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(54) **Heat-sensitive transferring recording medium.**

(57) A heat-sensitive transferring recording medium comprises a substrate and a solid coating film formed by applying a coating material mainly composed of an emulsion and a coloring agent overlying the substrate.

A heat-sensitive transferring recording medium is composed of a substrate, a heat-sensitive releasing layer and a heat-sensitive transferring ink layer laminated in the mentioned order.

A heat-sensitive transferring recording medium comprises a substrate, a heat-sensitive releasing layer, a coloring agent layer and a heat-sensitive cohesive layer.

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HEAT-SENSITIVE TRANSFERRING RECORDING MEDIUM

This invention relates to a heat-sensitive transferring recording medium used for heat-sensitive transferring recording apparatuses such as thermal facsimile, thermal printer and the like.

Heat-sensitive recording system which is of non-impact type has recently drawn attention since the system is free of noise and can be easily handled.

Indeed, conventional heat-sensitive recording systems are free of noise and neither development nor fixation of the images is necessary and, in addition, the handling is easy, but the resulting record is liable to be falsified and its durability is not so good.

For the purpose of solving these drawbacks, a particular heat-sensitive transferring recording method was proposed. That is, a heat melting layer is provided on a substrate, and said ink layer is contacted with a receiving paper (recording paper) followed by heating with a thermal head through the substrate to melt said ink layer resulting in transferring of the heated portion to a receiving paper which is an ordinary paper.

The above-mentioned heat-sensitive transferring recording method can give good printed letters where the smoothness of the receiving paper which is an ordinary paper is high, but where the smoothness is low,

for example, the Bekk smoothness test value is not higher than 50 sec., the heat melting ink layer contacts the receiving paper at some portion while said layer does not contact the receiving paper at other portions, because of the uneven surface receiving paper. This results in a low transferring effeciency, formation of void, and low sharpness. In addition, since the heat melting ink has a high fluidity, the ink penetrates into the inside of the receiving paper so that the density of the printed letters is low and good printed letters can not be obtained.

In conventional ink manufacturing methods, a hot melt type coating material or an organic solvent type coating material is used and the content of resin components is at most 20 % by weight. In the case of hot melt ink, the more the content of resin component, the higher is the melt viscosity, and thereby coating is not possible.

In the case of organic solvent type inks, it is difficult to dissolve or disperse waxes and, furhter, remove the organic solvent from the wax dissloved nor dispersed in the organic solvent for drying.

The present inventors have solved the above-mentioned drawbacks by providing a heat-sensitive transferring recording medium comprising a substrate and a heat-sensitive transferring image forming layer of a specified constitution.

According to one aspect of the present invention, there is provided a heat-sensitive transferring recording medium which comprises a substrate and a solid coating film formed by applying a coating material mainly composed of an emulsion and a coloring agent overlying the substrate.

In order to obtain printed letters of high density and less void on a paper of low smoothness, it is necessary to make the transferring layer in a form of block, and use a heat-sensitive transferring ink layer of high melt viscosity so as to decrease penetration of the ink into the paper. That is, the transferring is not effected in a form of point, but in a form of plane.

For effecting such plane-like transferring, a heat-sensitive transferring ink layer containing a larger amount of resin components is necessary in place of conventional heat-sensitive transferring ink layers mainly composed of waxes of low heat melting viscosity.

The substrate used in the present invention includes a thin paper of, for example, less than 20

μ thick, such as glassine paper, condenser paper and the like, and a heat resistant film of , for example, less than 10 μ thick, such as polyester, polyimide, nylon, polypropylene and the like. Plastic films of 2-10 μ thick are preferable.

The emulsion used in the present invention includes wax emulsion, for example, emulsion of a wax such as paraffin wax, microcrystalline wax, carbnauba wax, shellac wax, montan wax, higher fatty acides, higher fatty acid amides, metallic soaps of higher fatty acids and the like.

Further, resin emulsion also can be used as the emulsion of the present invention. Representative resin emulsions are polyethylene resin emulsion, ethylene-vinyl acetate copolymer emulsion, vinyl acetate resin emulsion, vinyl acetate-vinyl chloride copolymer emulsion, acrylic resin emulsion and the like.

Coloring agent used in the present invention includes pigments such as carbon black, iron oxides, prussian blue, lake red, titanium oxide and the like, and dyes such as basic dye, neozapon dye and the like.

