as hexane, heptane, iso-octane, cyclohexane, and the like; halogenated hydrocarbons such as methylene chlo-

ride, 1,2-dichloro ethane, dichloro propane, chloro benzene, and the like; sulfoxides such as dimethyl sulfoxide, and the like; pyrrolidone such as N-methyl -2-pyrrolidone, N-octyl-2-pyrrolidone; and the like.

[0095] Preparing the coating solution can be carried out by using known coating solution-dispersing unit such as paint shaker, ball mill, attritor, three-roll mill, Keddy mill, sand mill, dynamill, colloid mill and the like. Dispersing each material in the solvent by using the above coating solution-dispersing unit is allowed, or dispersing each material alone in the solvent and mixing is also allowed. Moreover, heating-dissolving, followed by a rapid quenching or an annealing (slow cooling), and followed by depositing is allowed.

[0096] The coating method for forming the recording layer is not limited, examples thereof including those known in the art such as blade coating, wire bar coating, spray coating, air knife coating, bead coating, curtain coating, gravure coating, kiss coating, reverse roll coating, dip coating, die coating, and the like.

[0097] As a support of the reversible thermosensitive recording medium of the present invention, paper, a resin film, a PET film, synthetic paper, metal foil, glass and a complex of these can be provided, and anything is applicable if it can hold a recording layer. Further, a material with necessary thickness can be used individually or by being attached together. In other words, a support with an optional thickness of from approximately several μm to approximately several mm is used. Further, a magnetic recording layer may be provided on the same side of the support as the reversible thermosensitive recording layer and/or on the opposite side. Further, the reversible thermosensitive recording medium of the present invention can be attached to other medium via a tacky layer or the like. Alternatively, a back coat layer is provided on one surface of the support, such as a PET film; and a peel-off layer used for the thermal transfer ribbon is provided on a surface of the support opposite to the back coat layer; a thermosensitive recording layer of the present invention is provided on the peel-off layer; and a resin layer that can be transferred to a paper, a resin film or a PET film is further provided on the thermosensitive recording layer to thereby be transferred to a paper, a resin film or a PET film. The reversible thermosensitive recording medium of the present invention may be processed to be in a sheet-state or card-state, and the configuration can be processed to be an optional one, or printing processing can be applied to the medium surface. Further, the reversible thermosensitive recording medium of the present invention can simultaneously use a non-reversible thermosensitive recording layer, and the color development tone of each recording layer can be the same or different in this case.

[0098] In drying and/or curing method for the recording layer, the curing processing is performed after coating and drying, if necessary. Thermal treatment can be performed at a comparatively high temperature for a short time using a high temperature bath, or it can be performed at a comparatively low temperature for an extended time. As a specific condition for a crosslinking reaction, it is preferable to heat for 1 minute to 150 hours at a temperature of approximately 30°C to 130°C in relation to the aspect of reactivity. It is more preferable to heat for 2 minutes to 120 hours at a temperature of 40°C to 100°C . Further, since productivity is considered to be important in manufacturing, it is difficult to take time until the crosslinking is sufficiently completed. Therefore, the crosslinking process can be established separately from the drying process. As a condition for the crosslinking process, it is preferable to heat for 2 minutes to 120 hours at a temperature of 40°C to 100°C .

[0099] It is preferable that the film thickness of the reversible thermosensitive recording layer be in the range of $1\mu\text{m}$ to $20\mu\text{m}$, and it is more preferable that it be in the range of $3\mu\text{m}$ to $15\mu\text{m}$.

[0100] For the improvement of adhesiveness between the reversible thermosensitive recording layer and the protective layer, the prevention of the deterioration of the recording layer due to the coating of the protective layer, and the prevention of the additive contained in the protective layer from shifting to the recording layer or the prevention of the additive contained in the recording layer from shifting to the protective layer; an intermediate layer can be provided between both layers. It is preferable that the film thickness of the intermediate layer be in the range of $0.1\mu\text{m}$ to $20\mu\text{m}$, and it is more preferable to be in the range of $0.3\mu\text{m}$ to $10\mu\text{m}$. For a solvent used for the coating solution of the intermediate layer, a dispersing device of the coating solution, a binder, the coating method and drying and/or curing method, the well-known method, solvent and devices used for the above-mentioned recording layer can be used.

[0101] In forming the protective layer, it is preferable that the thickness of the protective layer be in the range of $0.1\mu\text{m}$ to $20\mu\text{m}$, and it is more preferable to be in the range of $0.3\mu\text{m}$ to $10\mu\text{m}$. For the solvent used for the coating solution of the protective layer, a dispersing device of the coating, a binder, a coating method and a drying and curing method, the well-known method, solvent and devices used for the above-mentioned recording layer can be used.

[0102] Other filler, which has no ultraviolet ray absorbing performance or ultraviolet ray shielding performance, can be added to the reversible thermosensitive recording layer, the intermediate layer, and the protective layer. The fillers contain inorganic fillers and organic fillers summarily. Examples of the inorganic filler include, for example, calcium carbonate, magnesium carbonate, anhydrous silicic acid, hydrous silicic acid, hydrous aluminum silicate, hydrous calcium silicate, alumina, iron oxide, calcium oxide, magnesium oxide, chromium oxide, manganese oxide, silica, talc, and mica. Examples of the organic filler include silicone resins, cellulose resins, epoxy resins, nylon resins, phenol resins, polyurethane resins, urea resins, melamine resins, polyester resins, polycarbonate resins; styrene resins such as styrene, polystyrene, polystyrene-isoprene copolymer and styrene-vinylbenzene copolymer; acryl resins such as vinylidenechloride acryl, acrylurethane and ethyleneacryl; polyethylene resins; formaldehyde resins such as benzo-

guanamineformaldehyde and melamineformaldehyde; polymethylmethacrylate resins and vinyl chloride resins. In the present invention, these fillers may be used alone or in combination. When using a plurality of fillers, there is not particular limitation on the combination way of inorganic and organic filler. The shape of the filler may be sphere, granular, platelet or needle and the like. The content of filler in the protective layer is 5% by volume to 50% by volume.

[0103] The lubricant can be added to the reversible thermosensitive recording layer, the intermediate layer, and the protective layer. Specific examples of the lubricant include synthetic wax such as ester wax, paraffin wax and polyethylene wax; vegetable wax such as hardened castor oil; animal wax such as hardened beef tallow; higher alcohol such as stearyl alcohol and behenyl alcohol; higher fatty acid such as margaric acid, lauric acid, myristic acid, palmitic acid, stearic acid, and behenolic acid; higher fatty acid ester such as fatty acid ester of sorbitan; amide such as stearic acid amide, oleic acid amide, lauric acid amide, ethylenebisstearicamide, methylenebisstearicamide, methylolstearicacidamide. Content of the lubricant in the layer is 0.1% by volume to 95% by volume, more preferably 1% by volume to 75% by volume.

[0104] The reversible thermosensitive recording medium of the present invention can form the relatively coloring state and the relatively erasing state depending on the heating temperature and/or the cooling rate after heating. The basic color developing and erasing phenomenon of the composition composed of the coloring agent and the color developer used in the present invention will be explained as follows. Fig. 1 shows the relationship between the color optical density and the temperature of the recording medium. When the recording medium is heated from the initial erasing state (A), the recording medium comes to the melted coloring state (B), through an occurrence of coloring at the temperature T_1 at which the melting starts. When cooled rapidly from the melted coloring state (B), it can be cooled to room temperature while still in the coloring state, thereby a fixed coloring state (C) is induced. Whether or not this coloring state can be obtained depends upon the cooling rate from the melted state, and the erasing appears when the temperature gradually decreases, and the initial erasing state (A) or relatively low density than rapid cooling coloring state (C) is induced. On the other hand, when heated again from the rapid cooling coloring state (C), erasing occurs at a lower temperature T_2 than the coloring temperature (D to E), and when cooled from the temperature, resulting in the initial erasing state (A). The actual coloring temperature and erasing temperature may vary with the combination of the color developer and the coloring agent to be used, so these may be selected depending on the purpose. Further, the density in the melted coloring state and the color optical density upon rapid cooling may not necessarily coincide with each other, and they are different from each other in some cases.

