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IEEE INTERNATIONAL ELECTRONIC MANUFACTURING TECHNOLOGY SYMPOSIUM, San Francisco, CA, 15th-17th September 1986, pages 265-269, IEEE, New York, US; T.HARA et al.: "Reusable ribbon for thermal transfer printing"

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Description

The present invention relates to a thermal transfer ink necessary to a thermal transfer printer which is expanding the fields of application thereof because it is inexpensive, generates little noise, and is easy to handle.

Prior Art and the Problems thereof

Waxes such as paraffin and carnauba wax are predominantly used as the binders of conventional thermal transfer inks, which have a significantly low melt viscosity. Thus, when printing is made on a thermal transfer paper having a good smoothness, a clear print having a gloss peculiar to thermal transfer can be obtained. With expansion of the application field, however, there have arisen various requirements involving printing on a paper having a less surface smoothness, printing giving a fast print, printing at a high speed, and repeated printing.

Thus, as the level of requirements is enhanced, the conventional ink constituted of wax alone cannot cope with the requirements. Therefore, investigations on inks comprising a resin as the main component are being made in various fields.

Known resins include one which promises application to the printing on a paper having a rough surface because of its high cohesive force and high capability of forming film, one which promises application to the printing giving a fast print because of its high strength, one which promises application to the printing with a high transfer sensitivity because of its amorphousness, and one which promises application to the repeated printing because of its strong adhesion.

Thus, a possibility of application of a resin to a thermal transfer has been developed. In general, however, resins have a very high melt viscosity as compared with waxes. This tendency is particularly remarkable when they are formed into an ink. In the thermal transfer system, this melt viscosity is an important factor determining formation of a transferred image, thus directly influencing the quality of a print. If a resin ink has a low viscosity comparable to that of a wax ink in a heat-molten state, a sufficient contact area is secured, thus achieving printing with a high coverage. However, an ink containing a resin having a melting point suitable for thermal transfer as the main component does not generally have a low viscosity comparable to that of a wax when thermal transfer is carried out.

In order to enable the use of a high-viscosity resin ink by lowering its viscosity, a countermeasure such as addition of an oil (e.g. butyl cellosolve or spindle oil) has heretofore been adopted. However, this method presents problems of bleeding out and blocking during storage. Thus, a difficulty is experienced in adding an amount of oil enough to secure a sufficiently low viscosity.

From JP-A-60-115487 a colouring material layer is known which comprises 5-30 parts of weight of a resin (polyvinyl butyral) and 40 - 80 parts by weight, preferably 50 parts by weight of a viscosity depressant, (bee's wax). The colouring material, according to JP-A-60-115487 has a viscosity of 100 to 1000 Pa • s.

From EP-A-126906 a thermal transfer material is known, said transfer material containing a thermal transfer layer said layer containing 12-30 wt% of a wax with a melt viscosity of 150-200 mPa.s and 0.5-5 wt% of a resin with a melt viscosity of 150-200 mPa.s.

Summary of the Invention

The inventors of the present invention have made intensive investigations with a view to solving the above-mentioned problems, and as a result, have found that excellent printing performance can be obtained with an ink composition for thermal transfer which comprises 100 parts by weight of a resin having a melt viscosity of 10 to 1,000 Pa • s (10,000 to 1,000,000 cps), measured at 120° C and 5 to 250 parts by weight of a viscosity depressant having a melt viscosity of 10^{-3} to 0.6 Pa • s (1 to 600 cps), measured at 120° C, and being insoluble in a solvent usually used for inks added during the preparation of the ink composition, or so partially soluble in a solvent that not more than 1 gram of the viscosity depressant may be soluble in 100 grams of the solvent at 40° C, said viscosity depressant being selected from a resin, a wax, a higher fatty acid, a higher alcohol and a synthetic ester compound, whereby the ink composition contains after drying of a coated layer only traces of said solvent.

It is preferable that in the ink composition the insoluble portion of the depressant stands in the form of fine particles in the emulsion or the slurry. It may contain the solvent in a conventional amount and a colouring matter.

