



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 826 512 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.03.1998 Bulletin 1998/10

(51) Int. Cl.⁶: B41M 5/38, B41M 5/40

(21) Application number: 97114863.0

(22) Date of filing: 27.08.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

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(30) Priority: 28.08.1996 JP 226785/96

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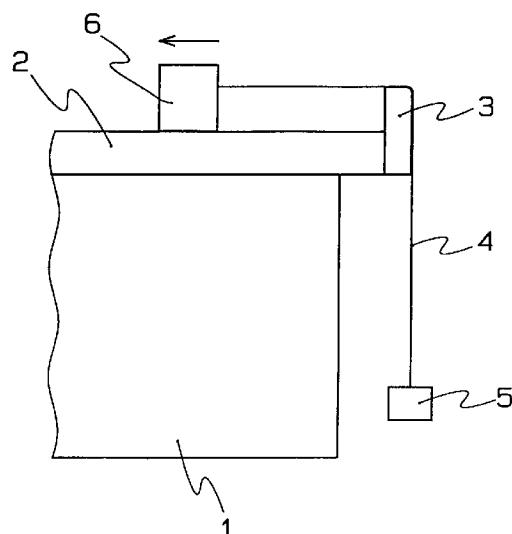
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(54) Thermal transfer recording material having an intermediate adhesive layer

(57) A thermal transfer recording medium which causes no ink-falling and is capable of providing printed images with high definition is disclosed which comprises a foundation having thereon a heat-meltable ink layer, and an intermediate adhesive layer provided between the foundation and the heat-meltable ink layer, the intermediate adhesive layer comprising 20 to 80 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 % by weight of at least one of a body pigment and carbon black.

FIG. 1



Description

The present invention relates to a thermal transfer recording medium. More particularly, it relates to a thermal transfer recording medium which does not cause the so-called "ink-falling" and is capable of providing printed images with high definition.

Recently thermal transfer recording system has been widely applied because thermal transfer printers used therein have characteristics such as easy maintenance, availability of small-sized and lightweight ones and low-cost.

In such a thermal transfer recording system, respective plural heating elements (dots) of a thermal head are allowed to selectively generate heat in response to picture signals, thereby selectively transferring the heat-melted ink layer of a thermal transfer recording medium in dots to give a printed image on a receptor. Therefore, improved dot-reproducibility is required to obtain printed images with high definition. This dot-reproducibility refers to the coincidence of the shape of dots of the transferred heat-melted ink with that of the heating elements.

Measures for improving the dot-reproducibility include selection of a heat-melted material showing a sharp peak in its DSC (differential scanning calorimetry) curve for the vehicle of the heat-melted ink layer. For example, carnauba wax (penetration: 1), which is a very hard wax, was used as a vehicle of the heat-melted ink layer, as a result of further consideration given to the scratch resistance of printed images and the like. A heat-melted ink layer containing carnauba wax as a vehicle thereof offers printed images with improved dot-reproduction because the wax shows a sharp peak in its DSC curve. However, the incorporation of a large amount of carnauba wax into a heat-melted ink layer results in a problem that the so-called "ink-falling" phenomenon occurs. The term "ink-falling" refers to a phenomenon in which, during traveling of the thermal transfer recording medium, which is loaded in a cassette, in a thermal transfer printer, portions of the heat-melted ink layer are peeled off from the foundation when the recording medium comes into sliding contact with guide members of the cassette, the thermal head, etc. and, hence, is subjected to external force. The ink-falling phenomenon is remarkable in using the recording medium in low-temperature environments.

The ink-falling phenomenon is undesirable because portions of the recording medium wherein the ink layer is peeled off cannot be used to form printed images and the generated ink powder is accumulated in the thermal head, resulting in a decrease in image quality or contamination in the inside of the printer.

Conventional measures for preventing the ink-falling phenomenon include (1) a method wherein the content of a resin component in the heat-melted ink layer is increased to improve adhesion of the ink layer, and (2) another method wherein a wax having a greater penetration is used in combination with carnauba wax to impart flexibility or softness to the heat-melted ink layer. However, the method (1) involves a problem that the viscosity of an ink coating liquid is increased with increasing content of the resin component and, hence, the application property of the coating liquid becomes poor, resulting in failure to form a uniform ink layer. The method (2) involves a problem that during exchange of the recording medium in using it in low-temperature environment, the ink thereof sticks to the hand.

