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(54) **Thermal transfer recording medium.**

(57) The improved thermal transfer recording medium comprises a support coated with a first heat-softening layer which in turn is coated with a second heat-softening layer, said first heat-softening layer containing a heat-fusible material and said second heat-softening layer containing a polymer based on an alkyl (meth)acrylate ester.

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THERMAL TRANSFER RECORDING MEDIUM

BACKGROUND OF THE INVENTION

This invention relates to a thermal transfer recording medium. More particularly, this invention relates to a thermal transfer recording medium that has not only high resolving power but also sufficient adhesion to allow prints to be fixed efficiently onto receiving media having low degrees of surface smoothness and that produces high print quality at high-speed printing by permitting the heat-softening layer to be rapidly transferred from the support onto the receiving media.

As word processors and other thermal transfer recording apparatus have become common printing tools in business and various other fields today, thermal transfer recording media having heat softening layer formed on a support have come to be used extensively. With the existing thermal transfer recording media, however, the print quality is highly susceptible to the influence of the surface smooth of receiving media (e.g. receiving sheet) and printed images cannot be efficiently fixed. Further, the deterioration of print quality is aggravated at increased printing speeds.

With a view to improving the fixability of printed images, various attempts have been made, chiefly on the basis of employing a multi-layered heat-softening layer in thermal transfer recording media or adding various additives to that layer. For example, it has been proposed that the heat-softening layer of a thermal transfer recording medium be formed of a dual structure consisting of an intermediate layer and a heat-fusible ink layer, with the intermediate layer which is the closer to a support being made of a material that has a lower melting point than the material of which the remote heat-fusible ink layer is made (see Unexamined Published Japanese Patent Application No. 60-189492). In this thermal transfer recording medium, release from the support is compensated by the intermediate layer, so compared to thermal transfer recording media having no such intermediate layer, the melting point of the heat-fusible ink layer can be sufficiently increased to achieve relative improvement in the fixability of printed image. However, even this thermal transfer recording medium is still unsatisfactory in terms of adhesion to receiving media and, in particular, when printing is done on receiving media having low degrees of surface smoothness or if it is done at high speed, background fouling or streaking is highly likely to occur to cause deterioration in print quality.

The present invention has been accomplished under these circumstances and its principal object is to provide a thermal transfer recording medium that has not only high resolving power but also sufficient adhesion to allow prints to be fixed efficiently onto receiving media having low degrees of surface smoothness and that produces high print quality at high-speed printing by permitting the heat-softening layer to be rapidly transferred from the support onto the receiving media.

In order to attain this object, the present inventors conducted intensive studies and found that a thermal transfer recording medium that has a specified first and a second heat-softening layer formed on a support has not only high resolving power but also sufficient adhesion to allow prints to be fixed efficiently onto receiving media having low degrees of surface smoothness and that produces high print quality at high-speed printing by permitting the heat-softening layer to be rapidly transferred from the support onto the receiving media. The present invention has been accomplished on this finding.

The present invention provides a thermal transfer recording medium that comprises a support coated with a first heat-softening layer which in turn is coated with a second heat-softening layer, and in this recording medium, the first heat-softening layer contains a heat-fusible material and the second heat-softening layer contains a polymer based on an alkyl (meth) acrylate ester.

The thermal transfer recording medium of the present invention has at least a first heat-softening layer and a second heat-softening layer formed on a support, with the first heat-softening layer being overlaid with the second heat-softening layer. the thermal transfer recording medium of the present invention may have other layers to the extent that will not compromise the characteristics of said recording medium. For example, the first heat-softening layer may be formed on the support, with a release layer or some other layer being interposed. Alternatively, an intermediate or some other layer may be provided under the second heat-softening layer.

The components of the thermal transfer recording medium of the present invention are described hereinafter in the order of the support, the first heat-softening layer and the second heat-softening layer.

Support

The support used in the thermal transfer recording medium of the present invention desirably has high heat resistance and good dimensional stability. The support may be made of various materials selected from the following: paper substrates such as plain paper, capacitor paper, laminated paper and coated paper; resin films such as polyethylene, polyethylene terephthalate, polystyrene, polypropylene and polyimide; composites of paper and resin films; and metal sheets such as an aluminum foil. Any of these materials may be used with advantage.

