(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 761 462 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.03.1997 Bulletin 1997/11

(51) Int. Cl.^{6}: **B41M 5/38**

(21) Application number: **96112490.6**

(22) Date of filing: **02.08.1996**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **03.08.1995 JP 198596/95**

(71) Applicant: **FUJICOPIAN CO., LTD.**
Osaka-shi, Osaka-fu (JP)

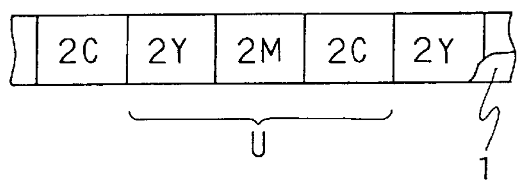
(72) Inventors:
- **Tago, Yasuo,**
  Techn. Ctr. of Fujicopian Co., Ltd.
  Osaka-shi, Osaka-fu (JP)
- **Tsuboi, Seiji,**
  Techn. Ctr. of Fujicopian Co., Ltd.
  Osaka-shi, Osaka-fu (JP)
- **Kurokawa, Kenji,**
  c/o Fujicopian Co., Ltd.
  Osaka-shi, Osaka-fu (JP)
- **Ikeda, Naohiro,**
  c/o Fujicopian Co., Ltd.
  Osaka-shi, Osaka-fu (JP)

(74) Representative: **Türk, Gille, Hrabal, Leifert**
Brucknerstrasse 20
40593 Düsseldorf (DE)

(54) Thermal transfer recording material

(57) A thermal transfer recording material is provided which comprises a foundation and, provided thereon, a heat-meltable ink layer comprising at least a heat-meltable material and a coloring agent, the heat-meltable material comprising 30 to 90 % by weight of an epoxy resin and 10 to 70 % by weight of an acrylic resin having a number average molecular weight of 30,000 to 300,000.

FIG. 1



EP 0 761 462 A1

Description

The present invention relates to thermal transfer recording materials for providing printed images having excellent fastness on diverse receptors.

Conventional thermal transfer recording materials, in general, include those comprising a foundation and, applied onto the foundation, a heat-meltable ink containing a vehicle composed mainly of a wax or another type of heat-meltable ink containing a vehicle composed mainly of a resin for ensuring printed images of good quality even on paper sheets having relatively poor surface smoothness or printed images of high scratch resistance.

Recently, bar code printers and label printers using thermal transfer recording materials have been used to print bar codes or like codes for management of parts or products in production processes of manufacturing factories, merchandise management in distribution field, management of articles at using sites, and the like. When used in, for example, distribution field, bar codes are frequently scratched or rubbed. Therefore, such bar codes are required to have particularly high scratch resistance.

As well as for the printing of bar codes, thermal transfer printers have been used in the production of diversified products in small quantities, including outdoor advertising materials, election posters, common posters, standing signboards, stickers, catalogs, pamphlets, calenders and the like in the commercial printing field; bags for light packaging, labels of containers for foods, drinks, medicines, paints and the like, and binding tapes in the packaging field; and labels for indicating quality characteristics, labels for process control, labels for product management and the like in the apparel field. These articles are also required to exhibit scratch resistance.

With respect to the receptors on which bar codes are formed by the thermal transfer method, there were used specialized receptors such as polyethylene terephthalate film subjected to a special surface treatment. Recently, plastic films subjected to no surface treatment such as usual polyethylene terephthalate film and vinyl chloride resin film have also been used, which leads to diversification of receptors. More recently, cutting plotters begin to spread and printed films wherein printed images are formed on vinyl chloride resin films by the thermal transfer method are frequently used therefor.

With the conventional thermal transfer recording materials using the heat-meltable ink containing a vehicle composed mainly of a wax, however, resulting printed images exhibit poor scratch resistance though the ink enjoys satisfactory transferability (separability of the ink layer). On the other hand, with the conventional thermal transfer recording materials using the heat-meltable ink containing a vehicle composed mainly of a resin such as ethylene-vinyl acetate copolymer, the transferability of the ink is inferior to the former ink due to its relatively high melt viscosity though resulting printed images enjoy relatively high scratch resistance. Moreover, both of the thermal transfer recording materials provide printed images having poor adhesion to common plastic films, resulting in poor scratch resistance.