The ink composition for thermal transfer of the present invention is obtained by a process wherein a resin is admixed with a slurry consisting of a solvent and a viscosity depressant being insoluble in said solvent or so partially soluble in the solvent that not more than 1 gram of said viscosity depressant is soluble in 100 grams of the solvent at 40° C, said viscosity depressant being selected from the group consisting of a resin, a wax, a higher fatter acid, a higher alcohol and a synthetic ester compound, wherein the ink composition comprises 100 parts by weight of said resin having a melt viscosity of 10 to 1,000 Pa • s (10,000 to 1,000,000 cps), measured at 120° C and 5 to 250 parts by weight of said viscosity depressant having a melt viscosity of 10^{-3} to 0.6 Pa • s (1 to 600 cps), measured at 120° C and whereby the ink composition contains after drying only traces of said solvent.

In this process it is preferable that the insoluble portion of the viscosity depressant is in form of fine particles in the emulsion of the slurry.

The thermal transfer ink of the present invention is applied to a base with a conventional means such as a gravure coater and dried to obtain a thermal transfer ink sheet without the need of paying attention to the compatibility of a high-viscosity resin with a viscosity depressant such as a wax.

According to the present invention, any combination of a high-viscosity base resin and a viscosity depressant such as a wax is possible, and any high-viscosity resin can be used as the thermal transfer ink binder.

A resin which can be used as the base binder in the present invention has a melt viscosity of 10 to 1,000 Pa • s (10,000 to 1,000,000 cps), measured at 120° C. Examples of such a resin include polyester, polyamide, acrylic, polystyrene, polystyrene-acrylic, polyvinyl chloride, polyvinyl butyral, epoxy, ethylene-vinyl acetate, polyurethane and polycarbonate resins, and mixtures thereof, said resins having melting points of 60 to 120° C.

The viscosity depressant having a low viscosity which can be used in the present invention is at least one member selected from the group consisting of resins, waxes, higher fatty acids, higher alcohols, and synthetic esters, which have a melt viscosity of 10^{-3} to 0.6 Pa • s (1 to 600 cps), measured at 120° C, and being insoluble in a solvent to use or so partially soluble in the solvent that more than 1 gram of the viscosity depressant may not be soluble in 100 grams of the solvent at 40° C.

More preferred are resins, waxes, higher fatty acids, higher alcohols, and synthetic esters which have a melt viscosity of 10^{-3} to 0.4 Pa • s (1 to 400 cps) at 120° C.

Any resin can be used as the low-viscosity resin in the present invention in so far as it has a low viscosity. Examples of such resins include polyethylene, polyester, ketone, ethylene-α-olefin copolymer α-olefin-maleic anhydride copolymer resins.

All kinds of waxes can be mentioned as the wax that may be used in the present invention. Examples of the waxes include natural plant waxes such as carnauba wax, candelilla wax, ouricury wax, sugarcane wax, and Japan wax; natural animal waxes such as bees-wax, spermaceti, Chineses wax, and wool wax; petroleum waxes such as paraffin wax, microcrystalline wax, oxidized paraffin wax, and oxidized micro-crystalline wax; mineral waxes such as montan wax, ozokerite, ceresine, and lignite wax; synthetic waxes such as ketone wax, Fischer-Tropsch wax, castor wax, opal wax, Armor wax, and Acra wax; and modifications thereof.

Any higher fatty acid which is usually used can be used in the present invention. Examples of such a higher fatty acid include palmitic acid, stearic acid, margaric acid, and behenic acid.

Any higher alcohol can be used in the present invention. Examples of such a higher alcohol include palmityl alcohol, stearyl alcohol, behenyl alcohol, margaryl alcohol, myricyl alcohol, and eicosanol.

Examples of synthetic esters that may be used in the present invention include monoesters synthesized from the above-mentioned higher fatty acid and higher alcohol, diesters synthesized from a bifuctional dicarboxylic acid and the above-mentioned higher alcohol, and diesters synthesized from a bifunctional diol and the above-mentioned higher fatty acid.

Any solvent which is usually used in an ink or a coating can be used in the present invention. Examples of such a solvent include alcohols such as ethanol and isopropyl alcohol; ketones such as methyl ethyl ketone and methyl isobutyl ketone; aromatic solvents such as toluene and xylene; and water. These solvents may be used in mixture if necessary.

A thermal transfer ink sheet can be produced from the thermal transfer ink of the present invention by applying at least one layer of the thermal transfer ink of the present invention to a base or a coating layer on a base and drying it. A combination of the thermal transfer ink layer with a top coat, a resistance layer for heating by passing electricity therethrough, or an electrically conductive layer may be employed.