In view of the foregoing, an object of the present invention is to provide a thermal transfer recording medium which causes no ink-falling in low-temperature environments and exerts excellent dot-reproducibility to form printed images with high definition.

This and other objects of the present invention will become apparent from the description hereinafter.

The present invention provides a thermal transfer recording medium comprising a foundation having thereon a heat-melted ink layer, and an intermediate adhesive layer provided between the foundation and the heat-melted ink layer, the intermediate adhesive layer comprising 20 to 80 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 % by weight of at least one of a body pigment and carbon black.

In an embodiment of the present invention, the polyester resin has a glass transition temperature of not higher than 0°C.

In another embodiment of the present invention, the heat-melted ink layer comprises a coloring agent and a vehicle, the vehicle comprising not less than 40 % by weight of carnauba wax.

In still another embodiment of the present invention, the vehicle comprises not less than 50 % by weight of carnauba wax.

In a further embodiment of the present invention, the intermediate adhesive layer comprises 40 to 70 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C and 30 to 60 % by weight of at least one of a body pigment and carbon black.

Fig. 1 is a schematic view illustrating a measuring device for examining the ink-falling of a thermal transfer recording medium.

The thermal transfer recording medium of the present invention is characterized in that between the foundation and the heat-melted ink layer is provided an intermediate adhesive layer comprising 20 to 80 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 % by weight of at least one of a body pigment and carbon black.

In the present invention, the intermediate adhesive layer maintains flexibility or softness even in low-temperature environments wherein the temperature is lower than normal temperature because a polyester resin having a glass

transition temperature of not higher than 20°C is used as the resin component and, hence, serves as some type of a buffer layer between the foundation and the heat-meltable ink layer, thereby causing no ink-falling even in the case that the heat-meltable ink layer is relatively hard. The use of a polyester resin having a glass transition temperature of higher than 20°C as the resin component for the intermediate adhesive layer results in ink-falling because the polyester resin 5 crystallizes in low-temperature environments and the function of the intermediate adhesive layer as a buffer layer is lost. From the viewpoint of retaining the flexibility or softness of the intermediate adhesive layer in low-temperature environments, a polyester resin having a glass transition temperature of not higher than 0°C is preferable.

In the present invention, the intermediate adhesive layer is incorporated with at least one of a body pigment and carbon black (hereinafter, in some cases, referred to as "particulate material") in addition to the polyester resin. The 10 incorporation of the particulate material produces fine unevenness on the surface of the intermediate adhesive layer to increase the contact area between the intermediate adhesive layer and the heat-meltable ink layer. As a result, the ink-falling can be more sufficiently prevented.

The intermediate adhesive layer in accordance with the present invention contains 20 to 80 % by weight, preferably 40 to 70 % by weight, of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 15 % by weight, preferably 30 to 60 % by weight, of a particulate material. When the content of the polyester resin having a glass transition temperature of not higher than 20°C is lower than the above range or the content of the particulate material is higher than the above range, the function of the intermediate adhesive layer as a buffer layer is degraded to fail to sufficiently exert the effect of preventing the ink-falling and a problem that the application property of a coating liquid for the intermediate adhesive layer is degraded is further invited. When the content of the polyester resin is higher 20 than the above range or the content of the particulate material is lower than the above range, the contact area between the intermediate adhesive layer and the ink layer is not increased due to the lower content of the particulate material to fail to sufficiently exert the effect of preventing the ink-falling and the so-called "layer-like transfer" which refers to the phenomenon wherein an excess portion of the ink layer that is not heated during the thermal transfer is also transferred, is prone to further occur, resulting in deterioration of the dot-reproducibility.

25 As the aforesaid polyester resin there can be used linear saturated polyester resins which are obtained by poly-condensation of a dibasic acid and a diol compound and have a glass transition temperature of not higher than 20°C, preferably not higher than 0°C. Examples of the dibasic acid are adipic acid, azelaic acid, sebacic acid, phthalic acid and Het acid (chlorendic acid). These dibasic acids can be used either alone or in combinations of two or more species thereof. Examples of the diol compounds are ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-30 cyclohexanedimethanol, hydrogenated bisphenol A and dibromoneopentylene glycol. These diol compounds can be used either alone or in combinations of two or more species thereof.

Examples of body pigments as the particulate material are silica, calcium carbonate, magnesium carbonate, barium sulfate and aluminium silicate. These body pigments can be used either alone or in combinations of two or more species thereof.