The support generally has a thickness of no more than 30 μm , with the range of 2 - 30 μm being preferred. If the thickness of the support exceeds 30 μm , heat conductivity decreases, causing occasional deterioration of the print quality.

The back side of the support may have any layer arrangement and if desired, it may be provided with a backing layer such as an anti-sticking layer.

The first heat-softening layer to be described below is formed on the support either in direct contact with the latter or with a conventionally known release layer or anchor layer interposed.

First heat-softening layer

One of the important features of the present invention is that the first heat-softening layer containing at least a heat-fusible material is provided between the support and the second heat-softening layer to be described later in this specification.

The first heat-softening layer provided in the present invention can be separated rapidly from the support to insure faster printing with the thermal transfer recording medium of the present invention.

This nature of the first heat-softening layer is principally imparted by the heat-fusible material contained in it.

Specific examples of the heat-fusible materials that can be used include: vegetable waxes such as carnauba wax, Japan wax, ouricury wax and esparto wax; insect and animal waxes such as bees wax, insect wax, shelleac and spermaceti wax; petroleum waxes such as paraffin wax, microcrystalline wax, polyethylene wax, ester waxes and acid waxes; and mineral waxes such as montan wax, ozokerite and ceresin. Other heat-fusible materials that can be used include: higher aliphatic acids such as palmitic acid, stearic acid, margaric acid and behenic acid; higher alcohols such as palmityl alcohol, stearyl alcohol, behenyl alcohol, margaryl alcohol, myricyl alcohol and eicosanol; higher aliphatic acid esters such as cetyl palmitate, myricyl palmitate, cetyl stearate and myricyl stearate; amides such as acetamide, propionic acid amide, palmitic acid amide, stearic acid amide and amide wax; and higher amines such as stearylamine, behenylamine and palmitylamine. These heat-fusible materials may be used either independently or as admixtures.

Among the waxes listed above, those which have melting points within the range of 50 - 100 °C as measured with Yanagimoto Model MJP-2 are preferred.

The first heat-softening layer contains the heat-fusible material in an amount that usually ranges from 5 to 95 wt%, preferably from 50 to 90 wt%, more preferably from 60 to 80 wt%, of the total amount of the composition of which the first heat-softening layer is made.

Besides the heat-fusible materials described above, the first heat-softening layer may contain a thermoplastic resin. Illustrative thermoplastic resins that can be used include: resins such as ethylenic copolymers, polyamide resins, polyester resins, polyurethane resins, polyolefinic resins, acrylic resins, vinyl chloride resins, cellulosic resins, rosin resins, ionomer resins and petroleum resins; elastomers such as natural rubber, styrene/butadiene rubber, isoprene rubber, chloroprene rubber and diene containing copolymers; rosin derivatives such as ester gum, rosin/maleic acid resin, rosin/phenolic resin and hydrogenated rosin; and high-molecular weight compounds having a softening point of 50 - 150 °C such as phenolic resins, terpene resins, cyclopentadiene resins and aromatic hydrocarbon resins. These thermoplastic resins may be used either on their own or as admixtures.

Among the various thermoplastic resins listed above, acrylic resins, diene-containing co-polymers and ethylenic copolymers are preferred since their use enable the production of thermal transfer recording media that yield good print quality at high speed. These preferred thermoplastic resins are described below more specifically.

Exemplary acrylic resins are those which are obtained by copolymerizing monobasic carboxylic acids (e.g. methacrylic acid) or esters thereof with at least one of the compounds that are capable of copolymerizing with such monobasic carboxylic acids or esters thereof. Illustrative monobasic carboxylic acids and esters thereof include: (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, amyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, hydroxyethyl

(meth)acrylate and hydroxyethyl (meth)acrylate. Examples of the compounds that are capable of copolymerizing with these monobasic carboxylic acids and esters thereof include: vinyl acetate, vinyl chloride, vinylidene chloride, maleic anhydride, fumaric anhydride, styrene, 2-methylstyrene, chlorostyrene, acrylonitrile, vinyltoluene, N-methylol(meth)acrylamide, N-butoxymethyl (meth)acrylamide, vinylpyridine, and N-vinylpyrrolidone.