It is, therefore, an object of the present invention to provide a thermal transfer recording material which is capable of exhibiting satisfactory transferability (separability of the ink layer) while at the same time forming printed images having excellent adhesion to diverse plastic films and excellent scratch resistance.

The foregoing and other objects of the present invention will be apparent from the following detailed description.

According to the present invention, there is provided a thermal transfer recording material comprising a foundation and, provided thereon, a heat-meltable ink layer comprising at least a heat-meltable material and a coloring agent,

the heat-meltable material comprising 30 to 90 % by weight of an epoxy resin and 10 to 70 % by weight of an acrylic resin having a number average molecular weight of 30,000 to 300,000.

In an embodiment of the present invention, the epoxy resin comprises at least one member selected from the group consisting of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether.

In another embodiment of the present invention, the epoxy resin comprises at least one member selected from the group consisting of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether and bisphenol F diglycidyl ether.

In still another embodiment of the present invention, the acrylic resin has a glass transition point of 30° to 120°C .

Fig. 1 is a partial plan view showing an example of an arrangement of color ink layers of respective colors in an embodiment of the thermal transfer recording material of the present invention.

The present invention will now be described in detail.

In the present invention, the heat-meltable ink layer comprises at least a heat-meltable material and a coloring agent, the heat-meltable material comprising 30 to 90 % by weight, preferably 40 to 60 % by weight of an epoxy resin and 10 to 70 % by weight, preferably 40 to 60 % by weight of an acrylic resin having a number average molecular weight of 30,000 to 300,000.

The combination use of the epoxy resin and the high molecular weight acrylic resin in the specific ratio in the heat-meltable ink layer improves the adhesion of the ink to a variety of plastic films as well as the transferability (separability) of the ink layer as compared with the conventional resin-type ink layer, resulting in printed images having excellent scratch resistance and like property. Herein, the term "separability of a heat-meltable ink lalyer" means the property that when being transferred, the heated portion of a heat-meltable ink layer is easily separated from the unheated portion of the heat-meltable ink layer and only the heated portion is transferred on a receptor to give a sharp print image.

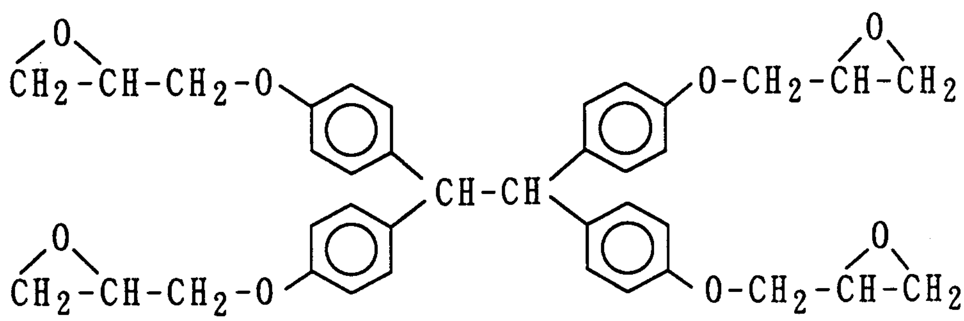
That is, the epoxy resin mainly contributes to the improvement of separability of the ink layer, leading to excellent transferability. The high molecular weight acrylic resin contributes to the improvement of scratch resistance of printed images formed on plastic films due to its excellent adhesion to a variety of plastic films and its excellent durability and toughness. Further, the ink layer is excellent in transparency, resulting in good adaptability to the formation of color images. In more detail, the use of such a high molecular weight acrylic resin as prescribed in the present invention is liable to degrade the separability of the resulting ink layer though the acrylic resin contributes to the improvement of scratch resistance of printed images. By virtue of the combination use of such a high molecular weight acrylic resin with an epoxy resin, however, it is made possible to obtain printed images having excellent scratch resistance while ensuring excellent separability of the ink layer.

When the proportion of the epoxy resin is smaller than the above range or the proportion of the acrylic resin is larger than the above range, the transferability of the ink layer is not satisfactorily improved because the amount of the epoxy resin contributing to an improvement in separability of the ink layer is small and the adhesion of the ink to the foundation is excessively strong. When the proportion of the epoxy resin is larger than the above range or the proportion of the acrylic resin is smaller than the above range, the fastness of the ink constituting printed images formed on various plastic films is not satisfactorily improved, resulting in poor scratch resistance.