35 The body pigment and carbon black may be used either alone or in combination as the particulate material. From the viewpoint of producing fine unevenness on the surface of the intermediate adhesive layer, the particulate material preferably has an average particle size of about 0.5 to about 10 µm.

The intermediate adhesive layer may be incorporated with a small amount of a dispersing agent or the like in addition to the aforesaid ingredients.

40 The thickness of the intermediate adhesive layer is preferably from 0.3 to 1.0 µm from the viewpoint of the adhesiveness and the transfer sensitivity.

The intermediate adhesive layer can be formed by applying onto a foundation a coating liquid which is prepared by dissolving or dispersing the polyester resin and the particulate material into an appropriate solvent, followed by drying.

As the heat-meltable ink layer in accordance with the present invention there can be used conventional ones without particular limitation so long as they are one-time type heat-meltable ink layers each comprising a coloring agent and a heat-meltable vehicle as main ingredients. However, preferred is a heat-meltable ink layer whose vehicle component contains not less than 40 % by weight, especially not less than 50 % by weight, of carnauba wax to form printed images having excellent durability with excellent dot-reproducibility as well as to prevent the ink-falling in combination with the aforesaid intermediate adhesive layer. When the content of carnauba wax in the vehicle component is lower than the 50 above range, the dot-reproducibility is prone to be deteriorated to fail to produce printed images with high definition and the durability of printed images is also prone to be decreased.

Usable as the vehicle component other than carnauba wax are waxes other than carnauba wax and/or resins. As the waxes there can be appropriately selected and used those conventionally used in this field, such as paraffin wax, microcrystalline wax, oxidized wax, ester wax, candelilla wax, rice wax and montan wax. As the resins there can be 55 appropriately selected and used those conventionally used in this field, such as polyethylene, ethylene-vinyl acetate resin, polyamide resins, polyester resins, epoxy resins and acrylic resins.

Carbon black as well as usual pigments and dyes can be appropriately selected and used as the coloring agent.

Suitable ranges for the contents of the foregoing ingredients in the heat-meltable ink layer in accordance with the

present invention are as follows:

Ingredient	% by weight
Carnauba wax	40 to 95 (preferably 50 to 90)
Other waxes	0 to 40 (preferably 10 to 30)
Resin	0 to 40 (preferably 10 to 30)
Coloring agent	5 to 20

5 The heat-meltable ink layer in accordance with the present invention can be formed by applying an ink of the foregoing formulation onto the aforesaid intermediate adhesive layer by means of a hot-melt coating method or a solvent coating method. The thickness of the heat-meltable ink layer is preferably from 1 to 5 μm from the viewpoint of the optical density of images and the transfer sensitivity.

10 In the present invention, as required, an overcoat layer may be provided on the heat-meltable ink layer. The overcoat layer is provided for the purpose of preventing smearing or the like. Usually the overcoat layer is an uncolored layer comprising a wax as a main ingredient.

15 Usable as the foundation in the present invention are highly heat-resistant plastic films such as polyethylene terephthalate film, polycarbonate films, polyimide films and nylon films, and cellophane, parchment paper and condenser paper. The thickness of the foundation is usually from 2 to 10 μm , preferably from 3.5 to 6 μm . From the viewpoint of good adhesion to the intermediate adhesive layer, polyethylene terephthalate film is especially preferred.

20 As required, on the back side (the side adapted to come into slide contact with a thermal head) of the foundation may be formed a heat-resistant layer comprising one or more resins selected from silicone resins, fluorine-containing resins, acrylic resins, epoxy resins, phenol resins, cellulose resins, and the like.

25 The present invention will be more fully described by way of Examples and Comparative Examples. It is to be understood that the present invention is not limited to the Examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

30 Examples 1 to 3 and Comparative Examples 1 to 3

35 Into a mixed solvent of toluene/methyl ethyl ketone was added each composition for intermediate adhesive layer of the formulation shown in Table 1 so that the total solid concentration became 10 % by weight. The resulting mixture was agitated at a high speed in an attritor for 60 minutes to give a coating liquid for intermediate adhesive layer. Onto one side of a 6 μm -thick polyethylene terephthalate film which was provided on the other side thereof with a heat-resistant layer composed of a silicone resin was applied the coating liquid by means of a solvent coater so that the coating amount after drying was 0.5 g/m^2 , followed by drying to give an intermediate adhesive layer. In Comparative Example 3, the resulting coating liquid failed to form a uniform layer due to its poor application property and, hence, subsequent treatments were not performed.