Exemplary diene-containing copolymers include: a butadiene-styrene copolymer, a butadiene-styrene-vinylpyridine copolymer, a butadiene-acrylonitrile copolymer, a chloroprene-styrene copolymer and a chloroprene-acrylonitrile copolymer.

Exemplary ethylenic copolymers include: an ethylene-vinyl acetate copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-methyl methacrylate copolymer, an ethylene-isobutyl acrylate copolymer, an ethylene-acrylic acid copolymer, an ethylene-vinyl alcohol copolymer, an ethylene-vinyl chloride copolymer and an ethylene-metal acrylate copolymer.

These thermoplastic resins may be used either on their own or as admixtures.

The first heat-softening layer contains the thermoplastic resin in an amount that usually ranges from 0.5 to 30 wt%, preferably from 1 to 20 wt%, more preferably from 2 to 15 wt%.

To control its releasability, the first heat-softening layer may also contain a surfactant such as a polyoxyethylene chain containing compound.

If desired, inorganic or organic fine particles (e.g. metal powderes and silica gel) or oils (e.g. linsed oil and mineral oils) may be incorporated in the first heat-softening layer.

In the thermal transfer recording medium of the present invention, the first heat-softening layer may contain a colorant. Illustrative colorants include pigments, both inorganic and organic, and dyes. Exemplary inorganic pigments include titanium dioxide, carbon black, zinc oxide, Prussian Blue, cadmium sulfide, iron oxide, as well as chromates of lead, zinc, barium and calcium. Exemplary organic pigments include pigments such as azo, thioindigoid, anthraquinose, anthanthrone and triphenyl dioxazine compounds, vat pigments, phthalocyanine dyes such as copper phthalocyanine, derivatives thereof, and quinacridone pigments. Exemplary dyes include acid dyes, direct dyes, disperse dyes, oil-soluble dyes, and metal-containing oil-soluble dyes.

If the first heat-softening layer is to contain colorants, their content usually ranges from 5 to 30 wt%, preferably from 10 to 25 wt%.

The first heat-softening layer can be formed by various coating techniques such as hot-melt coating, water-based coating and coating with the aid of organic solvents.

The thickness of the first heat-softening layer formed on the support by these coating methods is usually within the range of 0.6 - 8.0 μm , preferably in the range of 1.0 - 5.0 μm .

The thus formed first heat-softening layer is overlaid with the second heat-softening layer to be described below, either in direct contact with each other or with another layer such as an intermediate layer being interposed.

Second heat-softening layer

Another important feature of the present invention is that the second heat-softening layer which contains at least a polymer based on an alkyl (meth)acrylate ester (which is hereinafter sometimes referred to as "resin A") is formed on the above-described first heat-softening layer, either in direct contact with the latter or with a suitable layer such as an intermediate layer being interposed.

The second heat-softening layer used in the present invention has strong adhesion to receiving media such as rough paper having low degrees of surface smoothness and this insures sufficiently good fixability of prints to produce images of high quality.

This nature of the second heat-softening layer is principally imparted by resin A incorporated in it. Stated more specifically, when the second heat-softening layer is heated with, for example, the thermal head on a printer, resin A allows it to become soft enough to exhibit improved adhesion to receiving media.

Resin A can be obtained by polymerizing alkyl acrylates and/or alkyl methacrylates. Exemplary alkyl acrylates include: methyl acrylate, ethyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl acrylate, hydroxyethyl acrylate, polyethylene glycol diacrylate and trimethylolpropane triacrylate. Exemplary alkyl methacrylates include: methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, hexyl methacrylate, octyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate, hydroxyethyl methacrylate, polyethylene glycol dimethacrylate and trimethylolpropane trimethacrylate.

In order to impart other characteristics such as improved dispersibility of colorants, resin A may be prepared by copolymerizing the alkyl (meth)acrylates described above with other monomers. Examples of such comonomers include acrylic acid, methacrylic acid, maleic anhydride, etc.

Resin A preferably has a weight average molecular weight (Mw) of at least 200,000. If this condition is met, the desired advantage of the present invention can be attained more efficiently.

The second heat-softening layer contains resin A in an amount that usually ranges from 1 to 90 wt%, more preferably from 5 to 80 wt%.