[0105] In the recording medium of the present invention, the coloring state (C) obtained by rapidly cooling from the melted state is a state where the color developer and the coloring agent are combined such that they may react through molecular contact, and the coloring state is often solid state. In this state, the color developer and the coloring agent are cohered to represent a color development. It is believed that the color development is stabilized due to the formation of a cohesive structure. In the meantime, in the erasing state, both are in phase separation. It is believed that the molecules of at least one of the compounds are assembled to form a domain or are crystallized, and that the cohesion or the crystallization results in the separation of the coloring agent and the color developer and they are stabilized. With the present invention, in many cases, the phase separation of the coloring agent and the color developer and also the crystallization of the color developer results in complete erasure. In erasure due to the gradual cooling from the melted state and the erasure due to the heating from the coloring state as shown in Fig. 1, the cohesive structure is changed depending on this temperature in both cases, resulting in the phase separation and/or the crystallization of the color developer.

[0106] The reversible thermosensitive recording label of the present invention is formed by providing at least on of an adhesive layer or a tacky layer on the surface of the support opposite the thermosensitive layer, the support constituting the reversible thermosensitive recording medium. This reversible thermosensitive recording label includes a label having an adhesive layer or a tacky layer (non-peel-off sheet type) and another label having a peel-off sheet under the adhesive layer or tacky layer (peel-off sheet type), and as a material of the adhesive layer, a hot melt type is normally used.

[0107] For the material of the adhesive layer or the tacky layer, use may be made of generally used materials. Example of the material include, but are not limited to, urea resins, melamine resins, phenolic resins, epoxy resins, polyvinyl acetate resins, vinyl acetate-acrylic copolymers, ethylenevinyl acetate copolymers, acrylic resins, polyvinyl ether resins, vinyl chloride-vinyl acetate copolymers, polystyrene resins, polyester resins, polyurethane resins, polyamide resins, chlorinated polyolefin resins, polyvinyl butyral resins, acrylic ester copolymers, methacrylic ester copolymers, natural rubber, cyanoacrylate resins, silicone resins.

[0108] Next, the member that has the information-memorizing part and the reversible displaying part will be explained. The reversible display part is composed of the thermosensitive layer constituting the above-mentioned reversible thermosensitive recording medium.

[0109] The member comprising the information-memorizing part and the reversible displaying part may be classified in the following three types.

(1) A part of the member comprising the information-memorizing part is utilized as a support of the reversible thermosensitive recording medium, and the thermosensitive layer is disposed on the support directly.

(2) A thermosensitive layer is disposed separately on a support to form a reversible thermosensitive recording medium, and the support is adhered to the member comprising the information-memorizing part.

(3) The above-mentioned reversible thermosensitive recording label is adhered to the member comprising the information-memorizing part with adhesive layer or tacky layer.

[0110] In these cases of (1) to (3), the position of the disposed information-memorizing part may be the surface of the support of the reversible thermosensitive recording medium opposite the thermosensitive layer, between the support and the thermosensitive layer, or on a part of the thermosensitive layer, provided that the information-memorizing part and the reversible displaying part are designed to perform their functions.

[0111] Examples of the member comprising the information-memorizing part include, but are not particularly limited to, a card, a disc, a disc cartridge and a tape cassette in general. Specifically, examples of the member include a thicker card such as IC card and optical card; disc cartridge containing an information-rewritable disc such as flexible disc, optical magnetic disc (MD) and DVD-RAM; disc in which disc cartridge is not utilized, e.g. CD-RW; overwrite type disc such as CD-R; optical information recording medium with phase-changing recording material (CD-RW); and video cassette. Further, the member comprising the information-memorizing part and the reversible displaying part may exhibit remarkably increased availability as compared with the card without utilizing the reversible thermosensitive recording medium. That is, in case of card for example, the owner of the card can confirm the information only by viewing the card without a particular device through displaying on the thermosensitive layer a part of the information memorized in the information-memorizing part.

[0112] The information-memorizing part may be properly selected depending on the application without particular limitations, provided that the necessary information may be recorded, for example, a magnetic recording, contact type IC, non-contact type IC, and optical memory are exemplified. The magnetic recording layer may be formed by coating on a support a coating material comprising ordinary metallic compounds used in the art such as iron oxide, barium ferrite etc. and vinylchloride resins, urethane resins, nylon resins etc., otherwise by vapor deposition, sputtering etc. using the metallic compounds without using resins. Further, the thermosensitive recording layer of the reversible thermosensitive recording medium for displaying may be employed for the memorizing part in a form of barcode, two dimensional code and the like.

[0113] As an example of using the reversible thermosensitive recording label in the above-mentioned (3), in the case of a thicker support having attendant difficulties in coating the surface with the reversible thermosensitive recording layer, such as a vinyl chloride card with magnetic stripe; an adhesive layer or a tacky layer can be provided on the surface entirely or partially. This enables improving the convenience of this medium, such as the display of the partial information stored in the magnetism.

[0114] This reversible thermosensitive recording label on which the adhesive layer or the tacky layer is provided can be applied not only to the above-mentioned vinyl chloride card with magnetic stripe but also to a thicker card, such as an IC card or optical card.

[0115] The reversible thermosensitive recording label may be an alternative to a displaying label on a disc cartridge containing information-rewritable disc such as flexible disc, MD and DVD-RAM. FIG. 2 exemplifies the reversible thermosensitive recording label affixed to MD disc cartridge. Further, in a case of disc without disc cartridge such as CD-RW, the reversible thermosensitive recording label may be directly affixed to the disc, or the reversible thermosensitive recording layer may be directly disposed on the disc. In this case, such application is allowable that the displayed content is automatically altered depending the alternation of the memorized content.

[0116] FIG. 3 exemplifies the reversible thermosensitive recording label affixed to CD-RW.

[0117] In the reversible thermosensitive recording label of the invention, the recording label is affixed on a write-once disc such as CD-R, then a part of the memorized information in the CD-R may be rewritten and displayed.

[0118] Further, the recording label of the present invention may be used for a display label of a video cassette, as shown in Fig. 4.

[0119] As a method to provide a thermal reversible recording function on a thicker card, a disc cartridge or a disc, other than the above-mentioned method to attach the reversible thermosensitive recording label, a method to directly coat these discs with the reversible thermosensitive recording layer and another method in which the reversible thermosensitive recording layer is formed on a separate support in advance and the thermosensitive recording layer is transferred onto a thicker card, a disc cartridge or a disc are available.

[0120] In the case of transferring, an adhesive layer or a tacky layer, such as a hot melt type, can be provided on the reversible thermosensitive recording layer.

[0121] In the case of attaching the reversible thermosensitive recording label or providing the reversible thermosensitive recording layer on an inflexible material, such as a thicker card, a disc, a disc cartridge or a tape cassette, it is preferable to provide an elastic layer or sheet to be a cushion between the inflexible support and label or the reversible

thermosensitive recording layer to improve the contact-ability with a thermal head and to uniformly form an image.

[0122] The present invention further provides an image processing method characterized by forming and/or erasing an image due to heating using at least one of the above-mentioned reversible thermosensitive recording medium, the above-mentioned member having the information-memorizing part and the above-mentioned label, and also provides an image processing apparatus characterized by having at least one of the above-mentioned reversible thermosensitive recording medium, the above-mentioned member having the information-memorizing part and the above-mentioned label, and by forming and/or erasing an image due to heating.

[0123] For image forming, the image recording unit which is capable of partially heating the medium, such as thermal head, laser irradiation apparatus and the like may be used. For the image erasing, the image erasing unit may be selected from a hot stamp, ceramic heater, heat roller, hot blow, thermal head, laser irradiation apparatus and the like. Among these, the ceramic heater is preferred. By means of the ceramic heater, the apparatus may be miniaturized, the erasing state may be stabilized, and images with high contrast may be obtained. The operating temperature of the ceramic heater is preferably 100 °C or more, more preferably 110 °C or more, most preferably 115 °C or more, for example.