40 Each composition for heat-meltable ink layer of the formulation shown in Table 1 was sufficiently kneaded by means of a 3-roll mill to give a heat-meltalbe ink. The ink was applied in a coating amount of 3.0 g/m^2 onto the intermediate adhesive layer by means of a hot-melt coater to give a heat-meltable ink layer.

45 Each of the thus obtained thermal transfer recording media was evaluated for dot-reproducibility and ink-falling. The results are shown in Table 1.

(Dot-reproducibility)

50 Each of the thermal transfer recording media was used to form a printed image under the printing conditions mentioned below. The printed image was observed with a metallograph (XF(U)NR made by NIKON CORPORATION) at a magnification of 50 to determine the ratio of the area of one dot of the image to that of one dot of the heating elements (area of one dot of the image/area of one dot of the heating elements). The dot-reproducibility was evaluated according to the following criterion:

55 Printing conditions:

Thermal printer : line printer (B-30 made by TEC Corporation)
 Thermal head : line head type

Head pressure : 700 g/25.4 mm (1 inch)
Printing energy : 19.0 mJ/mm²
Printing speed : 10.2 cm (4 inches)/second
Receptor paper : TPKB (Bekk smoothness: 200 seconds)

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Evaluation criterion:

3 Area ratio: 0.95 to 1.05
2 Area ratio: 0.90 to less than 0.95
10 1 Area ratio: less than 0.90

(Ink-falling)

With respect to each of the thermal transfer recording media, the degree of ink-falling was examined in a low-temperature environment (dry room at 0°C) with use of a measuring device as shown in Fig. 1. This test is a substitute for a test for examining the degree of ink-falling when the thermal transfer recording medium is squeezed through a thermal head.

As shown in Fig. 1, a glass plate 3 was fixed to a support member 2 which was mounted on a table 1 with projecting out from an edge of the table 1. A ribbon-like thermal transfer recording medium 4 (width: 12.7 mm) was arranged so that it lay upward on the ink layer side and was brought into contact with the end surface of the glass plate 3 on the back side thereof. A weight 5 was attached to one end of the recording medium that hung down and a movable member 6 was attached to the other end of the recording medium. In such a state, the movable member 6 was moved at a speed of 1.3 m/minute in the direction indicated by the arrow to examine whether the ink-falling occurred. This examination operation was repeated while successively replacing the weight 5 with a heavier one by 50 g within the range of 50 to 25 300 g. The ink-falling was evaluated according to the following criterion:

Evaluation criterion:

4 Ink-falling does not occur when a 300-gram weight is used.
30 3 Ink-falling occurs when a 250-gram weight is used.
2 Ink-falling occurs when a 200-gram weight is used.
1 Ink-falling occurs when a 100-gram weight is used.

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Table 1

	EX.1	EX.2	EX.3	COM. EX.1	COM. EX.2	COM. EX.3
5	Composition of intermediate adhesive layer (% by weight)					
10	Polyester resin A ^{*1}	60	60	60	90	10
15	Polyester resin B ^{*2}		60			
20	Polyester resin C ^{*3}			60		
25	Aluminium silicate ^{*4}	40	40	40	10	90
30	Composition of heat-meltable ink-layer (% by weight)					
35	Carnauba wax	60	60	40	60	-
40	Ester wax	20	20	40	20	-
45	Ethylene-vinyl acetate copolymer	10	10	10	10	-
50	Carbon black	10	10	10	10	-
55	Evaluation					
60	Dot-reproducibility	3	3	2	2	-
65	Ink-falling	4	3	4	1	-

*1: Glass transition temperature: -20°C

2: Glass transition temperature: 13°C

3: Glass transition temperature: 60°C

4: Average particle size: 5.0 µm

35 In addition to the materials and ingredients used in the Examples, other materials and ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

As has been described, the thermal transfer recording medium of the present invention does not cause ink-falling when used in low-temperature environments and exerts excellent dot-reproducibility to give printed images with high-definition and excellent durability.

40 A thermal transfer recording medium which causes no ink-falling and is capable of providing printed images with high definition is disclosed which comprises a foundation having thereon a heat-meltable ink layer, and an intermediate adhesive layer provided between the foundation and the heat-meltable ink layer, the intermediate adhesive layer comprising 20 to 80 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 % by weight of at least one of a body pigment and carbon black.