The second heat-softening layer preferably contains a heat-softening resin having a softening point of 60 - 100 °C as an additional component. If the second heat-softening layer contains such a heat-softening resin, the desired advantage of the present invention can be attained more efficiently.

The heat-softening resin having a softening point of 60 - 100 °C is preferably at least one resin selected from the group consisting of polyester resins, phenolic resins, polystyrene resins, styreneacrylic resins, ketone resins and resin-modified resins.

The second heat-softening layer preferably contains an ethylene-vinyl acetate copolymer, with a vinyl acetate content of at least 28 wt%, preferably at least 35 wt%, or a derivative thereof (which ethylene-vinyl acetate copolymer or derivative thereof is hereinafter sometimes referred to as "resin B").

It is also preferred that the second heat-softening layer contains an ethylene-ethyl acrylate copolymer, with an ethyl acrylate content of at least 28 wt%, preferably at least 35 wt%, or a derivative thereof (which ethylene-ethyl acrylate copolymer or derivative thereof is hereinafter sometimes referred to as "resin C").

In yet another preferred embodiment, the second heat-softening layer contains an ethylene-methyl methacrylate copolymer, with a methyl methacrylate content of at least 28 wt%, preferably at least 35 wt%, or a derivative thereof (which ethylene-methyl methacrylate copolymer or derivative thereof is hereinafter sometimes referred to as "resin D").

If the second heat-softening layer contains at least one of resins B, C and D, it will become sufficiently soft upon heating to provide further enhanced adhesion to receiving media and this insures even more efficient fixation of printed images.

The ethylene-vinyl acetate copolymer or derivatives thereof that can advantageously be used in the present invention are not limited to any particular type as long as they have a vinyl acetate content of at least 28 wt%. For example, they may be an ethylene-vinyl acetate copolymer (EVA) obtained by reacting ethylene with vinyl acetate in the presence of an organic peroxide or oxygen, or they may be a graft-modified terpolymer obtained from EVA by reaction in the presence of a catalyst, an alcohol and an unsaturated carboxylic acid.

The ethylene-ethyl acrylate copolymer or derivatives thereof that can advantageously be used in the present invention are not limited to any particular type as long as they have an ethyl acrylate content of at least 28 wt%. For example, they may be an ethylene-ethyl acrylate copolymer (EEA resin) obtained by polymerization reaction between ethylene and ethyl acrylate, or they may be derivatives of the EEA resin.

The ethylene-methyl methacrylate copolymer or derivatives thereof are also not limited to any particular type as long as they have a methyl methacrylate content of at least 28%. For example, they may be an ethylene-methyl methacrylate copolymer (EMMA resin) obtained by polymerization reaction between ethylene and methyl methacrylate, or they may be derivatives of the EMMA resin.

Besides resin A, the second heat-softening layer preferably contains the heat-softening resin described above, as well as resins B, C and D. If desired, it may further contain a heat-fusible material, other thermoplastic resins, and a surfactant such as a polyoxyethylene-chain containing compound. These additional components may be selected from among those which can be used in the already described first heat-softening layer and any of them can also be used with advantage in the second heat-softening layer.

The second heat-softening layer may also contain a colorant. It should, however, be noted that if the content of colorant in the second heat-softening layer is excessive, the adhesion of the second heat-softening layer to a receiving medium will sometimes decrease, causing occasional deterioration in the efficiency of print fixation during high-speed printing with the thermal transfer recording medium of the present invention. Therefore, if a colorant is to be incorporated in the second heat-softening layer, its content generally is not higher than 30 wt%, preferably not higher than 25 wt%. The colorant that can be incorporated in the second heat-softening layer may be selected from among those colorants which can be incorporated in the already described first heat-softening layer.

The second heat-softening layer can be formed on the first heat-softening layer, either in direct contact with the latter or with another intermediate layer interposed, by using any of the coating methods that can be employed in forming the first heat-softening layer, and a particularly advantageous method is the one using organic solvents.

The thickness of the thus formed second heat-softening layer generally ranges from 0.1 to 3 μm,

preferably from 0.3 to 2 μm .

