

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 339 353
A2**

12

EUROPEAN PATENT APPLICATION

21 Application number: **89106336.4**

51 Int. Cl.4: **B41M 5/26**

22 Date of filing: **10.04.89**

30 Priority: **27.04.88 JP 104620/88**

43 Date of publication of application:
02.11.89 Bulletin 89/44

84 Designated Contracting States:
DE ES FR GB IT

71 Applicant: **Kao Corporation**
14-10, Nihonbashi Kayabacho 1-chome
Chuo-Ku Tokyo 103(JP)

72 Inventor: **Kawahito, Shiro**
44-1, Miyukimachi
Utsunomiya-shi Tochigi(JP)
Inventor: **Yashima, Hiroshi**
34-1, Izumimachi
Utsunomiya-shi Tochigi(JP)
Inventor: **Minato, Masanori**
4599-1, Aza Miyakoshimae Ohaza Ichihana
Ichikaimachi Haga-gun Tochigi(JP)
Inventor: **Suzuki, Atsushi**
4599-1, Aza Miyakoshimae Ohaza Ichihana
Ichikaimachi Haga-gun Tochigi(JP)
Inventor: **Kawabe, Kuniyasu**
1450, Nishihama
Wakayama-shi Wakayama(JP)

74 Representative: **Patentanwälte Dr. Solf & Zapf**
Zeppelinstrasse 53
D-8000 München 80(DE)

54 **Thermal transfer ink and film.**

57 An ink composition for thermal transfer comprises a coloring matter, a vehicle and a polyester having a melting point of 50 to 110 degree C, determined by the DSC method and a number-average molecular weight of 300 to 6,000 and containing 1 to 30 ethylenic unsaturations.

EP 0 339 353 A2

Thermal Transfer Ink and Film

The present invention relates to a thermal transfer ink and ink film. In particular, the present invention relates to a thermal transfer ink containing a specified polyester resin and an ink film containing it.

5 [Prior Art]

Thermal transfer ink films usually comprise a base such as a paper or plastic film having at least one coloring material layer (ink layer) formed thereon. In using such a film, a solid ink is molten by heating to transfer the ink onto a recording paper to thereby form a record. The ink film is heated by a process
10 wherein it is heated with a heating element placed either on a side opposite to the coloring material layer or on the coloring material layer side through a recording paper or, alternatively, a process wherein a resistant layer is formed among the ink film layers to conduct the heating by resistance heat generation.

The coloring material layer comprises a heat-fusible substance containing a pigment or dye as the coloring agent. The heat-fusible substances include, for example, carnauba wax and paraffin wax. The base
15 usually comprises a polyethylene terephthalate film or polycarbonate film having excellent surface smoothness and dimensional stability.

In forming a transferred image on plain paper or the like, a thermal transfer printer having a thermal head is usually used. It is desirable to control the thermal energy necessitated for the printing as low as possible. In particular, by adjusting the thermal energy necessitated for the printing to a value lower than
20 that of the prior art, the time of the cycle of heating the head and leaving it to cool is reduced and the printing speed is increased and, in addition, the thermal deterioration of the head can be inhibited and a power source of a line printer can be miniaturized. Further it makes up for an insufficient heat resistance of the base film.

However, when the ink composition is designed to have a low melting point in order to increase the transfer sensitivity of the thermal transfer ink film, the paper is greased with a low-melting component of the wax and the fixability and fastness of the print are reduced. Further when the ambient temperature is elevated during the storage, a so-called blocking phenomenon occurs. Thus such an ink composition having a low melting point cannot be easily realized.

It was proposed to use various thermoplastic polymers in order to solve these problems. For example, polyethylene wax (Japanese Patent Laid-Open No. 101094/1983), ethylene/alkyl acrylate copolymer (Japanese Patent Laid-Open No. 120092/1985) or 1,2-polybutadiene (Japanese Patent Laid-Open No. 127193/1985) is incorporated in the ink composition in order to conduct the printing with a low energy without greasing the paper. In these processes, the thermoplastic polymer is added to the low-melting wax (main component) to increase the coating film strength by virtue of the reticulate structure of the polymer
30 and to inhibit the greasing. The effects of these processes are thus limited.