45 Claims

1. A thermal transfer recording medium comprising a foundation having thereon a heat-meltable ink layer, and an intermediate adhesive layer provided between the foundation and the heat-meltable ink layer, the intermediate adhesive layer comprising 20 to 80 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C, and 20 to 80 % by weight of at least one of a body pigment and carbon black
2. The thermal transfer recording medium of Claim 1, wherein the polyester resin has a glass transition temperature of not higher than 0°C
3. The thermal transfer recording medium of Claim 1, wherein the heat-meltable ink layer comprises a coloring agent and a vehicle, the vehicle comprising not less than 40 % by weight of carnauba wax.

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4. The thermal transfer recording medium of Claim 3, wherein the vehicle comprises not less than 50 % by weight of carnauba wax.
5. The thermal transfer recording medium of Claim 1, wherein the intermediate adhesive layer comprises 40 to 70 % by weight of a polyester resin having a glass transition temperature of not higher than 20°C and 30 to 60 % by weight of at least one of a body pigment and carbon black.

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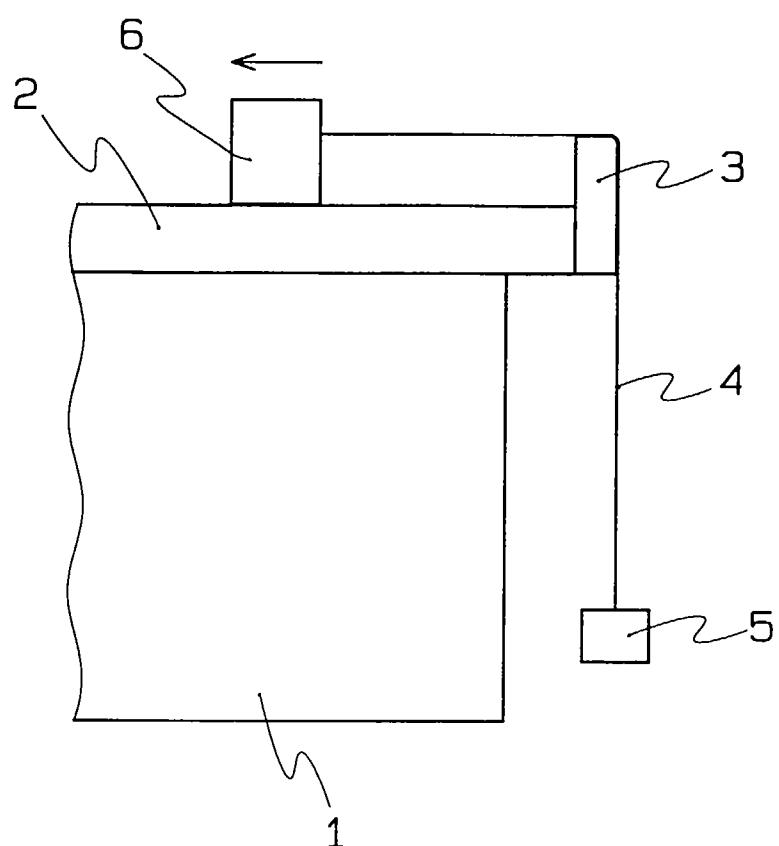
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FIG. 1





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 363 929 A (FUJITSU LIMITED) * column 7, line 54 - column 8, line 24 * * column 9, line 48 - column 10, line 12 * * column 13, line 17 - line 33 * * claims 1-10; figure 3 * ---	1,2	B41M5/40
X	EP 0 410 724 A (KONICA CORPORATION) * page 4, line 2 - line 16 * * page 5, line 15 - page 6, line 14 * * claims 1-5,11-20; examples 1,2 * * figures 1,2 * ---	1,2	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 379 (M-1012), 16 August 1990 & JP 02 141286 A (FUJITSU LIMITED), 30 May 1990, * abstract * ---	1-5	
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 378 (M-546), 17 December 1986 & JP 61 169283 A (FUJITSU LIMITED), 30 July 1986, * abstract * ---	1-5	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 66 (M-461), 15 March 1986 & JP 60 212393 A (FUJITSU K.K.), 24 October 1985, * abstract * -----	1-5	B41M
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	19 November 1997	Bacon, A	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			