As the heat resistant protective layer for the substrate, there may be used higher fatty acids, fluorocarbon polymers, silicone resin and the like.

The heat-sensitive transferring recording medium may be produced as shown below. The above-mentioned resin emulsion or wax emulsion and a coloring agent

are dispersed in water by a dispersing machine such as ball-mill, attritor and the like. In the case of using a commercially available color agent dispersion as the coloring agent, it is necessary only to mix and stir simply the above-mentioned components. The resulting ink coating material is applied to a substrate by means of an ordinaly coating machine and dried. When the heat resistant protective layer is formed on the surface of the substrate opposite to the ink layer, above material is mixed with and dispersed in a solvent, applied to the substrate and dried. The thickness of the heat-sensitive transferring layer may be 2 - 10 μ.

For the purpose of decreasing the energy necessary for thermal heads, it is effective to provide a heat-sensitive releasing layer between the substrate and the ink layer. The releasing layer may be formed by using silicone, celluloses and waxes, alone or in combination, if desired, a pigment such as carbon black, calcium carbonate, clay, talc and the like is dispersed in the above-mentioned material for a releasing layer.

In case that the heat-sensitive releasing layer is provided on the heat-sensitive transferring recording medium, the above-mentioned material is applied to the substrate by means of hot melt coating or solvent coating and dried before applying the heat-sensitive transferring ink layer.

According to this aspect of the present invention, since the melting temperature of the transferring ink layer is so high that penetration of the ink into the receiving paper is little and thereby the printed letter is of high density, and the transferring is effected in a form of block so that void is few, and in addition, the film shapeability is so weak that the printed letters have a sharp outline and are clear.

Further, according to the present invention where emulsion type coating materials are used, there can be produced a resin/ wax/ coloring agent ink containing more resin content than the prior art ink. Since the emulsion type coating material gives a heat-sensitive transferring ink layer having a less film shapeability than that produced from a hot melt organic solvent type coating material and therefore, printed letters of sharp outline can be obtained when printed by means of a thermal head.

According to another aspect of the present invention, there is provided a heat-sensitive transferring recording medium which comprises a substrate, a heat-sensitive releasing layer overlying the substrate, and a heat-sensitive transferring ink layer overlying the heat-sensitive releasing layer.

In order to obtain printed letters of high density and little void on a paper of low smoothness, it is necessary to make the transferring layer in a form of block and use a heat-sensitive transferring ink layer of high melt viscosity so as to decrease penetration of the ink into the paper. That is, the transferring is not effected in a form of point, but in a form of plane.

Further, it is necessary to facilitate releasing of the heat-sensitive transferring ink layer from the substrate and enhance the transferring efficiency.

In case that a heat-sensitive transferring ink layer has a high melt viscosity and is directly contacted with a substrate, releasing of the heat-sensitive transferring ink layer is liable to become difficult. Therefore, it is contemplated to make easy firstly the releasing of the heat-sensitive transferring ink layer from the substrate by means of the heat-sensitive releasing layer and then make higher the melt viscosity of the heat-sensitive transferring ink layer so as to decrease penetration of the ink into paper and effecting the transferring of ink in a form of block.

The heat-sensitive transferring recording medium comprises a substrate, a heat-sensitive releasing layer and a heat-sensitive transferring ink layer.