[0124] By means of the thermal head, the apparatus may be miniaturized still, in addition, the electric power consumption may be saved, and the power supply may be replaced to a battery-operated handy type. Further, the performance of image forming and erasing may be combined into one thermal head, thereby the apparatus may be miniaturized still more. In the case that the recording and erasing are achieved with one thermal head, once the prior images are erased entirely, then new images may be recorded; alternatively an overwrite type may be provided in which the individual image is erased all at once at variable energy level and new images are recorded. In the overwrite type, the total period for recording and erasing is relatively short, resulting in the speed-up of the recording.

[0125] In the case that the reversible thermosensitive recording card with the reversible thermosensitive layer and information-memorizing part is utilized, the reading unit and rewriting unit for the memories in the information-memorizing part are included in the above-noted apparatus.

[0126] FIG. 5 exemplifies an image-processing apparatus according to the present invention. FIG. 5 schematically shows an example in the case of erasing the image by means of the ceramic heater and forming the image by means of thermal head.

[0127] In the image processing apparatus shown in FIG. 5, the information memorized in the magnetic recording layer of the recording medium is read by means of the magnetic head initially. Then, heating by means of the ceramic heater erases the images recorded in the reversible thermosensitive layer. Further, the new information processed based on the information read by the magnetic head is recorded in the reversible thermosensitive layer by means of the thermal head. Thereafter, the information in the magnetic recording layer is replaced to the new information.

[0128] In the image processing apparatus shown in FIG. 5, the reversible thermosensitive recording medium, the magnetic recording layer being provided on the opposite side of the thermosensitive layer, is conveyed along the conveying root shown by back-forth arrows or conveyed in the reverse direction along the conveying root in the image processing apparatus.

[0129] The reversible thermosensitive recording medium is subjected to magnetic recording or erasing in the magnetic recording layer between the magnetic head 34 and the conveying roller 40, and subjected to a heat treatment for erasing images between the ceramic heater 38 and the conveying roller 40, and then images are formed between the thermal head 53 and conveying roller 47, thereafter discharged out of the apparatus. By the way, the rewriting of the magnetic recording may be before or after the image erasing by means of the ceramic heater. In addition, the recording medium is conveyed reversibly after passing between the ceramic heater 38 and conveying roller 40, or after passing between the thermal head 53 and conveying roller 47, if necessary. The duplicated heat treatment by means of ceramic heater 38, and the duplicated printing by means of thermal head 53 may be applied in some instances.

Example

[0130] The invention will be described in more detail below with reference to examples. Wherever "parts" or "%" are mentioned in the following examples, they are based on mass.

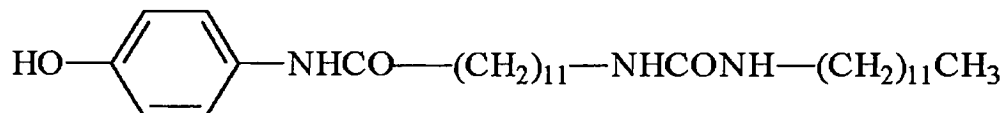
(Example 1)

<Formation of Reversible Thermosensitive Recording Layer>

[0131]

2-anilino-3-methyl-6-dibutyl amino fluoran 2 parts

Color developer represented by the following structure 8 parts



Vinylchloride-vinylacetate copolymer (branded as VYHH

manufactured by UNION CARBIDE CORPORATION) 20 parts

N, N'-dioctadecyl urea 0.4 parts

Methyl ethyl ketone 90 parts

[0132] The above compositions were pulverized and dispersed by means of a ball mill into particles having an average particle diameter of 0.1 μm to 3 μm . The coating solution for the reversible thermosensitive recording layer is prepared with the dispersing solution thus obtained.

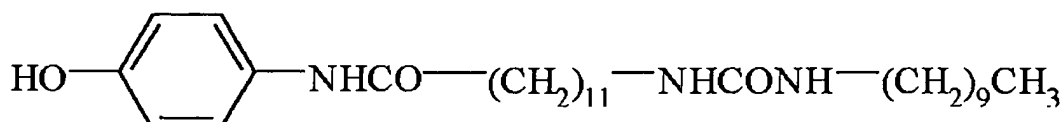
[0133] The coating solution for the recording layer with the above-mentioned composition was coated onto a white PET film with a magnetic layer with approximately 250 μm of thickness (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED) using a wire bar, and after drying the white PET film at 115°C for 1 minute, it was heated at 60°C for 36 hours, and the reversible thermosensitive recording layer with approximately 11.0 μm of film thickness was formed. The gel fraction of the resin of the thermosensitive recording layer was approximately 92%.

(Example 2)

[0134]

3-(4-dimethylamino-2-ethoxy phenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide 2 parts

Color developer represented by the following structure 8 parts



Methyl ethyl ketone (MEK) 15% solution of acrylic polyol resin

150 parts

(Hydroxyl value: 133, Acid value: 6.5, Molecular mass: 7000, Glass

transition temperature: 34 °C)

[0135] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except that the above-mentioned dispersing solution for the reversible thermosensitive recording layer was used instead of the dispersing solution which was used in Example 1. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

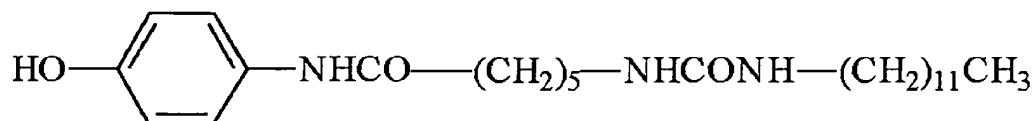
(Example 3)

[0136]

2-anilino-3-methyl-6-diethyl amino fluoran

2 parts

Color developer represented by the following structure 8 parts



THF 15% solution of acrylic polyol resin 150 parts

(Hydroxyl value: 70, Acid value: less than 1.0, Molecular mass:

35,000, Glass transition temperature: 52 °C, Monomer having hydroxyl

group: 2-hydroxyethylmethacrylate)

CORONATE HL

10 parts

[0137] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except that the above-mentioned dispersing solution for the reversible thermosensitive recording layer was used instead of the dispersing solution which was used in Example 1. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

(Example 4)

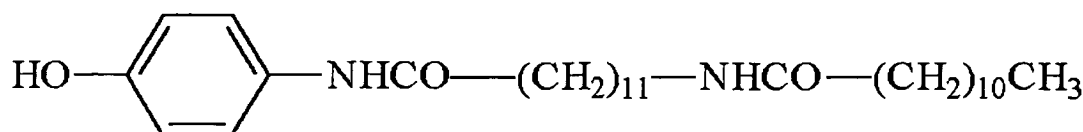
[0138]

3-(4-diethylamino-2-ethoxy phenyl)-3-(1-ethyl-2-methylindole-3-yl)-

4-azaphthalide

2 parts

Color developer represented by the following structure 8 parts

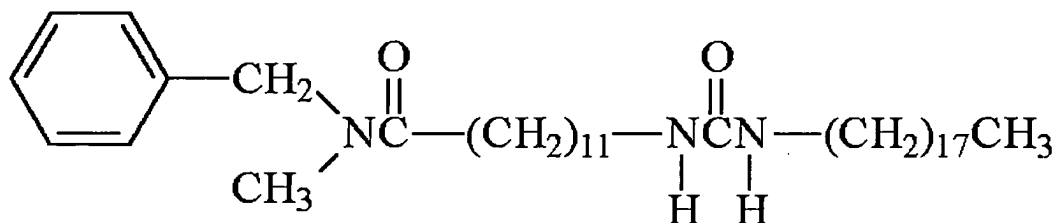


THF 15% solution of polyester resin 150 parts

(Hydroxyl value: 166, Acid value: 2.2)

CORONATE HL 10 parts

Erasure promoter represented by the following structure 8 parts



[0139] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except that the above-mentioned dispersing solution for the reversible thermosensitive recording layer was used instead of the dispersing solution which was used in Example 1. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

[0140] Further, the following coating solution for the protective layer was coated on the reversible thermosensitive recording layer by means of a wire bar, and then passed with conveying velocity of 12 m/minute under the ultraviolet ray lamp of irradiation energy 80 W/cm to cure the coating, thereby a protective layer about 3 μ m thick was provided. Thus the reversible thermosensitive recording medium of the present invention was prepared.