The epoxy resin used in the present invention is not limited to particular one, and any usual epoxy resins can be used. From the viewpoints of dispersibility of a coloring agent and transferability of the resulting ink, however, the epoxy resin component preferably comprises not less than 50 % (% by weight, hereinafter the same), more preferably not less than 70 % of at least one epoxy resin selected from the group consisting of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether. Herein, the epoxy resin used in the present invention is intended to mean an epoxy resin in an uncured or non-crosslinked state.

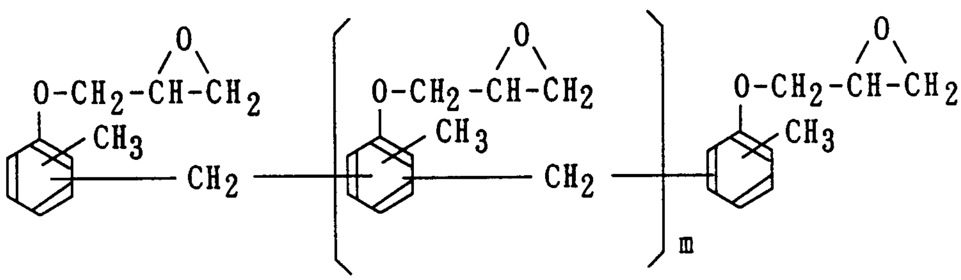
In the present invention it is particularly desirable that the epoxy resin component be entirely composed of at least one of the above-specified epoxy resins. It is, however, not necessarily required to do so, and the epoxy resin component comprising not less than 50 %, preferably not less than 70 % of at least one of the four specified epoxy resins can serve the purpose. If the proportion of such specified epoxy resin component in the overall epoxy resin is less than the foregoing range, poor dispersibility of a pigment in the heat-meltable material will result, thus deteriorating the transferability of the ink layer.

Tetraphenolethane tetraglycidyl ether (hereinafter referred to as "TPETGE" as the need arises) as aforementioned, having a softening point of 92°C, is a species of polyfunctional epoxy resins and represented by the formula (I):



(I)

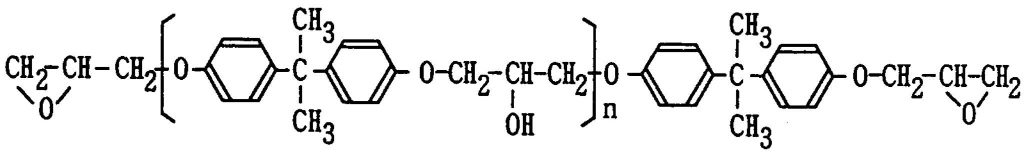
Cresol novolac polyglycidyl ether (hereinafter referred to as "CNPGE" as the need arises) as aforementioned is a species of polyfunctional epoxy resins. In the present invention examples of preferred cresol novolac polygylcidyl ethers include those represented by the formula (II):



(II)

wherein m is usually an integer of from 3 to 7. CNPGEs useful in the present invention include mixtures of those of the formula (II) wherein values for m are different from each other. CNPGE preferably has a softening point of 60° to 120°C.

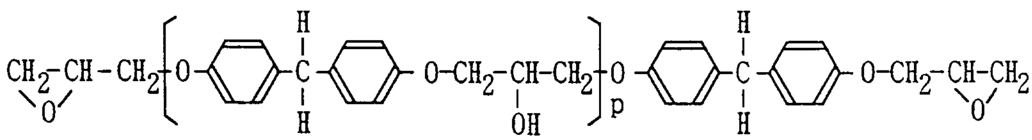
Bisphenol A diglycidyl ether (hereinafter referred to as "BPADGE" as the need arises) is a species of difunctional epoxy resins. Preferred are those represented by the formula (III):



(III)

wherein n is usually an integer of from 0 to 13. BPADGEs useful in the present invention include mixtures of those of the formula (III) wherein values for n are different from each other. BPADGE preferably has a softening point of 60° to 140°C .

Bisphenol F diglycidyl ether (hereinafter referred to as "BPFDGE" as the need arises) is a species of difunctional epoxy resins. Preferred are those represented by the formula (IV):



(IV)

wherein p is usually an integer of from 0 to 33. BPFDGEs useful in the present invention include mixtures of those of the formula (IV) wherein values for p are different from each other. BPFDGE preferably has a softening point of 60° to 140°C .