The thermal transfer ink of the present invention is usually applied to a base with a coater or a printer. When a viscosity depressant added is not soluble in a solvent used at all, the interaction between precipitated particles becomes so strong that the structural viscosity is increased, whereby problems of separation of the ink from the gravure meshes in coating or printing and levelling just after the application are presented. Thus, any clean coating film can hardly be obtained. According to the present invention, however, a viscosity depressant to be added is at least partially soluble in a solvent used, so that the structural viscosity can be suppressed. As a result, good applicability or printability is attained.

Examples

The following Examples will further exemplify the effectiveness of the present invention, but should not be construed as limiting the scope of the invention.

Example 1

A thermal transfer ink (1) of a solvent type comprising a polyester resin having a softening point of 90° C (melt viscosity at 120° C: 23 Pa s (23,000 cps) as the main component and having the following composition was prepared:

ink (1)	polyester resin	25.0%
	carbon black	4.5%
	dispersant	0.5%
	toluene	46.0%
	isopropyl alcohol	24.0%

Separately, a solution of a carnauba wax slurry (1) in toluene was prepared. From the aspect of performance, this slurry may be one prepared by completely dissolving carnauba wax in hot toluene and cooling the solution, or a slurry prepared by adding a fine carnauba wax powder and, if necessary, dispersing the mixture.

slurry (1)	carnauba wax	30.0%
	toluene	70.0%

Inks (2) to (4) here prepared by adding the slurry (1) to the ink (1).

	Ink (1)	Slurry (1)
Ink (2)	90%	10%
Ink (3)	75%	25%
Ink (4)	50%	50%

These inks were each applied to a 3.5 μ-thick polyethylene terephthalate (PET) film and dried to prepare a thermal transfer ink sheet.

The obtained thermal transfer ink sheet was evaluated as regards obtained prints by using a commercially available thermal transfer printer. The evaluation results are summarized in Table 1. It can be understood from the results that, with an increase in the amount of the carnauba wax slurry, a viscosity lowering effect was developed, whereby a thermally transferred image having a transfer rate and a resolution comparable to those of a wax ink was obtained while keeping the features of the resin, such as fastness.

Comparative Example 1

A thermally transferred image was obtained under the same conditions as those of Example 1 by using the ink (1).

The evaluation results as to obtained prints are shown in Table 1. In this case, since the ink has a very high viscosity, no sufficient transfer can be secured and hence a transferred image has a low coverage.

Table 1

	Ink	Resolution	Transfer rate	Fastness
Comp. Ex. 1	Ink (1)	x	x	O
Ex. 1	Ink (2)	x	O	O
	Ink (3)	O	O	O
	Ink (4)	O	O	O

Example 2

Solution type inks each comprising as the main component a polymide resin having a softening point of 86° C (melt viscosity at 120° C: 17,5 Pa • s (17,500 cps), a polystyreneacrylic resin having a softening point of 102° C (melt viscosity at 120° C: 50 Pa • s (50,000 cps), or a polystyrene resin having a softening point of 78° C (melt viscosity at 120° C: 11 Pa • s (11,000 cps) (in a 1/1 solvent mixture of toluene and methyl ethyl ketone) were admixed with 10, 20, 30, 40, and 50%, based on the resin, of a mixed slurry composed of polyethylene wax (melt viscosity at 120° C: $3 \cdot 10^{-2}$ Pa • s (30 cps) and carnauba wax prepared at a ratio of 1:1 in the same manner as that of Example 1 to prepare inks.

Evaluation of the obtained prints was made in the same manner as that of Example 1. The results as shown in Table 2 were obtained. It was evidently recognized that addition of the slurry provided a viscosity lowering effect.

Table 2

Performance in printing	Resolution					Transfer rate					Fastness				
Amount of addition (%)	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
Polyamide ink	×	×	○	○	○	×	○	○	○	○	○	○	○	○	○
Polystyrene-acrylic ink	×	○	○	○	○	×	○	○	○	○	○	○	○	○	○
Polystyrene ink	×	○	○	○	○	○	○	○	○	○	○	○	○	○	○

Example 3

A slurry of paraffin wax having a melting point of 105° C (melt viscosity at 120° C: 0.023 Pa • s) in toluene was prepared. The same polyester resin as that described in Example 1 was admixed with 30%, based on the weight of the resin, of the slurry. The evaluation of the obtained prints was made in the same manner as that of Example 1 to obtain results as shown in Table 3.