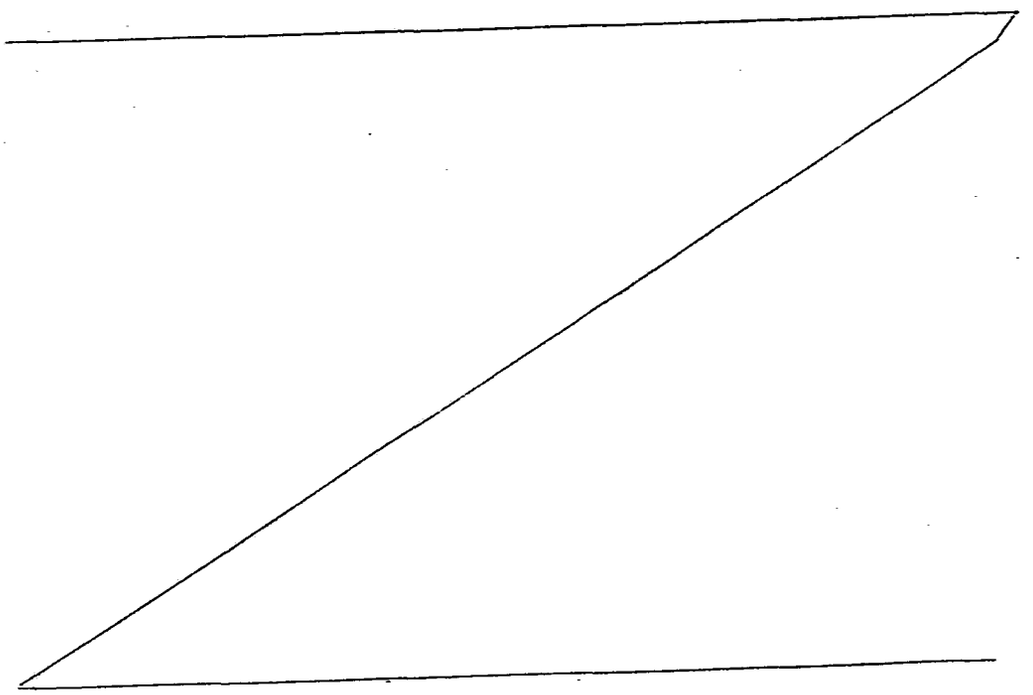
The substrate may be composed of a plastic film provided with a heat resistant protective layer.

The heat-sensitive releasing layer is preferably a layer which can be easily melted when heated and has a low melt viscosity. The heat-sensitive transferring ink layer is preferably a layer which becomes cohesive when heated, and has a melt viscosity higher than that of the heat-sensitive releasing layer.

The heat-sensitive releasing layer comprises, for example, 50 - 100 parts by weight of wax, 0 - 30 parts by weight of binder, and 0 - 50 parts by weight of coloring agent and pigment.

The heat-sensitive transferring ink layer comprises, for example, 0 - 50 parts by weight of wax, 30 - 80 parts by weight of binder and 5 - 50 parts by weight of coloring agent and pigment.

The thickness of the heat-sensitive releasing



layer is preferably 1 - 4 μ and that of the heat-sensitive transferring ink layer is preferably 2 - 8 μ.

The substrate in the present invention includes a thin paper of, for example, less than 20 μ thick, such as glassine paper, condenser paper and the like, and a heat resistant film of, for example, less than 10 μ thick, such as polyester, polyimide, nylon, polypropylene and the like.

Binders, waxes, and coloring agents which may be used in the present invention are exemplified in Table 1 below.

Table 1

Wax	Paraffine wax Microcrystalline wax Carnauba wax Shellac wax Montan wax Higher fatty acids Higher fatty acid amides Higher alcohols Metallic soap
Binder	Polyvinyl acetate Polyvinyl chloride Polyvinyl butyral Polyethylene

Binder	Polyamide Hydroxyethylcellulose Methylcellulose Nitrocellulose Polystyrene Polyesters Polyacrylate Vinyl chloride-vinyl acetate copolymer Ethylene-vinyl acetate copolymer Ethylene-organic acid copolymer Vinyl chloride-vinylidene chloride copolymer
Coloring agent and pigment	Coloring pigments such as carbon black, iron oxide, Prussian blue, titanium oxide, lake red, and the like; Dyes such as basic dyes, neozapon dyes and the like; Extender pigments such as calcium carbonate, clay, talc and the like

As materials for the heat resistant protective layer, there may be mentioned higher fatty acids, fluorocarbon polymers, and silicone resins.

The heat-sensitive transferring recording medium can be produced, for example, by the following procedure.

A coating composition for a heat-sensitive

releasing layer and a coating composition for a heat-sensitive transferring ink layer are dispersedly mixed by heated ball mills or attritors, or are dispersed in solvents or water, and then they are successively applied to a substrate by a hot melt coater, a solvent coater or an aqueous coater.

When a heat resistant protective layer is formed in a substrate, the above-mentioned material for the heat resistant protective layer may be dispersed in and mixed with a solvent and, before the heat-sensitive releasing layer and the heat-sensitive transferring ink layer are formed, the resulting coating material is applied by a solvent coater to a surface of the substrate opposite to the surface to which the above-mentioned layers are to be formed.