A polyester having a low molecular weight as disclosed in Japanese Patent Laid-Open No. 216790/1987 was proposed as a heat-fusible substance for the thermal transfer inks to make the printing with a high transfer sensitivity possible with a low energy. However, such a polyester having a low molecular weight has a defect that its solubility in a solvent at a temperature below 15°C is low and, therefore, crystals are liable
40 to be formed. As a result, the viscosity of the ink is high and it cannot be easily applied to the film. In addition, the ink coating film has a poor strength, since the resin is hard and brittle.

Printers of the thermal transfer type are widely used as small, lightweight, inexpensive popular ones. Particularly they are employed in almost all personal word processors in virtue of their maintenance-free characteristics.

Although the printing system of the thermal transfer type has thus many advantages when it is employed in the popular printers, it is expected that with the spread of the thermal transfer printers, it becomes the most serious problem that the costs of consumables are high and, therefore, the printing cost per sheet is high. Such high costs are due to the following facts: since cassettes suitable for the respective types of the printers must be supplied, the cassettes of various types must be produced each in small
50 amounts; the cost of the cassettes which are not consumables in the strict sense but peripheral parts is far higher than that of ribbons; it is difficult to automate a series of the subsequent steps such as slitting, winding round the core and packing in the cassettes and, therefore, a high labor cost is necessitated; and a high distribution cost is necessitated. Under these circumstances, it is demanded to reduce the printing cost by repeatedly using an ink ribbon.

[Summary of the Invention]

After intensive investigations made for the purpose of solving the above-described problems, the inventors have found that a thermal transfer ink capable of forming a coating film of a high strength and of printing with a low energy without causing the greasing can be produced by selecting a polyester resin having specified melting point and molecular weight ranges and specified bond(s) as a heat-fusible main component of the heat-fusible ink. In particular, the inventors have found that when a polyester resin having a melting point (determined by DSC method) of 50 to 110 °C, a number-average molecular weight of 300 to 6,000 and 1 to 30 ethylenically unsaturated bonds in the main chain and/or side chain(s) thereof is used, the following effects are obtained:

- 1) the solubility in a solvent is improved to inhibit both the crystallization at a low temperature and an increase in the viscosity of the ink and, therefore, the fluidity of the ink is kept high and the application thereof is easy even in winter, and
- 2) the polyester resin is soft and, therefore, it inhibits shrinkage upon drying of the ink when the ink is applied to a film to thereby increase the strength of the coating layer of the produced ink ribbon. The present invention has been completed on the basis of these findings.

The present invention provides a thermal transfer ink characterized by comprising a polyester resin having a melting point (determined by DSC method) of 50 to 110 °C, a number-average molecular weight of 300 to 6,000 and 1 to 30 ethylenically unsaturated bonds in the main chain and/or side chain(s) of the polymer, and a colorant as indispensable components, and a thermal transfer ink film characterized by comprising a base having a surface coated with the ink.

An ink composition for thermal transfer comprises, according to the invention, a coloring matter, a vehicle and a polyester having a melting point of 50 to 110 degree C, determined by the DSC method and a number-average molecular weight of 300 to 6,000 and containing 1 to 30 ethylenic unsaturations.

The composition preferably comprises 40 to 80 percent by weight, based on the entire solid components, of the polyester and 10 to 30 percent by weight, based on the entire solid components, of the coloring matter.

The invention further provides an ink film for thermal transfer which comprises a substrate and an ink layer, coated on the substrate, comprising the ink composition as defined above.

The ink of the present invention is usable as an ink for repeated printing to reduce the cost of the printing by using the ink ribbon repeatedly. In the printing system of the thermal transfer system, a heat-fusible ink applied to a base film such as a polyethylene terephthalate (PET) film is molten by heating with a thermal head on the other side of the base film to thoroughly penetrate it into a paper on which an image is to be formed or to adhere the ink to the paper and then the base film is mechanically peeled off from the paper to transfer the ink from the base film to the paper. When an ordinary ink ribbon is used, the whole of the molten ink is transferred to the paper, since the ink is cooled and solidified before the peeling and thus the ink ribbon is disposed of after using only once. On the contrary, when a ribbon made of the ink film of the present invention is used, the ink is kept in a molten state even when the film is peeled off from the paper. As a result, the flow of the ink is interrupted midway from the film to the paper, and the ink is transferred to the paper not wholly but partially to make the repeated printing possible.