As is apparent from Table 3, a sufficient viscosity lowering effect was developed and an ink having good performances in printing was obtained. Thus, it was found that even a high-melting wax having a melting point of higher than 100° C exhibited a viscosity lowering effect if the melt viscosity thereof was lowered.

Example 4

A polyamide resin having a softening point of 106° C (melt viscosity at 120° C: 120 Pa • s) was emulsified by the ordinary method to prepare an emulsion ink. Separately, a modified micro-crystalline wax having a melting point of 87° C (melt viscosity at 120°: 0.004 Pa • s) was emulsified with a common emulsifier to prepare an emulsion. 20%, based on the weight of the resin, of the emulsion was added to the above-mentioned emulsion ink. Evaluation of the obtained prints was made in the same manner as that of Example 1 to obtain results as shown in Table 3.

As is apparent from Table 3, the emulsion ink having good performances in printing was prepared.

Comparative Example 2

The same resin ink as that used in Example 1 was admixed with 30%, based on the resin, of a polyester resin having a melting point of 78° C (melt viscosity at 120° C: 2.3 Pa • s) to prepare an ink. Evaluation of the obtained prints was made in the same manner as that of Example 1 to obtain results as shown in Table 3.

As is apparent from Table 3, any viscosity lowering effect which will give good performances in printing could not be obtained though some decrease in viscosity was recognized. It was proved that a resin having a melt viscosity outside the scope of the present invention exhibited a remarkably low effect, even though it had a low melting point.

Table 3

	Base resin		Additive			Performance in printing		
	Kind	Viscosity (Pa • s)	Kind	Melting point (°C)	Viscosity (Pa • s)	Resolution	Transfer rate	Fastness
Ex. 3	polyester	23	paraffin wax	105	0.023	○	○	○
Ex. 4	polyamide	120	modified micro-crystalline wax	87	0.004	○	○	○
Comp. Ex. 2	polyester	23	polyester resin	78	2.3	×	×	○

Claims

1. An ink composition for thermal transfer which comprises 100 parts by weight of a resin having a melt viscosity of 10 to 1,000 Pa • s (10,000 to 1,000,000 cps), measured at 120° C and 5 to 250 parts by weight of a viscosity depressant having a melt viscosity of 10^{-3} to 0.6 Pa • s (1 to 600 cps), measured at 120° C, and being insoluble in a solvent usually used for inks added during the preparation of the ink composition or so partially soluble in the solvent that not more than 1 gram of the viscosity depressant may be soluble in 100 grams of the solvent at 40° C, said viscosity depressant being

selected from a resin, a wax, a higher fatty acid, a higher alcohol and a synthetic ester compound, whereby the ink composition contains after drying of a coated layer only traces of said solvent.

2. An ink composition as claimed in Claim 1, in which the insoluble portion of the depressant stands in the form of fine particles in the emulsion or the slurry.

3. A process for preparing an ink composition for thermal transfer wherein a resin is admixed with a slurry consisting of a solvent and a viscosity depressant being insoluble in said solvent or so partially soluble in the solvent that not more than 1 gram of said viscosity depressant is soluble in 100 grams of the solvent at 40° C, said viscosity depressant being selected from the group consisting of a resin, a wax, a higher fatty acid, a higher alcohol and a synthetic ester compound, wherein the ink composition comprises 100 parts by weight of said resin having a melt viscosity of 10 to 1,000 Pa • s (10,000 to 1,000,000 cps), measured at 120° C and 5 to 250 parts by weight of said viscosity depressant having a melt viscosity of 10^{-3} to 0.6 Pa • s (1 to 600 cps), measured at 120° C and whereby the ink composition contains after drying only traces of said solvent.

4. The process as claimed in Claim 3, wherein the insoluble portion of the viscosity depressant is in form of fine particles in the emulsion of the slurry.

Patentansprüche

1. Tintenzusammensetzung für die thermische Übertragung, umfassend 100 Gew.-Teile eines Harzes mit einer Schmelzviskosität von 10 bis 1000 Pa • s (10.000 bis 1.000.000 cP), gemessen bei 120° C, und 5 bis 250 Gew.-Teile eines Viskositätsverminderers mit einer Schmelzviskosität von 10^{-3} bis 0,6 Pa • s (1 bis 600 cP), gemessen bei 120° C, und der in einem üblicherweise für Tinten verwendeten Lösungsmittel unlöslich ist während der Herstellung der TintenzusammenSetzung, oder teilweise so löslich in dem Lösungsmittel ist, daß nicht mehr als 1 g des Viskositätsverminderers in 100 g Lösungsmittel bei 40° C löslich sind, wobei der Viskositätsverminderer ausgewählt ist aus einem Harz, einem Wachs, einer höheren Fettsäure, einem höheren Alkohol und einer synthetischen Esterverbindung, wobei die Tintenzusammensetzung nach Trocknen einer beschichteten Schicht nur Spuren des Lösungsmittels enthält.