<Preparation of coating solution for protective layer>

[0141]

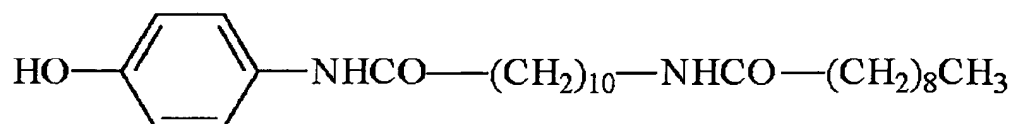
Urethane acrylate ultraviolet setting resin (branded as C7-157 manufactured by Dainippon Ink and Chemicals Incorporated)	10 parts
Silica (branded as P527 manufactured by MIZUSAWA INDUSTRIAL CHEMICALS, LTD.)	1.5 parts
Ethyl acetate	90 parts

(Example 5)

[0142]

2-anilino-3-methyl-6-diethyl amino fluoran 2 parts

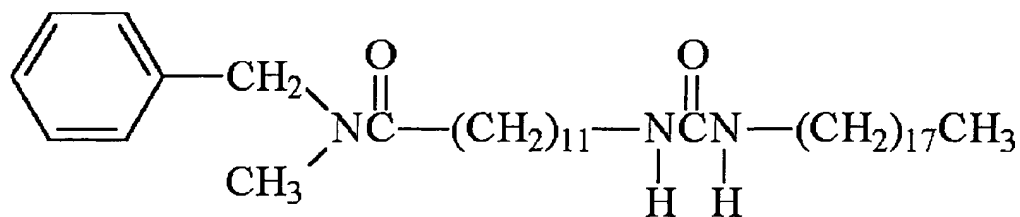
Color developer represented by the following structure 8 parts



Poly-n-butylmethacrylate resin (branded as BR102 manufactured
by MITSUBISHI RAYON CO., LTD.) 150 parts

CORONATE HL 10 parts

Erasure promoter represented by the following structure 8 parts



[0143] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except that the above-mentioned dispersing solution for the reversible thermosensitive recording layer was used instead of the dispersing solution which was used in Example 1. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%. Further, the protective layer was provided in the same manner with Example 4.

(Example 6)

[0144]

Methyl ethyl ketone (MEK) 15% solution of acrylic polyol resin (Hydroxyl value: 108, Acid value: less than 1.0, Molecular mass: 107,800, Glass transition temperature: 80 °C, Monomer having hydroxyl group: 2-hydroxyethylmethacrylate)	150 parts
CORONATE HL	10 parts

[0145] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except the above. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

[0146] Further, the following coating solution for the intermediate layer was coated on the recording layer by means of a wire bar, dried at 90 °C for 1 minute, followed by heating at 60 °C for 1 hour, thereby an intermediate layer with about 2 μm thick was provided.

< Preparation of coating solution for intermediate layer >

[0147]

Methyl ethyl ketone (MEK) 10% solution of polyesterpolyol resin (branded as Takelac U-21 manufactured by TAKEDA CHEMICAL INDUSTRIES LTD.)	100 parts
Zinc oxide (manufactured by SUMITOMO-OSAKA CEMENT K.K.)	10 parts
CORONATE HL	15 parts

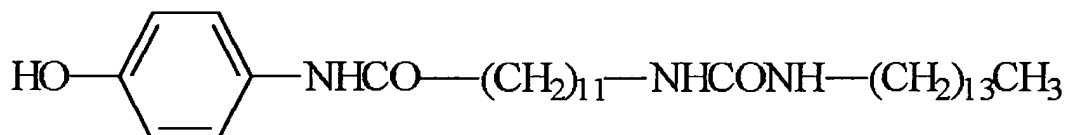
Further, the protective layer was provided on the intermediate layer in the same manner with Example 4.

(Example 7)

[0148]

2-anilino-3-methyl-6-diethyl amino fluoran 2 parts

Color developer represented by the following structure 8 parts



Methyl ethyl ketone (MEK) 15% solution of acrylic polyol resin

150 parts

(Hydroxyl value: 100, Acid value: less than 1.0, Molecular mass:

107,800, Glass transition temperature: 80 °C, Monomer having hydroxyl

group: 2-hydroxyethylmethacrylate)

CORONATE HL

25 parts

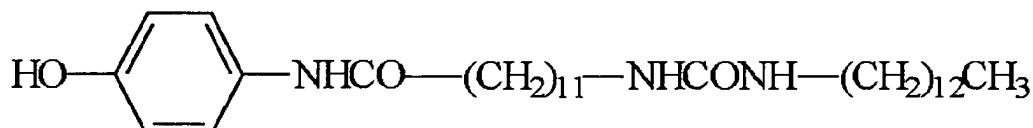
[0149] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except the above. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

(Example 8)

[0150]

3-(4-dimethylamino-2-ethoxy phenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide 2 parts

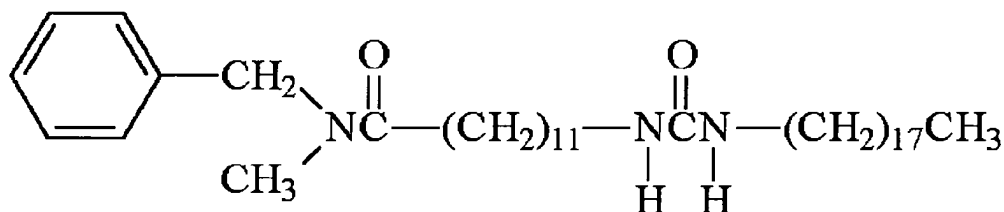
Color developer represented by the following structure 10 parts



Poly-n-butylmethacrylate resin (branded as BR102 manufactured by MITSUBISHI RAYON CO., LTD.) 150 parts

CORONATE HL 10 parts

Erasure promoter represented by the following structure 8 parts



[0151] The reversible thermosensitive recording layer was formed in the same manner with Example 1, except the above. The gel fraction of the resin of the thermosensitive recording layer was approximately 89%.

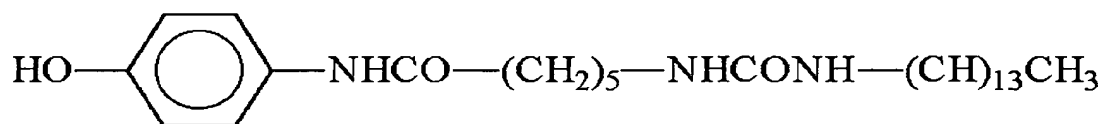
[0152] Further, the intermediate layer and the protective layer were provided in the same manner with Example 6.

(Example 9)

[0153] With the use of the reversible thermosensitive recording layer of Example 7, the intermediate layer and the protective layer were provided on the recording layer in the same manner with Example 6.

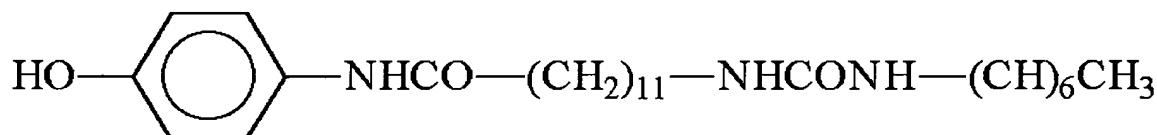
(Example 10)

[0154] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except that 8 parts of the color developer represented by the following structure was used.