The heat-sensitive transferring recording medium of the present invention has two layers, that is, a layer facilitating to release the ink layer (heat-sensitive releasing layer) on a substrate and a layer having cohesion and capable of cohering to receiving paper (heat-sensitive transferring ink layer) on the heat-sensitive releasing layer, and therefore, when heated by using a thermal head, the heat-sensitive transferring ink layer is released from the substrate and completely transferred to a receiving layer due to the cohesion of the heat-sensitive transferring ink layer to receiving paper. As a result, the transferring

efficiency is enhanced and printed letters free of void can be produced.

Since viscosity of the heat-sensitive transferring ink layer is high, penetration of the ink into receiving paper is little and printed letters of high density can be obtained. Even if a receiving paper of less smoothness is used, the heat-sensitive transferring recording medium can give a clear record of high density and free of void at a high transferring efficiency.

According to a further aspect of the present invention, there is provided a heat-sensitive transferring recording medium which comprises a substrate, a heat-sensitive releasing layer overlying the substrate, a coloring agent layer overlying the heat-sensitive releasing layer, and a heat-sensitive cohesive layer overlying the coloring agent layer.

In order to obtain printed letters of high density and little void on a paper of low smoothness, it is necessary that the transferring efficiency is high, the transferring is effected in a form of block, i.e. the transferring is not effected in a form of point, but in a form of plane, and penetration of the ink into the paper is prevented.

The heat-sensitive transferring recording medium can satisfy the above-mentioned conditions.

The substrate of heat-sensitive transferring

recording medium may be composed of a plastic film provided with a heat resistant protective layer.

It is preferable that the heat-sensitive releasing layer is easily melted when heated and has a low melt viscosity. It is preferable that the coloring agent layer does not melt or has a high melt viscosity. Further it is preferable that the heat-sensitive cohesive layer becomes cohesive when heated and the value of the melt viscosity is between that of the heat-sensitive releasing layer and that of the coloring agent layer.

The heat-sensitive releasing layer comprises, for example, 50 - 100 parts by weight of wax, 0 - 30 parts by weight of binder and 0 - 50 parts by weight of coloring agent. The coloring agent layer comprises, for example, 0 - 30 parts by weight of wax, 20 - 50 parts by weight of binder and 40 - 80 parts by weight of pigment. The heat-sensitive cohesive layer comprises, for example, 0 - 50 parts by weight of wax, 50 - 80 parts by weight of binder, 0 - 50 parts by weight of pigment.

The thickness of the heat-sensitive releasing layer is preferably 1 - 4 μ, that of the coloring agent layer is preferably 1 - 8 μ and that of the heat-sensitive cohesive layer is preferably 1 - 8 μ.

The heat-sensitive transferring recording medium has preferably the following constitution. That is, the

heat-sensitive releasing layer is mainly composed of a easily melting wax having a low melt viscosity; the coloring agent layer is mainly composed of a pigment which hardly melts and has a weak film-shapability; and the heat-sensitive cohesive layer is mainly composed of a binder which becomes cohesive when heated by a thermal head; and these layers are successively formed on a substrate in the mentioned order.

The coloring agents contained in the heat-sensitive releasing layer may be dyes or coloring pigments. The pigments contained in the coloring agent layer and the heat-sensitive cohesive layer may be coloring pigments or extender pigments.

The substrate in the present invention includes a thin paper of, for example, less than 20 μ thick, such as glassine paper, condenser paper and the like, and a heat resistant film of, for example, less than 10 μ thick, such as polyester, polyimide, nylon, polypropylene and the like.

A plastic film of 2 - 10 μ thick is preferable.

Waxes, binders and coloring agents and pigment which may be used are exemplified in Table 1 above.

As materials for the heat-resistant protective layer, there may be mentioned higher fatty acids fluorocarbon polymers, and silicone resins.

The heat-sensitive transferring recording medium can be produced, for example, by the following procedure.

A coating composition for a heat-sensitive releasing layer, a coating composition for a coloring agent layer, and a coating composition for a heat-sensitive cohesive layer are dispersedly mixed by heated ball mills or attritors, or are dispersed in solvents or water, and then they are successively applied to a substrate by a hot melt coater, a solvent coater or an aqueous coater.

When a heat resistant protective layer is formed in a substrate, the above-mentioned material for the heat resistant protective layer may be dispersed in and mixed with a solvent and, before the heat-sensitive releasing layer, coloring agent layer and heat-sensitive cohesive layer are formed, the resulting coating material is applied by a solvent coater to a surface of the substrate opposite to the surface to which the above-mentioned layers are to be formed.