The polyester resin used in the present invention is produced by polycondensing a saturated polyhydric alcohol and/or a polyhydric alcohol having an ethylenically unsaturated bond with a saturated polybasic carboxylic acid and/or a polybasic carboxylic acid having an ethylenically unsaturated bond. The polyester resin must have an ethylenically unsaturated bond in at least one of the alcohol moiety and acid moiety. A saturated polyhydric alcohol and/or a polyhydric alcohol having a branched saturated hydrocarbon chain are useful here, too.

The presence of the ethylenically unsaturated bond in the polyester resin of the present invention produced by polymerizing the compounds having the ethylenically unsaturated bond can be confirmed by NMR or IR analysis. The polyester resin of the present invention must have 1 to 30 ethylenically unsaturated bonds in the main chain and/or side chains of the polymer. When the number of the ethylenically unsaturated bonds exceeds 30, the melting point is too low unfavorably. In fact, it is difficult to introduce more than 30 ethylenically unsaturated bonds thereinto.

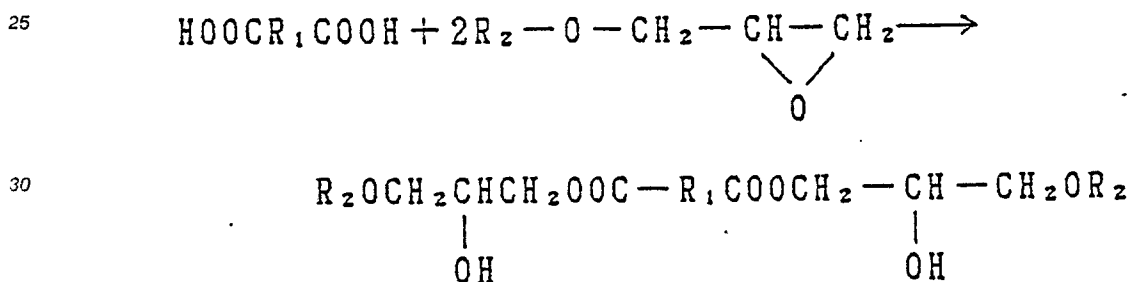
The saturated polybasic carboxylic acids constituting the polyester resin of the present invention include, for example, oxalic, malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, nonanedicarboxylic, decanedicarboxylic, undecanedicarboxylic, dodecanedicarboxylic, diglycolic, n-butylsuccinic, isobutylsuccinic, n-octylsuccinic, isooctylsuccinic, n-dodecylsuccinic, isododecylsuccinic and hexahydroterephthalic acids as well as esters of them with a lower alcohol or anhydrides of them. The saturated polybasic

carboxylic acids can be used either singly or in the form of a mixture of two or more of them.

The polybasic carboxylic acids having ethylenically unsaturated bond(s) constituting the polyester resins used in the present invention include, for example, dibasic acids having ethylenically unsaturated bond(s) and 4 to 24 carbon atoms (such as fumaric, maleic, itaconic, citraconic and traumatic acids, and
 5 ULB-20 and IPU-22 of Okamura Seiyu Co. as well as their esters with a lower alcohol and their anhydrides; polymeric fatty acids usually produced by the polymerization of drying oil or semi-drying oil fatty acids (such as tall oil fatty acids); alkenylsuccinic acids such as butenyl-, octenyl- and dodecenylsuccinic acids and anhydrides of them; muconic acid; polybutadienedicarboxylic acid; and tetrahydrophthalic acid and its anhydride.

10 The saturated polyhydric alcohols constituting the polyester resins usable in the present invention include, for example, ethylene glycol, propylene glycol, butanediol, triethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol, octamethylene glycol, non-
 15 amethylene glycol, decamethylene glycol, undecamethylene glycol, dodecamethylene glycol, tridecamethylene glycol, tetradecamethylene glycol, octadecamethylene glycol, eicosamethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, hexaethylene glycol, glycerol, pentaerythritol, neopentyl glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol and cyclohexanedimethanol. These saturated polyhydric alcohols can be used either alone or in the form of a mixture of two or more of them.