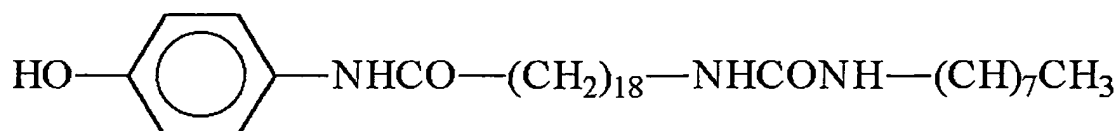
(Example 11)

[0155] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except that 8 parts of the color developer represented by the following structure was used.



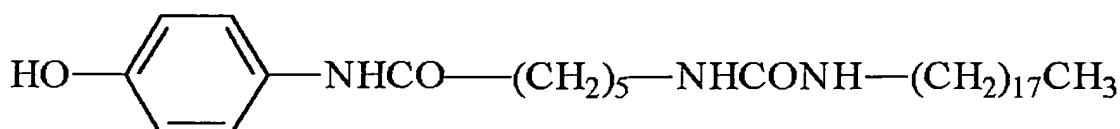
(Example 12)

[0156] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except that 8 parts of the color developer represented by the following structure was used.



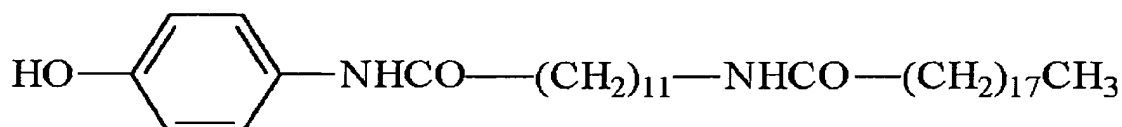
(Comparative Example 1)

[0157] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except that 8 parts of the color developer represented by the following structure was used.



(Comparative Example 2)

[0158] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except that 8 parts of the color developer represented by the following structure was used.

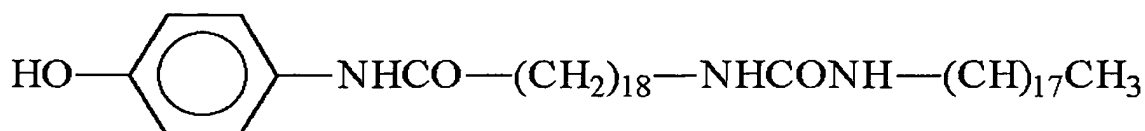


(Comparative Example 3)

[0159] The reversible thermosensitive recording medium was formed in the same manner with Example 1, except

that 8 parts of the color developer represented by the following structure was used.

[0160] Each gel fraction of the resins of the thermosensitive recording layers of the comparative examples 1 to 3 was 80% or more.



[0161] Printing was performed on the recording medium produced as mentioned above by a thermal head with 8 dots/mm at 13.3 V of voltage and at 1.2 msec of pulse width using a thermosensitive printer manufactured by Okura Electric Co., Ltd. Erasure was performed under the condition at 110 °C for 1 second using a heat gradient tester manufactured by Toyo Seiki Seisaku-Sho, Ltd. Then, the optical density at this printed portion, the erased portion and a background portion was measured using Macbeth densitometer RD-914. Printing and erasure were performed into/ from this recording medium in an environment at normal temperature and normal humidity (22°C, 60% RH) and at high temperature and high humidity (35°C, 85% RH).

[0162] Further, the above-mentioned printing and erasure were repeated 50 times in an environment at normal temperature and normal humidity, and the state of the image density and the state of recording medium surface were visually observed and evaluated according to the following ranks:

Rank 1: The image portion was in the excellent coloring state, and no dent was also observed.

Rank 2: There was no change in the image portion

Rank 3: The color development at the image portion was uneven, and dent also occurred.

Rank 4: The coloring state at the image portion was extremely poor, and dent drastically occurred.

[0163] The results are shown in Table 15.

Table 15

	Normal temperature and Normal humidity			High Temperature and High Humidity		Durability
	Color Optical Density	Erasing Optical Density	Density of Background portion	Color Optical Density	Erasing Optical Density	
Example 1	1.08	0.14	0.11	1.09	0.13	Rank 1
Example 2	0.88	0.14	0.12	0.89	0.14	Rank 1
Example 3	0.96	0.14	0.11	0.93	0.14	Rank 1
Example 4	1.07	0.13	0.11	1.08	0.13	Rank 1
Example 5	1.09	0.14	0.11	1.10	0.13	Rank 1
Example 6	1.04	0.13	0.11	1.06	0.13	Rank 1
Example 7	1.09	0.13	0.12	1.08	0.12	Rank 1
Example 8	1.07	0.12	0.11	1.06	0.12	Rank 1
Example 9	1.08	0.12	0.11	1.08	0.12	Rank 1
Example 10	0.95	0.32	0.12	0.82	0.37	Rank 1
Example 11	0.86	0.26	0.11	0.79	0.23	Rank 1
Example 12	1.02	0.22	0.11	0.89	0.25	Rank 1
Compara. Ex. 1	0.93	0.04	0.11	0.41	0.16	Rank 2
Compara. Ex. 2	0.85	0.14	0.11	0.53	0.16	Rank 2
Compara. Ex. 3	0.92	0.14	0.11	0.50	0.11	Rank 2

[0164] Concerning Examples 1 to 12, humidity does not affect printing and erasure under all environmental conditions, and the color optical density and the erasing optical density are stable. Further, concerning the durability test, the diminishment of the printing density and the rise of erasing optical density were hardly observed, and it was in the excellent condition without dent.

(Example 13)

<Formation of Reversible Thermosensitive Recording Layer>

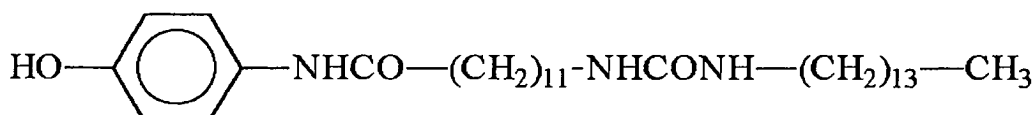
[0165] The following compositions were pulverized and dispersed by means of a ball mill into particles having an average particle diameter of about 1 μm to 4 μm.

[Solution A]

[0166]

2-anilino-3-methyl-6-dibutyl amino fluoran 2 parts

Color developer represented by the following structure 8 parts



Color developing and erasing controlling agent represented by the following structure 2 parts



Methyl ethyl ketone (MEK) 15% solution of acrylic polyol resin

(Hydroxyl value: 133, Acid value: 6.5, Molecular mass: 7,000, Glass transition temperature: 34 °C) 150 parts

[0167] To the dispersing solution thus obtained, 10 parts of adduct-type hexamethylenediisocyanate 75 % solution in ethyl acetate (COLONATE HL, by NIPPON URETHANE K.K.) was added and stirred well to prepare a coating liquid for recording layer. Then the resulting coating solution for recording layer with the above-mentioned composition was coated on a white PET film (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED) with a magnetic layer with about 250 μm thick by means of a wire bar, dried at 115 °C for 1 minute, followed by heating at 60 °C for 36 hours, thereby a reversible thermosensitive recording layer about 11.0 μm thick was provided. The gel fraction of the resin of the thermosensitive recording layer was approximately 90%.

[0168] The coating solution for the intermediate layer with the following composition was coated on the resulting recording layer by means of a wire bar, was dried at 90 °C for 1 minute, followed by heating at 60 °C for 2 hours, thereby a recording layer about 2 μm thick was provided. Further, the coating solution for protective layer with the following composition was coated on the intermediate layer by means of a wire bar, was passed with conveying velocity of 12 m/minute under the UV ray lamp of irradiation energy 80 W/cm to cure the coating, thereby a protective layer about 3 μm thick was provided, and thus the reversible thermosensitive recording medium of the present invention was prepared.