Examples of epoxy resins usable in combination with the aforementioned specified epoxy resins are:

(1) Glycidyl ether type epoxy resins including, for example, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, glycerol triglycidyl ether, pentaerythritol diglycidyl ether and naphthol-modified cresol novolac polyglycidyl ether;
(2) Glycidyl ether ester type epoxy resins including, for example, p-oxybenzoic acid glycidyl ether ester;
(3) Glycidyl ester type epoxy resins including, for example, phthalic acid diglycidyl ester, tetrahydrophthalic acid diglycidyl ester, hexahydrophthalic acid diglycidyl ester and dimer acid diglycidyl ester;
(4) Glycidyl amine type epoxy resins including, for example, glycidylaniline, triglycidyl isocyanurate and tetraglycidylaminodiphenylmethane;
(5) Linear aliphatic epoxy type epoxy resins including, for example, epoxidized polybutadiene and epoxidized soybean oil; and
(6) Alicyclic epoxy type epoxy resins including, for example, 3, 4-epoxy-6-methylcyclohexylmethyl 3, 4-epoxy-6-methylcyclohexanecarboxylate and 3, 4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate.

These epoxy resins may be used either alone or as mixtures of two or more species thereof. Preferable as epoxy resins usable in combination with the above-specified epoxy resins are those having softening points of not lower than 60°C. However, an epoxy resin in a liquid state can also be used so long as the overall heat-meltable material resulting from mixing it with the specified epoxy resin or the epoxy resin usable in combination therewith or the acrylic resin has a softening point of not lower than 60°C .

The acrylic resin usable in the present invention has a number average molecular weight of 30,000 to 300,000. More preferable are acrylic resins having a number average molecular weight of 30,000 to 150,000, particularly 40,000 to 150,000. When the number average molecular weight of the acrylic resin is smaller than the above range, the resulting ink is prone to provide printed images having unsatisfactory scratch resistance. When the number average molecular weight is larger than the above range, the resulting ink is prone to offer poor transferability. The acrylic resin preferably has a glass transition point of 30° to 120°C .

Examples of the acrylic resin include homopolymers or copolymers of one or more acrylic monomers such as (meth)acrylic acid, (meth)acrylic acid alkyl esters (wherein examples of the alkyl group are those having 1 to 25 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, amyl, octyl and stearyl), and (meth)acrylonitrile; and copolymers of one or more of the foregoing acrylic monomers and one or more other monomers copolymerizable therewith, such as styrene, butadiene, vinyl monomer containing siloxane bond and fluorine-containing vinyl monomer. Typical examples of the acrylic resins are, for instance, acrylic acid resin, methacrylic acid resin, alkyl acrylate resins, alkyl methacrylate resins, acrylonitrile resin, acrylonitrile-styrene copolymer resin and acrylonitrile-styrene-butadiene copolymer resin.

The heat-meltable material according to the present invention may be incorporated with one or more heat-meltable resins other than the above-mentioned so long as the purpose of the present invention is attained. Examples of such heat-meltable resins include ethylene-vinyl acetate copolymer resin, vinyl chloride-vinyl acetate copolymer resin, phenolic resin, polyester resin and polyamide resin. Such heat-meltable resins are used in an amount of preferably not greater than 30 %, more preferably not greater than 15 %, most preferably not greater than 5 %, based on the amount of the overall heat-meltable material.

The softening point of the overall heat-meltable material is preferably within the range of from 60° to 120°C in terms of the storage stability and transferability of the thermal transfer recording material.

The proportion of the overall heat-meltable material in the heat-meltable ink is preferably from about 40 to about 95 % in terms of the transferability and like properties of the ink layer.

Usable as the coloring agent in the present invention are various organic and inorganic pigments, inclusive of carbon black. Examples of such organic and inorganic pigments include azo pigments (such as insoluble azo pigments, azo lake pigments and condensed azo pigments), phthalocyanine pigments, nitro pigments, nitroso pigments, anthraquinonoid pigments, nigrosine pigments, quinacridone pigments, perylene pigments, isoindolinone pigments, dioxazine pigments, titanium white, calcium carbonate and barium sulfate. Such pigments may be used in combination with dyes. The proportion of the coloring agent in the ink layer is suitably within the range of from 5 to 60 %.