Other layers

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The thermal transfer recording medium of the present invention may adopt various layer arrangements. For example, a conventionally known release or anchor layer may be provided between the support and the first heat-softening layer. If desired, an intermediate layer may be provided between the first heat-softening layer and the second heat-softening layer. An overcoating layer may be formed over the second heat-

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softening layer. An advantageous overcoating layer may be a colorant-free wax or polymer layer. After forming the necessary layers in the manner described above, the web is optionally dried, has its surface smoothed and otherwise processed before it is cut to a desired shape and size to make the thermal transfer recording medium of the present invention. The thus obtained thermal transfer recording medium may be used in a suitable form such as tape or a ribbon on typewriters.

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The thermal transfer recording medium of the present invention may be processed by any of the thermal transfer methods that are commonly employed to perform thermal transfer recording. The following explanation assumes the case of using a thermal head which is the most typical heat source.

First, the heat-softening layer in the thermal transfer recording medium is brought into intimate contact with a receiving medium, say, receiving sheet. Heat pulses are applied from the heat-softening layer, with additional heat pulses being applied, as required, to the back side of the receiving sheet by means of a

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platen, so that the heat-softening layer is locally heated according to a desired printing or transfer pattern. The temperature of the heated areas of the heat-softening layer rises so that it rapidly softens and is transferred onto the receiving sheet. Since the first heat-softening layer contains the heat-fusible material described herein, it will separate rapidly from the support even if printing is done at high speed. Further, the second heat-softening layer contains resin A as an essential ingredient, so it exhibits strong adhesion to receiving media if they have a low degree of surface smoothness and this leads to the formation of high-

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quality prints by insuring effective fixation of printed images.

Examples

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The following examples and comparative examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

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Example 1

A first heat-softening layer was formed on a polyethylene terephthalate film 3.5 μm thick by coating it with a composition for the first heat-softening layer (for its formula, see below) to give a dry thickness of 2.0

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μm . The application of said composition was conducted by a hot-melt coating method using a wire bar.

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Composition for the First Heat-softening Layer	
Carbon black	15 wt%
Paraffin wax (m.p. 70° C)	70 wt%
Ethylene-vinyl acetate copolymer (vinyl acetate content, 20 wt%)	15 wt%

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Subsequently, a second heat-softening layer was formed on the first heat-softening layer by coating it with a composition for the second heat-softening layer (for its formula, see below) to give a dry thickness of 1.5 μm .

The application of said composition was conducted by a coating method using an organic solvent (MEK, 35° C).

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Composition for the Second Heat-softening Layer	
Poly (stearyl acrylate) (average molecular weight, Mw = 180,000)	80 wt%
Carbon black	20 wt%

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The thus fabricated thermal transfer recording medium was set in a commercial high-speed printer (24-dot-serial head; energy application, 25 mJ/head) and alphabets were transferred (printed) onto sheets of copy paper and Lancaster paper (Bekk smoothness, 2 sec) to evaluate the high-speed printability of the medium with respect to rough paper. The results are shown in Table 1.

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The procedure of high-speed printability evaluation was as follows.

15 High-speed printability

Printing was conducted at a platen pressure of 350 g/head, with the printing speed being varied as shown in Table 1. The print quality of the image obtained was visually evaluated. The fixation of the printed image was also evaluated by performing a peel test with an adhesive tape ("Post-it" of Sumitomo 3M, Ltd.)

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The symbols used in Table 1 respectively have the following meanings:

Print quality

⊙, no void or interruption of characters, with improved edge sharpness;

○, no void or interruption of characters;

Δ, some voids;

×, too many voids to produce legible characters.

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Image fixation

⊙, no change at all in the print after tape was pulled off;

○, practically no change in the print after tape was pulled off;

Δ, some ink separation occurred;

×, printed characters were dislodged.

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Example 2

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The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

Composition for the second heat-softening layer	
Poly(ethyl methacrylate) (average molecular weight, Mw = 85,000)	85 wt%
Carbon black	15 wt%

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Example 3

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

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Composition for the second heat-softening layer	
Poly(buthyl methacrylate) (average molecular weight, Mw = 360,000)	40 wt%
Ethylene-vinyl acetate copolymer (vinyl acetate content, 35 wt%)	40 wt%
Carbon black	20 wt%

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Example 4

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

Composition for the second heat-softening layer	
Poly(buthyl methacrylate) (average molecular weight, Mw = 360,000)	30 wt%
Resin modified resin (s.p. 90 ° C)	50 wt%
Carbon black	20 wt%

Example 5

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below, and that the thickness of the second heat-softening layer was changed from 1.5 to 0.7 μm . The results are shown in Table 1.