Coating solution for intermediate layer

[0169]

Methyl ethyl ketone (MEK) 10% solution of polyesterpolyol resin (branded as Takelac U-21 manufactured by TAKEDA CHEMICAL INDUSTRIES LTD.)	100 parts
Zinc oxide (manufactured by SUMITOMO-OSAKA CEMENT K.K.)	10 parts
CORONATE HL	15 parts

Coating solution for the protective layer

[0170]

Urethane acrylate ultraviolet setting resin	10 parts
Silica (branded as P527 manufactured by MIZUSAWA INDUSTRIAL CHEMICALS, LTD.)	1.5 parts
Ethyl acetate	90 parts

(Examples 14 to 25)

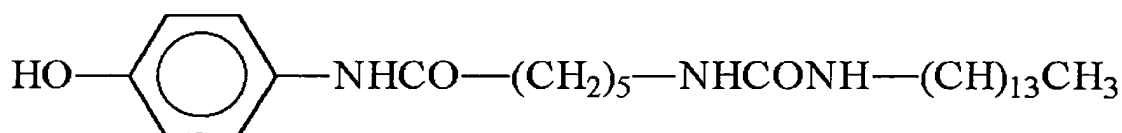
[0171] The reversible thermosensitive recording media were prepared in the same manner with Example 13, except of using the erase promoter compounds with the structure shown in Table 16.

Table 16

	Erase Promoter
Ex. 14	$C_{15}H_{31}CONHC_{16}H_{33}$
Ex. 15	$C_{11}H_{23}CONHCH_2HNOCC_{11}H_{23}$
Ex. 16	$(CH_3)_2CHC_{14}H_{35}CONHC_2H_4HNOCC_{14}H_{35}(CH_3)_2$
Ex. 17	$C_{17}H_{35}CONHC_2H_4HNOCC_{17}H_{35}$
Ex. 18	$C_{17}H_{33}CONHCH_2HNOCC_{17}H_{33}$
Ex. 19	$C_{18}H_{37}NHCOOC_2H_4CONHC_{18}H_{37}$
Ex. 20	$C_{18}H_{37}OCONHC_{18}H_{37}$
Ex. 21	$C_{22}H_{45}OCONHC_{18}H_{37}$
Ex. 22	$C_{18}H_{37}NHCOOC_6H_4OCONHC_{18}H_{37}$
Ex. 23	$C_{18}H_{37}NHCOOC_2H_4OC_2H_4OCONHC_{18}H_{37}$
Ex. 24	$C_{18}H_{37}OCOHNHC_6H_4NHCOOC_{18}H_{37}$
Ex. 26	$\begin{array}{c} CH_2-OCONHC_{18}H_{37} \\ \\ CH-OCONHC_{18}H_{37} \\ \\ C_4H_8-OCONHC_{18}H_{37} \end{array}$

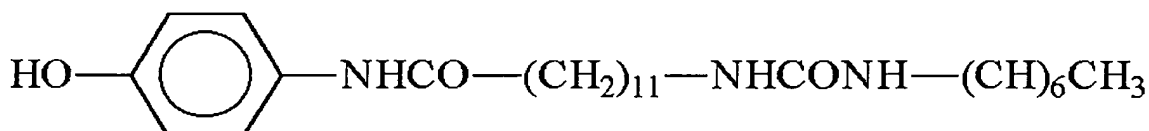
(Example 26)

[0172] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



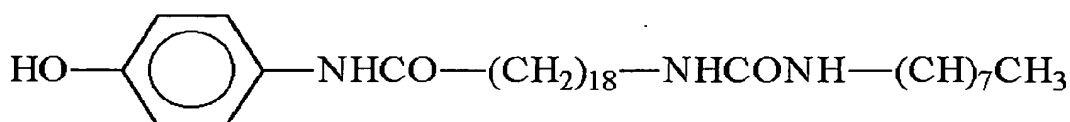
(Example 27)

[0173] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



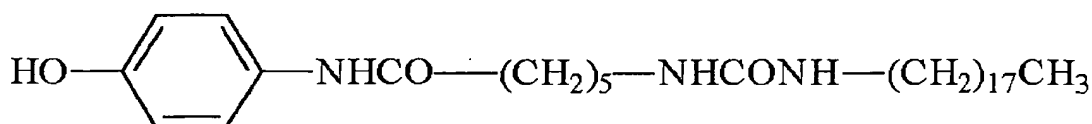
(Example 28)

[0174] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



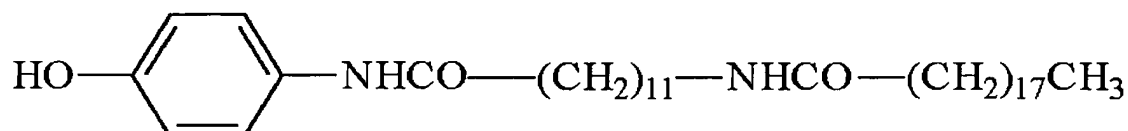
(Comparative Example 4)

[0175] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



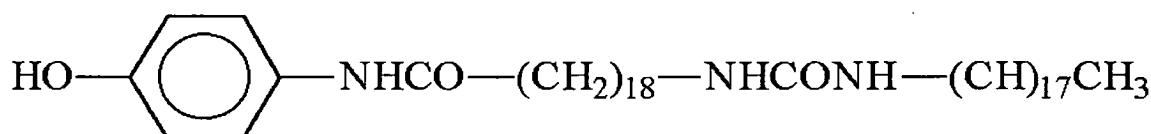
(Comparative Example 5)

[0176] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



(Comparative Example 6)

[0177] The reversible thermosensitive recording medium was prepared in the same manner with Example 13, except of using 8 parts of the color developer represented by the following structure.



[0178] Printing and erasure were performed into/from the recording medium produced as mentioned above at the following evaluation condition using by a thermosensitive printing simulator manufactured by Yashiro Ltd. with an edge type thermal head EUX-ET8A9AS1 (resistance value: 1152 ohm) manufactured by Matsushita Electronic Components Co., Ltd. Then, the optical density at the printed portion, the erased portion and the background portion were measured using Macbeth densitometer RD-914.

[0179] "The density of the erasing remainder" = "the density at the erased portion" - "the density at the background portion" Evaluation Condition: 2 msec of pulse width, 2.86 msec of line cycle, 43.10 mm/sec of printing speed, 8 dots/mm of sub-scanline density

[0180] Printing and erasure were performed into/from this recording medium in an environment at normal temperature and normal humidity (22°C, 60% RH) and at high temperature and high humidity (35°C, 85% RH).

[0181] Further, the above-mentioned printing and erasure were repeated 10 times in an environment at normal temperature and normal humidity, and the state of the image density and the state of recording medium surface were visually observed and evaluated according to the following ranks:

Rank 1: The image portion was in the excellent coloring state, and no dent was also observed.

Rank 2: There was no change in the image portion

Rank 3: The color development at the image portion was uneven, and dent also occurred.

Rank 4: The coloring state at the image portion was extremely poor, and dent drastically occurred.

[0182] The results are shown in Table 17.

Table 17

	Normal Temperature and Normal Humidity			High Temperature and High Humidity		Durability
	Color Optical Density	Erasing Optical Density	Density of Background portion	Color Optical Density	Erasing Optical Density	
Example 13	1.07	0.14	0.11	1.05	0.14	Rank 1
Example 14	1.06	0.14	0.12	1.06	0.15	Rank 1
Example 15	1.18	0.13	0.11	1.15	0.13	Rank 1
Example 16	1.21	0.17	0.12	1.20	0.17	Rank 1
Example 17	1.15	0.16	0.11	1.11	0.15	Rank 1
Example 18	1.18	0.13	0.11	1.18	0.14	Rank 1
Example 19	1.10	0.16	0.12	1.09	0.16	Rank 1
Example 20	1.05	0.16	0.11	1.03	0.15	Rank 1
Example 21	1.00	0.18	0.12	0.98	0.19	Rank 1
Example 22	1.05	0.16	0.11	1.00	0.17	Rank 1
Example 23	1.10	0.12	0.10	1.11	0.13	Rank 1
Example 24	1.09	0.14	0.11	1.02	0.15	Rank 1
Example 25	1.02	0.13	0.11	1.00	0.13	Rank 1

Table 17 (continued)