Yellow pigments, magenta pigments, and cyan pigments, and optionally black pigments are used for forming multicolor or full-color printed images utilizing subtractive color mixture.

The pigments for yellow, magenta and cyan for use in the ink layer are preferably transparent, while the pigments for black are usually opaque.

Examples of transparent yellow pigments include organic pigments such as Naphthol Yellow S, Hansa Yellow 5G, Hansa Yellow 3G, Hansa Yellow G, Hansa Yellow GR, Hansa Yellow A, Hansa Yellow RN, Hansa Yellow R, Benzidine Yellow, Benzidine Yellow G, Benzidine Yellow GR, Permanent Yellow NCG and Quinoline Yellow Lake. These pigments may be used either alone or in combination of two or more species thereof.

Examples of transparent magenta pigments include organic pigments such as Permanent Red 4R, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Carmine FB, Lithol Red, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Rhodamine Lake B, Rhodamine Lake Y, Arizalin Lake and Quinacridone Red. These pigments may be used either alone or in combination of two or more species thereof.

Examples of transparent cyan pigments include organic pigments such as Victoria Blue Lake, metal-free Phthalocyanine Blue, Phthalocyanine Blue and Fast Sky Blue. These pigments may be used either alone or in combination of two or more species thereof.

The term " transparent pigment" means a pigment which gives a transparent ink when dispersed in a transparent vehicle.

Examples of black pigments include inorganic pigments having insulating or conductive properties such as carbon black, and organic pigments such as Aniline Black. These pigments may be used either alone or in combination of two or more species thereof.

The proportion of the coloring agent in respective color ink layers is usually from about 5 to about 60 %.

When bisphenol A diglycidyl ether is used as the specified epoxy resin, it is preferable to use a pigment, such as carbon black, having an oil absorption of not less than 80. Pigments such as carbon black do not necessarily exert good dispersibility against bisphenol A diglycidyl ether. A pigment having an oil absorption of not less than 80 is good in dispersibility against bisphenol A diglycidyl ether and, hence, provides a heat-meltable ink wherein the pigment is uniformly dispersed and which exhibits good transferability. Herein, the term " oil absorption of a pigment" means the amount ($m\ell$) of dibutyl phthalate which is absorbed by 100 g of the pigment. With at least one of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether and bisphenol F diglycidyl ether, particularly at least one of tetraphenolethane tetraglycidyl ether and cresol novolac polyglycidyl ether among the above-specified epoxy resins, dispersibility of pigments such as carbon black is good regardless of the oil absorption of the pigment used.

In the present invention the heat-meltable ink layer may be incorporated with appropriate additives such as dispersing agent as well as the aforementioned ingredients.

The heat-meltable ink layer can be formed by applying onto a foundation a coating liquid prepared by dissolving the epoxy resin and the acrylic resin in a solvent which is capable of dissolving the resins or dispersing the epoxy resin and the acrylic resin in a solvent (inclusive of water) which is incapable of dissolving the resins and then dissolving or dispersing the coloring agent together with other additives, followed by drying.

The coating amount (on a solid basis, hereinafter the same) of the heat-meltable ink layer in the present invention is usually 0.02 to 5 g/m^2, preferably 0.5 to 3 g/m^2.

As the foundation for the thermal transfer recording material of the present invention, there can be used polyester films such as polyethylene terephthalate film, polybutylene terephthalate film, polyethylene naphthalate film, polybutylene naphthalate film and polyarylate film, polycarbonate film, polyamide film, aramid film, polyether sulfone film, polysulfone film, polyphenylene sulfide film, polyether ether ketone film, polyether imide film, modified polyphenylene ether film and polyacetal film, and other various plastic films commonly used for the foundation of ink ribbons of this type. Alternatively, thin paper sheets of high density such as condenser paper can also be used. The thickness of the foundation is usually from about 1 to about 10 μm. From the standpoint of reducing heat spreading to increase the resolution of printed images, the thickness of the foundation is preferably from 1 to 6 μm.

Where the thermal transfer recording material of the present invention is to be used in a thermal transfer printer with a thermal head, a conventionally known stick-preventive layer is preferably provided on the back side (the side to be brought into slide contact with the thermal head) of the foundation. Examples of materials for the stick-preventive layer include various heat-resistant resins such as silicone resins, fluorine-containing resins and nitrocellulose resins, and other resins modified with these heat-resistant resins such as silicone-modified urethane resins and silicone-modified acrylic resins, and mixtures of the foregoing heat-resistant resins and lubricating agents.