Composition for the second heat-softening layer	
Poly(stearyl acrylate) (average molecular weight, Mw = 300,000)	30 wt%
Ketone resin (s.p. 90 ° C)	50 wt%
Carbon black	20 wt%

Example 6

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

Composition for the second heat-softening layer	
Poly(buthyl methacrylate) (average molecular weight, Mw = 360,000)	30 wt%
Ethylene-vinyl acetate copolymer (vinyl acetate content, 35 wt%)	20 wt%
Resin modified resin (s.p. 90 ° C)	50 wt%

Example 7

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

Composition for the second heat-softening layer	
Poly(ethyl methacrylate) (average molecular weight, Mw = 480,000)	20 wt%
Ethylene-ethyl acrylate copolymer (ethyl acrylate content, 35 wt%)	40 wt%
Ketone resin (s.p. 90 ° C)	20 wt%
Carbon black	20 wt%

Example 8

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

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Composition for the second heat-softening layer	
Poly(butyl methacrylate) (average molecular weight, Mw = 230,000)	30 wt%
Ethylene-methyl methacrylate copolymer (methyl methacrylate content, 38 wt%)	20 wt%
Alkylphenolic resin (s.p. 75 °C)	30 wt%
Carbon black	20 wt%

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Example 9

The procedure of Example 1 was repeated except that the composition for the second heat-softening layer was replaced by the formula shown below. The results are shown in Table 1.

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Composition for the second heat-softening layer	
Poly(butyl methacrylate) (average molecular weight, Mw = 360,000)	25 wt%
Ethylene-vinyl acetate copolymer (vinyl acetate content, 40 wt%)	20 wt%
Rosin modified resin (s.p. 80 °C)	30 wt%
Polystyrene resin (s.p. 80 °C)	25 wt%

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Comparative Example 1

A thermal transfer recording medium was fabricated by repeating the procedure of Example 1 except that the composition for the second heat-softening layer was replaced by the formula shown below. The high-speed printability of this medium on rough paper was evaluated as in Example 1. The results are shown in Table 1.

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Composition for the second heat-softening layer	
Ethylene-vinyl acetate copolymer (vinyl acetate content, 40 wt%)	80 wt%
Carbon black	20 wt%

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Comparative Example 2

A thermal transfer recording medium was fabricated by repeating the procedure of Example 1 except that the composition for the second heat-softening layer was replaced by the formula shown below. The high-speed printability of this medium on rough paper was evaluated as in Example 1. The results are shown in Table 1.

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Composition for the second heat-softening layer	
Ethylene-vinyl acetate copolymer (vinyl acetate content, 40 wt%)	40 wt%
Resin-modified resin (s.p. 80 °C)	40 wt%
Carbon black	20 wt%

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Comparative Example 3

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A thermal transfer recording medium was fabricated by repeating the procedure of Example 1 except that the composition for the second heat-softening layer was replaced by the formula shown below. The high-speed printability of this medium on rough paper was evaluated as in Example 1. The results are shown in Table 1.

Composition for the second heat-softening layer	
Ethylene-vinyl acetate copolymer (vinyl acetate content, 40 wt%)	20 wt%
Ketone resin (s.p. 90 °C)	30 wt%
Polystyrene (s.p. 80 °C)	30 wt%
Carbon black	20 wt%

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Table 1

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	Printing speed (cps)							
	10				30			
	Copy paper		Lancaster paper		Copy paper		Lancaster paper	
	Print quality	Fixation	Print quality	Fixation	Print quality	Fixation	Print quality	Fixation
Example 1	⊙	⊙	⊙	○	○	○	○	Δ
2	⊙	⊙	⊙	○	○	○	○	Δ
3	⊙	⊙	⊙	⊙	⊙	⊙	○	○
4	⊙	⊙	⊙	⊙	⊙	⊙	○	○
5	⊙	⊙	⊙	⊙	⊙	⊙	○	○
6	⊙	⊙	⊙	⊙	⊙	⊙	○	○
7	⊙	⊙	⊙	⊙	⊙	⊙	○	○
8	⊙	⊙	⊙	⊙	⊙	⊙	○	○
9	⊙	⊙	⊙	⊙	⊙	⊙	○	○
Comparative Example 1	○	○	○	Δ	○	Δ	Δ	×
2	○	○	Δ	Δ	Δ	Δ	×	×
3	○	○	Δ	Δ	Δ	Δ	×	×

As is clear from Table 1, the thermal transfer recording media fabricated in accordance with the present invention could successfully be used in high-speed printing on Lancaster paper and other receiving media that had low degrees of surface smoothness and images were effectively fixed to produce satisfactory print quality.