The polyhydric alcohols having ethylenically unsaturated bond(s) constituting the polyester resin usable
 20 in the present invention include, for example, 1,4-butanediol, polybutadienediol, dimer diols (hydrogenation products of dimer acids) and reaction products of the above-described polybasic carboxylic acid having ethylenically unsaturated bond(s) with an alkyl glycidyl ether, such as compounds obtained by the reaction of the following reaction formula:



35 wherein R₁ represents an alkylene group having an ethylenically unsaturated bond and R₂ represents an alkyl group.

A particularly preferred combination of the constituents of the polyester resins used in the present invention comprises a saturated polyhydric alcohol selected from the group consisting of ethylene glycol, butanediol, hexamethylene glycol and decamethylene glycol, a saturated polybasic carboxylic acid selected
 40 from the group consisting of succinic acid, adipic acid and sebacic acid, and a polybasic acid having ethylenically unsaturated bond(s). More particularly, following combinations (1) to (3) are preferred:

(1) combination of 1 mol of ethylene glycol, 0.9 mol of sebacic acid and 0.1 mol of a polybasic acid having ethylenically unsaturated bond(s),

45 2) combination of 1 mol of hexamethylene glycol, 0.9 mol of sebacic acid and 0.1 mol of a polybasic acid having ethylenically unsaturated bond(s), and

(3) combination of 1 mol of decamethylene glycol, 0.9 mol of adipic acid and 0.1 mol of a polybasic acid having ethylenically unsaturated bond(s).

50 The polyester resins produced from the above-described combinations and having a melting point of 50 to 110 °C and a number-average molecular weight of 300 to 6,000 are particularly useful as the heat-fusible material for the thermal transfer ink.

The polyester resin of the present invention is an ester oligomer having a degree of polymerization lower than that of an ordinarily used polyethylene terephthalate type of polyester resin and a relatively low
 55 melting point in a narrow range suitable for the heat-fusible material of the thermal transfer ink. The polyester resin of the present invention has a number-average molecular weight calculated from the terminal groups of usually 300 to 6,000, preferably 500 to 4,000 and a melting point determined by DSC method of 50 to 110 °C, preferably 55 to 100 °C. The polyester resin can be produced by any known process. When the polyester resin has a melting point lower than 50 °C, the blocking of the thermal transfer

ink film occurs to reduce the stability during the storage or at the time of the use. When the melting point exceeds 110°C, the sensitivity is insufficient for the practical use, though the heat stability is excellent.

When the number-average molecular weight of the polyester resin is less than 300, the melting point thereof is often lower than 50°C to cause the blocking. On the contrary, when it exceeds 6,000, the cohesive power is too strong for the transfer and the sensitivity is reduced in many cases.

The polyester resin of the present invention is a so-called crystalline polymer having a well-defined melting point as determined by DSC method and its properties are utterly different from those of amorphous polyesters having no well-defined melting point described in Japanese Patent Laid-Open No. 13384/1987.

The polyester resin may contain a component having an aromatic double bond so far as it still has a well-defined melting point.

Polyesters usually have -COOH and -OH groups at the molecular chain ends thereof. The polyesters can be converted into modified polyesters, block copolymers containing the polyester or graft copolymers to be used as the heat-fusible material for the thermal transfer ink of the present invention by condensation, ion reaction or polymer reaction of these functional groups. Further they can be modified or converted into graft copolymers containing the polyester usable as the heat-fusible material for the thermal transfer ink of the present invention by the reaction of the double bonds in the molecule.

For example, the -COOH or -OH group at the ends of the polyester molecule can be reacted with a fatty acid such as stearic acid or a higher alcohol such as stearyl alcohol to modify the polyester, it can be reacted with an isocyanate or an amine to modify it, or it can be reacted with a silicone compound, an epoxy compound or a phenol to conduct the modification. In addition, the polyester can be further condensed with mainly a crystalline aliphatic polyester to form a block copolyester, or one or more polymerizable styrenes such as styrene and α -methylstyrene or polymerizable vinyl monomers such as methacrylates and acrylates, e.g. methyl methacrylate and butyl acrylate, can be polymerized in the presence of the polyester, taking advantage of the double bond(s) in its molecular chain to form a graft copolymer containing the polyester. In addition, zinc acetate, zinc oxide or the like can be added thereto to form an ionic crosslinkage with the terminal carboxylic acid group or the like.