The term " thermal transfer recording material" as used herein means to include a thermal transfer recording material for forming monochromatic images, and a thermal transfer recording material for forming multi-color or full-color images utilizing subtractive color mixture.

The thermal transfer recording material for forming monochromatic images is of a structure in which a monochromatic heat-meltable ink layer is provided on a foundation. Colors for the monochromatic heat-meltable ink layer include black, red, blue, green, yellow, magenta and cyan.

An embodiment of the thermal transfer recording material for forming multi-color or full-color images is of a structure in which on a single foundation are disposed a yellow heat-meltable ink layer, a magenta heat-meltable ink layer and a cyan heat-meltable ink layer and, optionally, a black heat-meltable ink layer in a side-by-side relation. Such color ink layers can be disposed in various manners on a foundation depending on the kind of printer.

Fig. 1 is a partial plan view showing an example of the thermal transfer recording material according to the foregoing embodiment. As shown in Fig. 1, on a single foundation 1 are disposed a yellow heat-meltable ink layer 2Y, a magenta heat-meltable ink layer 2M and a cyan heat-meltable ink layer 2C in a side-by-side relation. These ink layers 2Y, 2M and 2C, each having a predetermined constant size, are periodically disposed longitudinally of the foundation 1 in recurring units U each comprising ink layers 2Y, 2M and 2C arranged in a predetermined order. The order of arrangement of these color ink layers in each recurring unit U can be suitably determined according to the order of transfer of the color ink layers. Each recurring unit U may comprise a black ink layer in addition to the layers 2Y, 2M and 2C.

Another embodiment of the thermal transfer recording material for forming multi-color or full-color images is a set of thermal transfer recording materials comprising a first thermal transfer recording material having a yellow heat-meltable ink layer on a foundation, a second thermal transfer recording material having a magenta heat-meltable ink layer on another foundation, and a third thermal transfer recording material having a cyan heat-meltable ink layer on yet another foundation, and, optionally a fourth thermal transfer recording material having a black heat-meltable ink layer on still another foundation.

The use of any of the foregoing embodiments of the thermal transfer recording materials will give multi-color or full-color images having excellent scratch resistance. Further, individual color heat-meltable ink layers in the present invention are excellent in superimposing properties, thus ensuring multi-color or full-color images of superior color reproducibility.

To form printed images using the thermal transfer recording material of the present invention the ink layer is superimposed on an image-receiving body and heat energy is applied imagewise to the ink layer. A thermal head is typically used as a heat source of the heat energy. Alternatively, any conventional heat sources can be used such as laser light, infrared flash and heat pen.

Where the image-receiving body is not a sheet-like material but a three-dimensional article, or one having a curved surface, thermal transfer method using laser light is advantageous since application of heat energy is easy.

The formation of multi-color or full-color images with use of the thermal transfer recording material of the present invention is performed, for example, as follows. With use of a thermal transfer printer with one or plural thermal heads the yellow ink layer, the magenta ink layer and the cyan ink layer are selectively melt-transferred onto a receptor in a predetermined order in response to separation color signals of an original multi-color or full-color image, i.e., yellow signals, magenta signals and cyan signals to form yellow ink dots, magenta ink dots and cyan ink dots on the receptor in a predetermined order, thus yielding a yellow separation image, a magenta separation image and a cyan separation image superimposed on one another on the receptor. The order of transfer of the yellow ink layer, magenta ink layer and cyan ink layer can be determined as desired. When a usual multi-color or full-color image is formed, all the three color ink layers are selectively transferred in response to the corresponding three color signals to form three color separation images on the receptor. When there are only two color signals, the corresponding two of the three color ink layers are selectively transferred to form two color separation images.

Thus there is obtained a multi-color or full-color image comprising: (A) at least one region wherein a color is developed by subtractive color mixture of at least two superimposed inks of yellow, magenta and cyan, or (B) a combination of the region (A) and at least one region of a single color selected from yellow, magenta and cyan where different color inks are not superimposed. Herein a region where yellow ink dots and magenta ink dots are present in a superimposed state develops a red color; a region where yellow ink dots and cyan ink dots are present in a superimposed state develops a green color; a region where magenta ink dots and cyan ink dots are present in a superimposed state develops a blue color; and a region where yellow ink dots, magenta ink dots and cyan ink dots are present in a superimposed state develops a black color. A region where only yellow, magenta or cyan ink dots are present develops a yellow, magenta or cyan color.