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Advantages of the Invention

The thermal transfer recording medium of the present invention has at least a first heat-softening layer and a second heat-softening layer on a support and it offers the following advantages.

(1) The first heat-softening layer contains at least a heat-fusible material and can be separated efficiently from the support upon heating. Therefore, it allows for high-speed printing with improved response and higher resolution.

(2) The second heat-softening layer contains at least a polymer based on an alkyl (meth)acrylate ester, so it exhibits satisfactory adhesion to receiving media even if they have low degrees of surface smoothness, and this leads to the formation of high-quality prints by insuring effective fixation of printed images.

(3) The recording medium of the present invention is highly adaptive to high-speed printing since it will experience only limited deterioration in print quality even if the printing speed is increased.

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Claims

1. In a thermal transfer recording medium that comprises a support coated with a first heat-softening layer which in turn is coated with a second heat-softening layer, the improvement wherein said first heat-softening layer contains a heat-fusible material and said second heat-softening layer contains a polymer based on an alkyl (meth)acrylate ester.

2. A thermal transfer recording medium according to claim 1 wherein said polymer based on an alkyl acrylate ester is obtained by polymerizing at least one monomer selected from the group consisting of methyl acrylate, ethyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate 2-ethylhexyl acrylate, decyl acrylate, dodecyl acrylate, hydroxyethyl acrylate, polyethylene glycol diacrylate and trimethylolpropane triacrylate.

3. A thermal transfer recording medium according to claim 1 wherein said polymer based on an alkyl methacrylate ester is obtained by polymerizing at least one monomer selected from the group consisting of methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, hexyl methacrylate, octyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate, hydroxyethyl methacrylate, polyethylene glycol dimethacrylate and trimethylolpropane trimethacrylate.

4. A thermal transfer recording medium according to claim 1 or 2 wherein said polymer based on an alkyl (meth)acrylate ester has a weight average molecular weight of at least 200,000.

5. A thermal transfer recording medium according to claim 1, 2 or 3 wherein said polymer based on an alkyl (meth)acrylate ester is contained in said second heat-softening layer in an amount ranging from 1 to 90 wt%.

6. A thermal transfer recording medium according to claim 1 or 5 wherein said polymer based on an alkyl (meth)acrylate ester is contained in said second heat-softening layer in an amount ranging from 5 to 80 wt%.

7. A thermal transfer recording medium according to claim 1 or any of claims 2 to 6 wherein said second heat-softening layer contains a heat-softening resin having a softening point of 60-100 °C.

8. A thermal transfer recording medium according to claim 7 wherein said heat-softening resin is at least one member selected from the group consisting of polyester resins, phenolic resins, polystyrene resins, styrene-acrylic resins, ketone resins and resin-modified resins.

9. A thermal transfer recording medium according to claim 1 or any of claims 2 to 8 wherein second heat-softening layer contains an ethylene-vinyl acetate copolymer with a vinyl acetate content of at least 28 wt% or a derivative thereof.

10. A thermal transfer recording medium according to claim 1 or any of claims 2 to 8 wherein said second heat-softening layer contains an ethylene-ethyl acrylate copolymer with an ethyl acrylate content of at least 28 wt% or a derivative thereof.

11. A thermal transfer recording medium according to claim 1 or any of claims 2 to 8 wherein said

second heat-softening layer contains an ethylene-methyl methacrylate copolymer with a methyl methacrylate content of at least 28 wt% or a derivative thereof.

12. A thermal transfer recording medium according to claim 1 or any of claims 2 to 11 wherein said second heat-softening layer contains a colorant.

5 13. A thermal transfer recording medium according to claim 12 wherein said colorant is an inorganic pigment, an organic pigment or a dye.