In the present invention, the polyester resins can be used either alone or as a combination of two or more of them or as a combination with an ordinary wax such as paraffin or carnauba wax, a rosin derivative such as hydrogenated rosin or ester gum, polyethylene wax or an ethylene/alkyl acrylate.

The thermal transfer ink of the present invention comprises at least one of the above-described polyester resin and at least one colorant as the indispensable components. The amount of the polyester resin is preferably 40 to 80 wt.% based on the solid components of the ink and the amount of the colorant (in terms of the total of pigment and dye) is preferably 10 to 30 wt.% based on the solid components of the ink.

The colorants usable in the present invention include well-known dyes and pigments for printing inks, etc., for example, black dyes and pigments such as carbon black, oil black and graphite; acetoacetate arylamide monoazo yellow pigments (fast yellow pigments) such as C. I. Pigment Yellow 1, 3, 74, 97 and 98; acetoacetate arylamide disazo yellow pigments such as C. I. Pigment Yellow 12, 13 and 14; yellow dyes such as C. I. Solvent Yellow 19, 77 and 79, and C. I. Disperse Yellow 164; red or crimson pigments such as C. I. Pigment Red 48, 49:1, 53:1, 57:1, 81, 122 and 5; red dyes such as C. I. Solvent Red 52, 58 and 8; and blue dyes and pigments such as copper phthalocyanine, e.g. C. I. Pigment Blue 15:3 and derivatives thereof and modifications thereof; as well as colored or colorless subliming paints.

These colorants can be used either alone or in the form of a mixture of two or more of them. As a matter of course, they can be mixed with an extender pigment or white pigment to adjust the color tone. Further in order to improve the dispersibility of the colorant in the heat-fusible component, the surface of the colorant can be treated with a surfactant, a coupling agent such as a silane coupling agent or a polymer material, or a polymeric dye or a polymeric graft pigment can be used.

The thermal transfer ink film of the present invention has at least one coloring material layer prepared by the application of the ink as described above in contact with the base film or with a coating film layer formed on the base film. It may further have a topcoating layer or a resistant layer for resistance heat generation.

The base used for forming the thermal transfer ink film of the present invention is preferably one having high heat resistance, dimensional stability and surface smoothness. Preferred examples thereof include films of polyethylene terephthalate mainly used as the base films of the thermal transfer ink films as well as films of resins such as polycarbonate, polyethylene, polystyrene, polypropylene and polyimide. These resin films have a thickness of preferably 2 to 20 μ .

As described above, a high transfer sensitivity is obtained, low-energy printing is made possible and the

printing speed is increased by using the thermal transfer ink film of the present invention, since it comprises as the heat-fusible material a polyester resin having a melting point (determined by DSC method) of 50 to 110 °C, a number-average molecular weight of 300 to 6,000 and 1 to 30 ethylenically unsaturated bonds in the main chain and/or side chains of the polymer. Other merits of the thermal transfer ink film of the present invention is that the even transfer is possible, the fastness of the print is not reduced and blocking is not caused, since the content of low-melting components having a melting point lower than 50 °C is very low.

Further the viscosity of the ink is not so increased even at a low temperature (15 °C or lower). Therefore, the fluidity of the ink to be applied to the base is excellent even in winter and it can be applied easily. The coating film strength of the ink film is sufficient for the practical use.

The ribbon comprising the ink film prepared from the thermal transfer ink of the present invention can be used repeatedly many times to reduce the printing cost.

Brief Description of the Drawings:

Fig. 1 is a graph showing the results of Test Example 1, Fig. 2 is a graph showing the results of Test Example 2, Fig. 3 is a graph showing changes in the printing density with the number of times of the repetition of the printing with the ink films prepared in Example 4 and Comparative Example 3, Fig. 4 shows the NMR spectrum of the polyester resin prepared in Example 1, Fig. 5 shows the IR spectrum of the polyester resin prepared in Example 1, Fig. 6 is the NMR spectrum of the polyester resin prepared in Comparative Example 2, and Fig. 7 is the IR spectrum of the polyester resin prepared in Comparative Example 2.

[Examples]

The following Examples will illustrate the effects of the present invention, which by no means limit the invention. In the Examples, parts are given by weight.