In the present invention, on the substrate there are formed a layer for facilitating to release an ink layer (i.e. heat-sensitive releasing layer), a layer which substantially does not have fluidity (i.e. coloring agent layer), and a layer which is cohesive and can adhere to a receiving paper (i.e. heat-sensitive cohesive

layer). Such three-layered heat-sensitive transferring recording medium acts in such a manner that the ink layer (a coloring agent layer and a heat-sensitive cohesive layer) is released from the substrate by heating with a thermal head and the cohesion of the heat-sensitive cohesive layer enables to completely transfer the ink layer to a receiving paper. Thus, printed images of high transferring efficiency and free of void can be produced.

In addition, the medium has a layer substantially incapable of becoming fluidized by heating (the coloring agent layer) and thereby, printed images of high density can be produced.

The following examples are given for illustrating the present invention. Parts and % are by weight.

Reference Example

Paraffin wax	40	parts by weight
Carnauba wax	30	parts by weight
Ethylene-vinyl acetate copolymer (90:10)	10	"
Carbon black	20	"

An ink composed of the above-mentioned ingredients was applied to a polyester film of 6 μ thick in the thickness of 4 μ by means of hot melt coating.

Example 1

	Amount (parts by weight)	Solid content (%)
Ethylene-vinyl acetate (90:10) copolymer emulsion (solid content, 45%)	30	39.1
Paraffin emulsion (solid content, 30%)	30	26.1
Carnauba emulsion (solid content, 30%)	20	17.4
Carbon black dispersion (solid content, 30%)	20	17.4

An ink composed of the above-mentioned ingredients was applied to a polyester film of 6 μ thick and dried to produce a heat-sensitive transferring ink layer of 4 μ thick.

Example 2

A paraffin wax (m.p. 65°C) was applied to a polyester film of 6 μ thick in the thickness of 1 μ by hot melt coating.

To the surface of the resulting paraffin wax layer was applied an ink composed of the following ingredients:

	Amount (parts by weight)	Solid content (%)
Ethylene-vinyl acetate (90:10) copolymer emulsion (solid content, 45%)	60	69.2
Carnauba emulsion (solid content, 20%)	20	15.4
Carbon black dispersion (solid content 30%)	20	15.4

by Mayer bar coating and dried to form a heat-sensitive transferring ink layer of 4 μ thick.

Example 3

Paraffin wax was applied to a polyester film of 6 μ thick in the thickness of 1μ by a hot melt coating method to form a heat-sensitive releasing layer.

Ethylene-vinyl acetate (90:10) copolymer	70 parts

Carnauba wax	10	parts
Carbon black	20	"
Ethyl acetate	100	"
Toluene	200	"

To the surface of the heat-sensitive releasing layer was applied a composition composed of the above-mentioned components by a mayer bar method, followed by drying to form a heat-sensitive transferring ink layer.

Example 4

Paraffin wax	70	parts
Ethylene-vinyl acetate (90:10) copolymer	10	parts
Carbon black	20	parts

A composition composed of the above-mentioned components was applied to a polyester film of 6 μ thick in the thickness of 2 μ by a hot melt coating method to form a heat-sensitive releasing layer.

To the surface of the heat-sensitive releasing layer was applied a composition composed of the following components by a mayer bar method and dried to form a heat-sensitive transferring ink layer of 3 μ thick.

	Component (parts)	Solid matter(%)
Ethylene-vinyl acetate (90:10) emulsion (solid matter 45%)	160	(68.6)
Carnauba emulsion (solid matter 30%)	50	(14.3)
Carbon black dispersion (solid matter 30%)	60	(17)

Example 5

To a polyester film of 6 μ thick were successively applied the following layers.

Heat-sensitive releasing layer:

Paraffin wax was applied in the thickness of 1 μ by hot melt coating.

Coloring agent layer:

Ethylene-vinylacetate (90:10) Copolymer	40	parts by weight
Carbon black	30	"
Calcium carbonate light	30	"
Toluene	200	"

The above-mentioned components were applied by solvent coating and dried. Thickness was 2 μ.

Heat-sensitive cohesive layer:

Ethylene-vinylacetate (90:10) Copolymer	60	parts by weight
Carnauba wax	20	"
Carbon black	20	"
Ethyl acetate	100	"
Toluene	200	"

The above-mentioned components were applied by solvent coating and dried. Thickness was 2 μ.