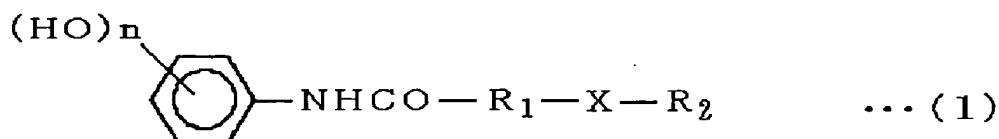
	Normal Temperature and Normal Humidity			High Temperature and High Humidity		Durability
	Color Optical Density	Erasing Optical Density	Density of Background portion	Color Optical Density	Erasing Optical Density	
Example 26	1.05	0.29	0.10	0.92	0.31	Rank 1
Example 27	0.95	0.27	0.11	0.89	0.30	Rank 1
Example 28	1.08	0.27	0.10	1.00	0.29	Rank 1
Compara. Ex. 4	1.06	0.15	0.11	0.51	0.14	Rank 2
Compara. Ex. 5	1.00	0.17	0.11	0.60	0.15	Rank 2
Compara. Ex. 6	1.02	0.17	0.11	0.61	0.15	Rank 2

Industrial Applicability

[0183] As evident from the detailed concrete descriptions given above, the present invention can provide a reversible thermosensitive recording medium in which humidity does not affect color optical density and erasing optical density; high contrast is excellent; the occurrence of dents to the recording medium and the density change due to the repetitive use are less; durability is excellent. Further, the invention can provide a reversible thermosensitive recording medium, wherein it is possible to perform erasure by a thermal head; and high speed erasure is excellent.

Claims

1. A reversible thermosensitive recording medium comprising a reversible thermosensitive recording layer which comprises a reversible thermosensitive composition on a support,
 - wherein the reversible thermosensitive composition comprises a an electron-donating coloring compound and an electron-accepting compound and is capable of forming a relatively coloring state depending on the difference of heating temperatures and/or the difference of cooling rates after heating, and
 - wherein the electron-accepting compound is a phenol compound expressed by the general formula (1) below, and when the reversible thermosensitive recording medium is printed in an environment of $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at relative humidity from 70% to 90%, a color optical density is 0.80 or more and an erasing optical density is 0.15 or less;

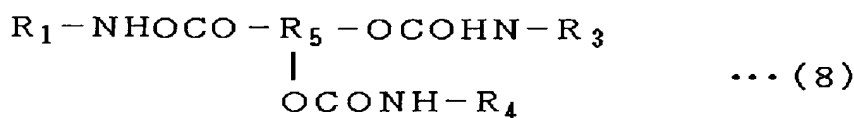


where, in the formula (1), 'n' represents an integer of 1 to 3 and 'X' represents a divalent group containing either N atoms or O atoms, 'R₁' represents an aliphatic hydrocarbon group having 2 or more carbon atoms, which may have a substituents, and 'R₂' represents an aliphatic hydrocarbon group having 1 to 14 carbon atoms.

2. The reversible thermosensitive recording medium according to claim 1, wherein 'R₁' is an aliphatic hydrocarbon group having 10 to 16 carbon atoms and 'R₂' is an aliphatic hydrocarbon group having 8 to 14 carbon atoms in the general formula (1).
3. The reversible thermosensitive recording medium according to claim 1 or 2, wherein 'X' in the general formula (1) is a urea group.
4. The reversible thermosensitive recording medium according to any one of claims 1 to 3, wherein the reversible

thermosensitive recording layer contains a resin being in the cross-linking state.

- 5 5. The reversible thermosensitive recording medium according to claim 4, wherein the resin contained in the reversible thermosensitive recording layer has 70 (KOHmg/g) or more of hydroxyl value.
6. The reversible thermosensitive recording medium according to any one of claims 4 and 5, wherein the resin contained in the reversible thermosensitive recording layer is acrylic polyol resin.
- 10 7. The reversible thermosensitive recording medium according to any one of claims 1 to 3, wherein a gel fraction of the resin is 30 % or more.
8. The reversible thermosensitive recording medium according to any one of claims 1 to 7, wherein a compound having a secondary amide group is comprised as an erasure promoter.
- 15 9. The reversible thermosensitive recording medium according to any one of claims 1 to 7, wherein another erasure promoter having at least one of -NHCO- group and -OCONH- group in a molecule is additionally comprised.
- 20 10. The reversible thermosensitive recording medium according to claim 9, wherein the erasure promoter containing at least one of -NHCO-group and -OCONH- group in a molecule is any one of the compounds expressed by general formulae (2) to (8);



where, in the formulae, R_1 , R_2 , and R_4 represent linear alkyl group, branched alkyl group or unsaturated alkyl group having 7 to 22 carbon atoms, R_3 represents a divalent functional group having 1 to 10 carbon atoms and R_5 represents a trivalent functional group having 4 to 10 carbon atoms.

11. The reversible thermosensitive recording medium according to any one of claims 1 to 10, wherein a protective layer for protecting the thermosensitive recording layer is provided on the reversible thermosensitive recording layer, and the protective layer comprises a resin in the cross-linking state.
12. A member comprising:

an information-memorizing part; and

a reversible displaying part,

wherein the reversible displaying part comprises the reversible thermosensitive recording medium according to any one of claims 1 to 11.

13. The member according to claim 12, wherein the member comprising the information-memorizing part and the reversible displaying part is any one of a card, a disc, a disc cartridge and a tape cassette.

14. A reversible thermosensitive recording label, comprising:

the reversible thermosensitive recording medium according to any one of claims 1 to 11; and
at least one of an adhesive layer and a tacky layer, which is provided on a surface of the support opposite the reversible thermosensitive recording layer.

15. The member according to any one of claims 12 and 13, wherein the reversible thermosensitive recording label according to claim 14 is used for the reversible displaying part.

16. An image processing method, comprising

forming and/or erasing an image on/from a reversible thermosensitive recording layer by heating the reversible thermosensitive recording layer,
wherein the reversible thermosensitive recording layer is at least one of the reversible thermosensitive recording layers of the reversible thermosensitive recording medium according to any of claims 1 to 11, the reversible thermosensitive recording label according to claim 14, and the member according to any of claims 12, 13 and 15.

17. The image processing method according to claim 16, wherein the image is formed on the reversible thermosensitive recording layer using a thermal head.

18. The image processing method according to claim 16, wherein the image is erased using a thermal head or a ceramic heater.

19. An image processing apparatus, comprising

an image forming and/or erasing unit configured to form and/or erase an image on/from a reversible thermosensitive recording layer,
wherein the reversible thermosensitive recording layer is at least one of the reversible thermosensitive layers of the reversible thermosensitive recording medium according to any of claims 1 to 11, the reversible thermosensitive recording label according to claim 14, and the member according to any of claims 12, 13 and 15.

20. The image processing apparatus according to claim 19, wherein the image forming unit is a thermal head.

21. The image processing apparatus according to claim 19, wherein the image erasing unit is at least one of a thermal head and a ceramic heater.