In the above manner a black color is developed by the superimposing of yellow ink dots, magenta ink dots and cyan ink dots. A black color may otherwise be obtained by using only black ink dots instead of three color ink dots. Further alternatively, a black color may be obtained by superimposing black ink dots on at least one of yellow, magenta and cyan ink dots, or on superimposed ink dots of at least two of yellow, magenta and cyan ink dots.

In forming printed images with use of the thermal transfer recording material, the printed images may be directly formed on a final object, or alternatively by previously forming the printed images on a sheet-like image-receiving body (receptor) and then bonding the image-receiving body thus bearing the printed images to a final object with suitable means such as an adhesive.

Usable as the receptor are a variety of plastic films (this term is intended to include sheets, hereinafter the same) including usual polyethylene terephthalate film and vinyl chloride resin films such as polyvinyl chloride film. Of course, receptors subjected to a surface treatment for thermal transfer can be used.

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 these Examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

Examples 1-9 and Comparative Examples 1-2

A 5 μm-thick polyethylene terephthalate film was formed on one side thereof with a stick-preventive layer composed of a silicone resin with a coating amount of 0.25 g/m^2. Onto the opposite side of the polyethylene terephthalate film with respect to the stick-preventive layer was applied an ink coating liquid of the formula shown in Table 1, followed by drying to form a heat-meltable ink layer with a coating amount of 2 g/m^2, yielding a thermal transfer recording material.

Table 1

Formula of ink coating liquid (%)	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Com. Ex.1	Com. Ex.2
Araldite ECN1280*1	12.5	-	-	-	-	-	-	-	-	-	-
EOCN-7000*2	-	9	-	-	-	-	-	-	-	-	-
Epikote 1031S*3	-	-	7	-	-	6	7	7	7	-	-
Epikote 4007P*4	-	-	-	5	-	-	-	-	-	-	-
Epikote 1003*5	-	-	-	-	7	-	-	-	-	14	3
Acrylic resin A*6	1.5	-	7	-	-	-	7	7	7	-	-
Acrylic resin B*7	-	5	-	-	-	-	-	-	-	-	-
Acrylic resin C*8	-	-	-	9	7	4	-	-	-	-	9
Vylon 200*9	-	-	-	-	-	4	-	-	-	-	-
Carbon black	6	6	6	6	6	6	-	-	-	6	6
Yellow pigment*10	-	-	-	-	-	-	6	-	-	-	-
Magenta pigment*11	-	-	-	-	-	-	-	6	-	-	-
Cyan pigment*12	-	-	-	-	-	-	-	-	6	-	-
Methyl ethyl ketone	80	80	80	80	80	80	80	80	80	80	80

*1 CNPGE made by Asahi-CIBA Limited, softening point: 80℃

*2 Naphthol-modified cresol novolac polyglycidyl ether made by Nippon Kayaku Co., Ltd., softening point: 90℃

*3 TPETGE made by Yuka Shell Epoxy Kabushiki Kaisha, softening point: 92℃

*4 BPFDGE made by Yuka Shell Epoxy Kabushiki Kaisha, softening point: 109℃

*5 BPADGE made by Yuka Shell Epoxy Kabushiki Kaisha, softening point: 89℃

*6 Polymethyl methacrylate made by Mitsubishi Rayon Co., Ltd., number average molecular weight: 90,000, glass transition point: 105℃

*7 Polymethyl methacrylate made by Mitsubishi Rayon Co., Ltd., number average molecular weight: 280,000, glass transition point: 105℃

*8 Styrene-acryl resin made by Rohm and Haas Inc., number average molecular weight: 40,000, glass transition point: 50℃

*9 Polyester resin made by Toyobo Co., Ltd., softening point: 163℃

*10 Sanyo Color Works, Ltd., C.I. Pig. No. Y-12

*11 Sanyo Color Works, Ltd., C.I. Pig. No. R-122

*12 Sanyo Color Works, Ltd., C.I. Pig. No. B-15-2

Using each of the thermal transfer recording materials thus obtained, printing was performed to print bar code patterns on the receptor mentioned below with a thermal transfer type bar code printer (B-30 made by TEC Corp.) under the following conditions:

Printing conditions

Applied energy: 22.6 mJ/mm^2
Printing speed: 2 inches/second
Platen pressure: "High" in terms of an indication prescribed in the printer

Receptor

A: 70 μm-thick soft polyvinyl chloride film (subjected to no surface treatment) (hereinafter referred to as "PVC film")
B: 100 μm-thick polyethylene terephthalate film (subjected to no surface treatment) (hereinafter referred to as "PET film")

The resulting printed images were evaluated for their transferability and scratch resistance (crocking resistance and smear resistance).