Example 6

To a polyester film of 6 μ thick were successively applied the following layers.

Heat-sensitive releasing layer:

Paraffin wax	80 parts by weight
Calcium carbonate	20 "

The above-mentioned components were applied by hot melt coating in the thickness of 2 μ.

Coloring agent layer:

	Component (parts by weight)	Solid matter(%)
Ethylene-vinyl acetate (90:10) copolymer emulsion (solid matter 45%)	50	30.6
Zinc stearate dispersion (solid matter 30%)	50	20.4
Carbon black dispersion (solid matter 30%)	120	49.0

The above-mentioned components were applied by solvent coating in the thickness of 2 μ.

Heat-sensitive cohesive layer:

	Component (parts by weight)	Solid matter(%)
Ethylene-vinyl acetate (90:10) copolymer emulsion (solid matter 45%)	100	71.4
Carnauba emulsion (solid matter 30%)	30	14.3
Carbon black dispersion (solid matter 30%)	30	14.3

The above-mentioned components were applied by solvent coating and dried. The thickness was 2 μ.

Test method

The heat-sensitive transferring recording mediums as prepared above were tested by means of a heat-sensitive printer (cycle, 1.2 m sec.; applied pulse width, 0.9 m sec., power, 0.5 W/Dot) with a receiving paper (Bekk test, 16 sec; Hammer Mill Bond paper) (JIS P8119).

The heat-sensitive transferring recording medium prepared in Reference Example gave many voids and low density while that prepared in each of Examples 1 - 6 gave good printed letters of few voids and high density.

CLAIMS:

1. A heat-sensitive transferring recording medium which comprises a substrate and a solid coating film formed by applying a coating material mainly composed of an emulsion and a coloring agent overlying the substrate.

2. A recording medium according to claim 1 in which the substrate is composed of a plastic film and a heat resistive protecting layer provided on the plastic film.

3. A heat-sensitive transferring recording medium according to claim 1 or claim 2 in which the emulsion is a wax emulsion and/or a resin emulsion.

4. A recording medium according to any preceding claim in which the emulsion contains a resin emulsion and the resin emulsion contains 80-30% solid content.

5. A recording medium which comprises a substrate, a heat-sensitive releasing layer overlying the substrate, and a heat-sensitive transferring ink layer overlying the heat-sensitive releasing layer.

6. A recording medium according to claim 5 in which the substrate is composed of a plastic film provided with a heat resistant protective layer.

7. A heat-sensitive transferring recording medium according to claim 5 or 6 in which the heat-sensitive releasing layer is easily melted when heated, and the melt viscosity is low while the heat-sensitive transferring ink layer becomes cohesive when heated, and the melt viscosity is higher than that of the heat-sensitive releasing layer.

8. A recording medium according to claim 5, 6 or 7 in which the heat-sensitive releasing layer comprises wax : binder : coloring agent and pigment = 50-100 : 0-30 : 0-50 (parts by weight) and the heat-sensitive transferring ink layer comprises wax : binder : coloring agent and pigment = 0-50 : 30-80 : 5-50 (parts by weight).

9. A heat-sensitive transferring recording medium which comprises a substrate, a heat-sensitive releasing layer overlying the substrate, a coloring agent layer overlying the heat-sensitive releasing layer, and a heat-sensitive cohesive layer overlying the coloring agent layer.

10. A recording medium according to claim 9 in which the substrate is composed of a plastic film provided with a heat resistant protective layer.

11. A heat-sensitive transferring recording medium according to claim 9 or 10 in which the heat-sensitive releasing layer is easily melted when heated and has a low melt viscosity, the coloring agent layer does not melt or has a high melt viscosity, and the heat-sensitive cohesive layer becomes cohesive when heated and has a melt viscosity the value of which is between that of the heat-sensitive releasing layer and that of the coloring agent layer.

12. A heat-sensitive transferring recording medium according to claim 9, 10 or 11 in which the heat-sensitive releasing layer comprises wax : binder : coloring agent = 50-100 : 0-30 : 0-50 (parts by weight), the coloring agent layer comprises wax : binder : pigment = 0-30 : 20-50 : 40-80 (parts by weight), and the heat-sensitive cohesive layer comprises wax : binder : pigment = 0-50 : 50-80 : 0-50 (parts by weight).