FIG. 1

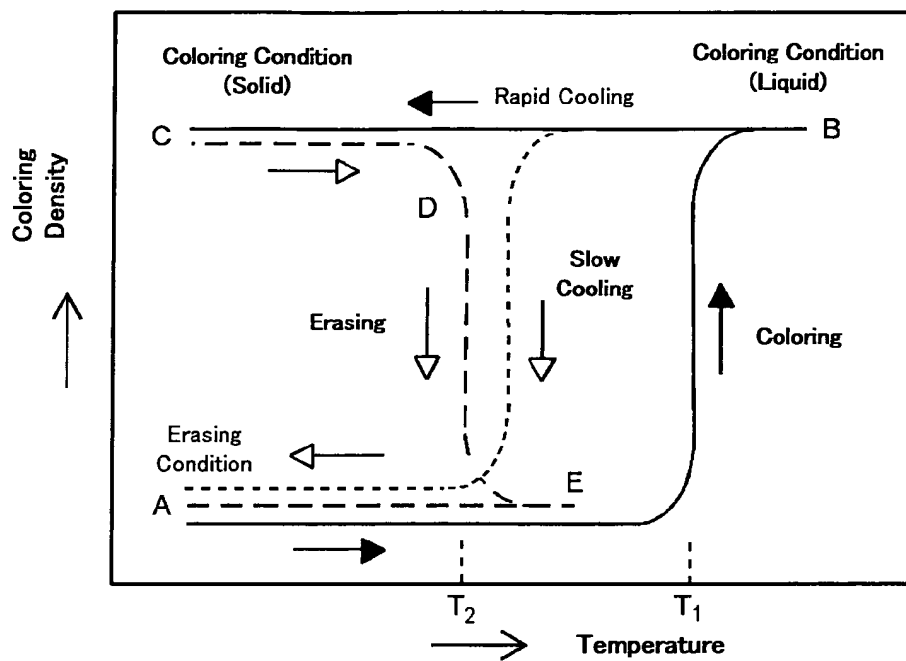


FIG. 2

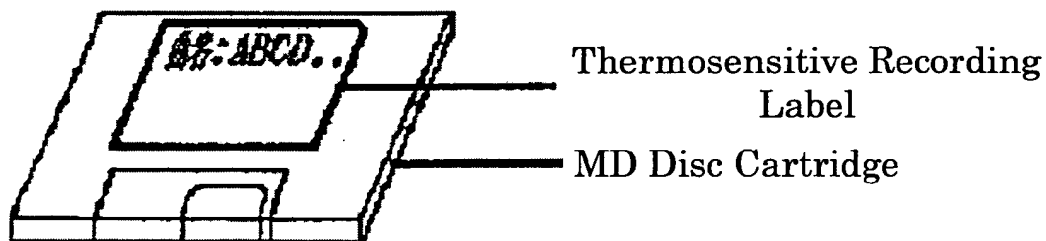


FIG. 3

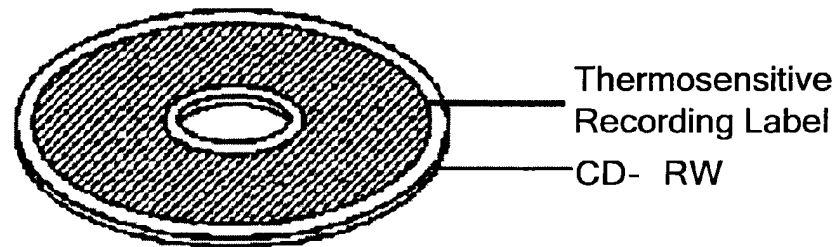


FIG. 4

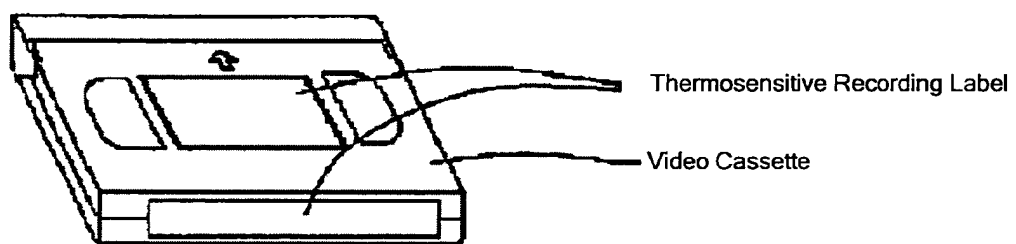
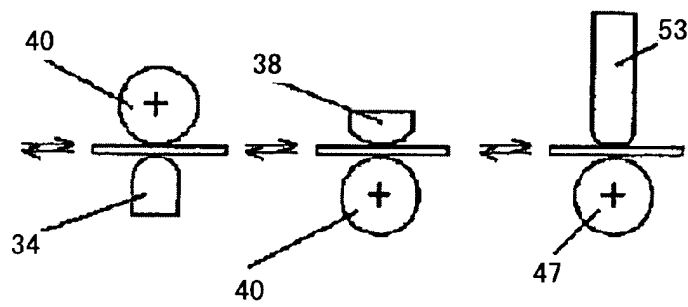


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/13636

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ B41M5/30, B41J2/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.⁷ B41M5/28-5/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003
Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6090192 A (Ricoh Co., Ltd.), 18 July, 2000 (18.17.00), Full text & JP 10-95175 A	1-3, 11-21
X	JP 10-315623 A (Ricoh Co., Ltd.), 02 December, 1998 (02.12.98), Par. Nos. [0049] to [0051], [0083] (Family: none)	1-3, 11-21
X	JP 10-315625 A (Ricoh Co., Ltd.), 02 December, 1998 (02.12.98), Par. Nos. [0038] to [0040], [0081] (Family: none)	1-3, 11-21

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
 "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed
 "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "&" document member of the same patent family

Date of the actual completion of the international search
21 January, 2004 (21.01.04)

Date of mailing of the international search report
03 February, 2004 (03.02.04)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/13636

Box I Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-3, 11-21.

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/13636

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10-315626 A (Ricoh Co., Ltd.), 02 December, 1998 (02.12.98), Par. Nos. [0043] to [0045], [0086] (Family: none)	1-3, 11-21
X	JP 10-315627 A (Ricoh Co., Ltd.), 02 December, 1998 (02.12.98), Par. Nos. [0043] to [0045], [0091] (Family: none)	1-3, 11-21
X A	JP 2001-113829 A (Mitsubishi Paper Mills Ltd.), 02 December, 1998 (02.12.98), Claim 1; Par. Nos. [0028], [0076] (Family: none)	1, 2, 11-21 3

Form PCT/ISA/210 (continuation of second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/13636

Continuation of Box No. II of continuation of first sheet(1)

The matter common to all the claims 1-21 is a reversible thermal recording material claimed in claim 1.

Although the combination with definition as to coloring and decoloring densities exhibited when printing is effected in high temperature high humidity environment defined in claim 1 of this application per se is not described in the published literature, it can be accomplished by the use of phenol compound of the general formula (1) as an electron-accepting compound and is not a constituent of the reversible thermal recording material.

The reversible thermal recording material using the phenol compound of the general formula (1) is disclosed in, for example, the references indicated in attached sheet: JP 2000-345067 A (Mitsui Chemicals, Inc.) 12 December, 2000 (12.12.00) and US 5721910 A (Ricoh Co., Ltd.) 24 February, 1998 (24.02.98).

Consequently, since in all the claims there exist no other common matters considered as special technical features within the meaning of PCT Rule 13.2, second sentence, no technical relationship within the meaning of PCT Rule 13 can be found between the distinct inventions thereof.

Therefore, the claims 1-21 do not satisfy the requirement of unity of invention.

It appears that at least the following three inventions are claimed.

Claims 1-3: invention relating to a reversible thermal recording material wherein use is made of an electron-accepting compound that is a phenol compound of known general formula whose carbon quantity and substituents have been selected;

Claims 4-7: invention relating to a reversible thermal recording material wherein use is made of an electron-accepting compound that is a phenol compound of known general formula and wherein the resin contained in reversible thermal recording layer is specified (with respect to claim 7, although "claims 1 to 3" are quoted, "claims 4 to 6" would have to be quoted instead); and

Claims 8-10: invention relating to a reversible thermal recording material wherein use is made of an electron-accepting compound that is a phenol compound of known general formula, this electron-accepting compound employed in combination with a decoloring accelerator, for example, one having a secondary amido group.

Claims 11-21 relate to thermal recording materials of claims 1-10 and are directed to those provided with a protective layer, a member or label including the same, a method of image processing wherein image formation or deletion is conducted on the thermal recording materials and an image processor for the image formation or deletion. These have no relation to the constitution of thermal recording material and relate to application of publicly known technology. These are considered as being dependent from the inventions of claims 1-10 and searched without charging additional fees.

The matters claimed in claims 4-7 and 8-10 are not searched.

This international search report is prepared on only the matter of claims 1-3 and portion of claims 11-21 relating to claims 1-3.