14. A thermal transfer recording medium according to claim 13 wherein said inorganic pigment is at least one member selected from the group consisting of titanium dioxide, carbon black, zinc oxide, Prussian Blue, cadmium sulfide, iron oxide and a chromate of lead, zinc, barium or calcium.

10 15. A thermal transfer recording medium according to claim 13 wherein said organic pigment is selected from the group consisting of azo pigments, thioindigoid pigments, anthraquinone pigments, anthanthrone pigments, triphenyl dioxazine pigments, vat pigments, phthalocyanine pigments and quinacridone pigments.

16. A thermal transfer recording medium according to claim 13 wherein said dye is selected from the group consisting of acid dyes, direct dyes, disperse dyes, oil-soluble dyes and metal-containing oil-soluble dyes.

17. A thermal transfer recording medium according to claim 12 or any of claims 13 to 16 wherein said colorant is contained in said second heat-softening layer in an amount of no more than 30 wt%.

18. A thermal transfer recording medium according to claim 1 or any of claims 2 to 17 wherein said second heat-softening layer has a thickness of 0.1 - 3 μm .

19. A thermal transfer recording medium according to claim 1 or 18 wherein said second heat-softening layer has a thickness of 0.3 - 2 μm .

20. A thermal transfer recording medium according to claim 1 or any of claims 2 to 19 wherein said heat-fusible material is selected from among waxes, higher aliphatic acids, higher alcohols, higher aliphatic acid esters, amides, and higher amines.

21. A thermal transfer recording medium according to claim 1 or any of claims 2 to 20 wherein said heat-fusible material has a melting point of 50 - 100°C.

22. A thermal transfer recording medium according to claim 1 or any of claims 2 to 21 wherein said heat-fusible material is contained in said first heat-softening layer in an amount ranging from 5 to 95 wt%.

23. A thermal transfer recording medium according to claim 1 or 22 wherein said heat-fusible material is contained in said first heat-softening layer in an amount ranging from 50 to 90 wt%.

24. A thermal transfer recording medium according to claim 1 or any of claims 2 to 23 wherein said first heat-softening layer contains a thermoplastic resin selected from among acrylic resins, diene-containing copolymers and ethylenic copolymers.

25. A thermal transfer recording medium according to claim 24 wherein said thermoplastic resin is contained in said first heat-softening layer in an amount ranging from 0.5 - 30 wt%.

26. A thermal transfer recording medium according to claim 1 or any of claims 2 to 25 wherein said first heat-softening layer contains a colorant.

27. A thermal transfer recording medium according to claim 26 wherein said colorant is an inorganic pigment, an organic pigment or a dye.

28. A thermal transfer recording medium according to claim 27 wherein said inorganic pigment is at least one member selected from the group consisting of titanium dioxide, carbon black, zinc oxide, Prussian Blue, cadmium sulfide, iron oxide and a chromate of lead, zinc, barium or calcium.

29. A thermal transfer recording medium according to claim 27 wherein said organic pigment is selected from the group consisting of azo pigments, thioindigoid pigments, anthraquinone pigments, anthanthrone pigments, triphenyl dioxazine pigments, vat pigments, phthalocyanine pigments and quinacridone pigments.

30. A thermal transfer recording medium according to claim 27 wherein said dye is selected from the group consisting of acid dyes, direct dyes, disperse dyes, oil-soluble dyes and metal-containing oil-soluble dyes.

31. A thermal transfer recording medium according to claim 26 or any of claims 27 to 30 wherein said colorant is contained in said first heat-softening layer in an amount ranging from 5 to 30 wt%.

32. A thermal transfer recording medium according to claim 1 or any of claims 2 to 31 wherein said first heat-softening layer has a thickness of 0.6 - 8.0 μm .

33. A thermal transfer recording medium according to claim 1 or 32 wherein said first-heat-softening layer has a thickness of 1.0 - 5.0 μm .

34. A thermal transfer recording medium according to claim 1 or any of claims 2 or 33 wherein said support is made of paper, resin films, composites of paper and resin films, or a metal sheet.

35. A thermal transfer recording medium according to claim 1 or any of claims 2 to 34 wherein said

support has a thickness of 2 - 30 μm .

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