2. Tintenzusammensetzung nach Anspruch 1, wobei der unlösliche Teil des Verminderers in Form feiner Partikel in der Emulsion oder der Aufschlämmung vorliegt.

3. Verfahren zur Herstellung einer Tintenzusammensetzung für die thermische Übertragung, wobei ein Harz mit einer Aufschlämmung, bestehend aus einem Lösungsmittel und einem Viskositätsverminderer, der in dem Lösungsmittel unlöslich ist oder in dem Lösungsmittel teilweise so löslich ist, daß nicht mehr als 1 g des Viskositätsverminderers in 100 g des Lösungsmittels bei 40° C löslich sind, vermischt wird, wobei der Viskositätsverminderer ausgewählt ist aus der Gruppe, bestehend aus einem Harz, einem Wachs, einer höheren Fettsäure, einem höheren Alkohol und einer synthetischen Esterverbindung, und die Tintenzusammensetzung 100 Gew.-Teile des Harzes mit einer Schmelzviskosität von 10 bis 1000 Pa • s (10.000 bis 1.000.000 cP), gemessen bei 120° C, und 5 bis 250 Gew.-Teile des Viskositätsverminderers mit einer Schmelzviskosität von 10^{-3} bis 0,6 Pa • s (1 bis 600 cP), gemessen bei 120° C, umfaßt und wobei die Tintenzusammensetzung nach dem Trocknen nur Spuren des Lösungsmittels enthält.

4. Verfahren nach Anspruch 3, wobei der unlösliche Teil des Viskositätsverminderers in Form feiner Partikel in der Emulsion oder der Aufschlämmung vorliegt.

Revendications

1. Composition d'encre pour le transfert thermique, qui comprend 100 parties en poids d'une résine, ayant une viscosité à l'état fondu de 10 à 1 000 Pa.s (10 000 à 1 000 000 cP) mesurée à 120°C, et 5 à 250 parties en poids d'un réducteur de viscosité, ayant une viscosité à l'état fondu de 10^{-3} à 0,6 Pa.s (1 à 600 cP) mesurée à 120°C et étant insoluble dans un solvant généralement utilisé pour les encres ajouté lors de la préparation de la composition d'encre ou partiellement soluble dans le solvant dans la mesure où pas plus de 1 g du réducteur de viscosité peut être soluble dans 100 g du solvant à

40 °C, ledit réducteur de viscosité étant choisi parmi une résine, une cire, un acide gras supérieur, un alcool supérieur ou un ester synthétique, si bien que la composition d'encre ne contient, après séchage d'une couche de revêtement, que des traces dudit solvant.

2. Composition d'encre selon la revendication 1, dans laquelle la portion insoluble du réducteur de viscosité demeure sous forme de particules fines dans l'émulsion ou la suspension.

3. Procédé pour préparer une composition d'encre pour le transfert thermique, dans lequel on mélange une résine avec une suspension constituée d'un solvant et d'un réducteur de viscosité qui est insoluble dans ledit solvant ou qui n'est que partiellement soluble dans le solvant, dans la mesure où pas plus de 1 g dudit réducteur de viscosité est soluble dans 100 g du solvant à 40 °C, ledit réducteur de viscosité étant choisi dans le groupe constitué par une résine, une cire, un acide gras supérieur, un alcool supérieur et un ester synthétique, dans lequel la composition d'encre comprend 100 parties en poids de ladite résine, ayant une viscosité à l'état fondu de 10 à 1 000 Pa.s (10 000 à 1 000 000 cP) mesurée à 120 °C, et 5 à 250 parties en poids dudit réducteur de viscosité, ayant une viscosité à l'état fondu de 10^{-3} à 0,6 Pa.s (1 à 600 cP) mesurée à 120 °C, et grâce à quoi la composition d'encre ne contient, après séchage, que des traces dudit solvant.

4. Procédé selon la revendication 3, dans lequel la portion insoluble du réducteur de viscosité est sous forme de particules fines dans l'émulsion ou la suspension.