The results are shown in Table 2.

Transferability

Using a bar code reader (Codascan II produced by RJS ENTERPRISES, INC), the printed images were subjected to a reading test according to the following judgment criteria:

○ :	completely readable;
△ :	partially readable; and
X :	impossible to read.

Scratch resistance (crocking resistance)

The printed images were rubbed under the following conditions and then subjected to the reading test as above.

Tester:	A.A.T.C.C. Crock Meter Model CM-1 produced by ATLAS ELECTRIC DEVICE COMPANY
Rubbing material:	Cotton cloth
Pressure:	500 g/cm^2
Number of reciprocations:	300

Scratch resistance (smear resistance)

The printed images were rubbed under the following conditions and then subjected to the reading test as above.

Tester:	Rub Tester produced by Yasuda Seiki Seisakusho Ltd.
Rubbing material:	Corrugated fiberboard
Pressure:	250 g/cm^2
Number of reciprocations:	300

Table 2

	PVC film			PET film
	Transferability	Crocking Resistance	Smear resistance	Transferability
Ex.1	○	○	○	○
Ex.2	○	○	○	○
Ex.3	○	○	○	○
Ex.4	○	○	○	○
Ex.5	○	○	○	○
Ex.6	○	○	○	○
Ex.7	○	○	○	○
Ex.8	○	○	○	○
Ex.9	○	○	○	○
Com. Ex.1	△	△	△	△
Com. Ex.2	X	X	X	X

As seen from the foregoing, the thermal transfer recording material of the present invention offers excellent transferability of the ink layer thereof (separability of the ink layer) and provides printed images exhibiting good adhesion to diverse plastic films and high scratch resistance and hence is highly useful in printing images such as bar codes.

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

Claims

1. A thermal transfer recording material comprising a foundation and, provided thereon, a heat-meltable ink layer comprising at least a heat-meltable material and a coloring agent,

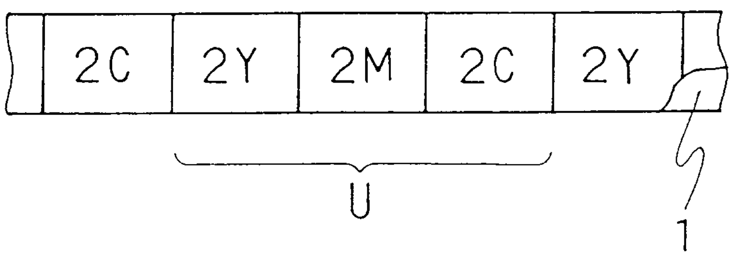
the heat-meltable material comprising 30 to 90 % by weight of an epoxy resin and 10 to 70 % by weight of an acrylic resin having a number average molecular weight of 30,000 to 300,000.

2. The thermal transfer recording material of Claim 1, wherein the epoxy resin comprises at least one member selected from the group consisting of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether.

3. The thermal transfer recording material of Claim 1, wherein the epoxy resin comprises at least one member selected from the group consisting of tetraphenolethane tetraglycidyl ether, cresol novolac polyglycidyl ether and bisphenol F diglycidyl ether.

4. The thermal transfer recording material of Claim 1, wherein the acrylic resin has a glass transition point of 30° to 120°C .

FIG. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 2490

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)
A	DE 41 41 017 A (KAO CORP.) * page 12, line 51 - line 53 * ---	1	B41M5/38
A	FR 2 637 095 A (RICOH COMPANY) * claim 25 * ---	1	
P,X	EP 0 696 517 A (FUJICOPIAN CO.) * page 11, line 26 - line 30 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 November 1996	Heywood, C

CATEGORY OF CITED DOCUMENTS

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

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

EPO FORM 1503 03.82 (P04C01)