In the following Examples, the melting point, number-average molecular weight, NMR and IR were determined as follows:

Melting point [differential scanning calorimetry (DSC)]:

4.5 mg of a sample was heated at a temperature elevation rate of 5 °C/min with a DSC-10A measuring apparatus of Rigaku Denki Co., Ltd. The temperature at the top of the endothermic peak was employed as the melting point.

Number-average molecular weight:

The acid value (AV, JIS K 8006) and hydroxyl value (OHV, JIS K 8006) of the polyester resin were determined and the number-average molecular weight was determined according to the following formula:

$$\text{number-average molecular weight} = \frac{112200}{(\text{AV} + \text{OHV})}$$

NMR:

The polyester resin was dissolved in deuterated chloroform containing 1% of TMS and proton NMR thereof was determined with a Varian T-60 NMR spectrometer.

IR:

IR was determined by the KBr method with a Hitachi Model 270-30 infrared spectrophotometer.

Example 1

354 g of hexamethylene glycol, 485 g of sebacic acid, 70 g of fumaric acid and 450 mg of hydroquinone were placed in a 1-l four-necked flask, which was then provided with a thermometer, stirrer, condenser and nitrogen-inlet tube. The polycondensation was conducted at 180° C in a nitrogen stream in a mantle heater to obtain a polyester resin having a number-average molecular weight of 2500 and a melting point of 61° C.

The NMR of the polyester resin was determined and a proton assignable to an ethylenically unsaturated bond was confirmed (chemical shift δ = 6.8 ppm) (Fig. 4). In the IR spectrum, an absorption peak assignable to the C=C stretching vibration of a non-conjugated olefin was confirmed at 1660 cm⁻¹ (Fig. 5). Namely, it was confirmed that the polyester resin had an ethylenically unsaturated bond.

A mixture of the following composition containing the polyester resin was kneaded with a ball mill for 12 h to prepare a thermal transfer ink:

polyester resin	15 parts
ethylene/vinyl acetate resin	3 parts
carnauba wax	6 parts
carbon black	6 parts
toluene	70 parts

The ink was applied to a polyethylene terephthalate film (Lumirror, a product of Toray Industries, Inc.) having a thickness of 6 μ with a wire bar to form a coloring material layer having a dry coating film thickness of about 3 g/m². Thus a thermal transfer ink film was prepared.

The prepared thermal transfer ink film was used for printing on a plain paper (BEKK 160 sec) with a line-type thermal transfer printer (NIP 5234, 9.4 dots/mm; a product of Nippon Electric Co., Ltd.) and the density of the transferred image was determined. In order to examine the relationship between the printing energy and the density of the transferred image, the pulse duration of the applied voltage was changed by 0.65 to 0.85 sec by means of a density control lever and the density of the transferred image was determined with a Macbeth densitometer (RD 918 type). It was thus found that the pulse duration of the applied voltage necessitated for forming the transferred image having a density of 1.2 was 0.66 sec.

No greasing was observed at all in the course of the printing. To examine the blocking resistance, five sheets of the above-described thermal transfer ink films were put together to form a laminate, which was kept under a pressure of 500 g/cm² for one week. The films were then taken out and examined to reveal that no blocking occurred at all. Even when the ink films were crumpled up with hands, no ink came off to exhibit a high coating film strength.

Example 2

236 g of hexamethylene glycol, 384 g of sebacic acid and 56 g of a dimer acid (Unidyme 22; a product of Union Camp) were placed in a flask of 1 liter and polycondensation was conducted at 180° C in the same manner as that of Example 1 to obtain a polyester resin having a melting point of 63° C and a number-average molecular weight of 1745.

An ink having the same composition as that of Example 1 except that the polyester resin prepared in this example was used was prepared. An ink film was prepared therefrom and the printability thereof was examined in the same manner as that of Example 1. The density after the transfer was determined with a Macbeth densitometer (RD 918) to reveal that the pulse duration of the applied voltage necessitated for forming a transferred image having a density of 1.2 was 0.66 sec.

Even when the ink film was crumpled up with hands, no ink came off to exhibit a high coating film strength.

Example 3

354 g of 1,6-hexanediol, 546 g of sebacic acid and 40 g of dodecenylsuccinic anhydride (a product of Sanyo Chemical Industries, Ltd.) were placed in a 1-l four-necked flask and polycondensation was conducted at 180° C in the same manner as that of Example 1 to obtain a polyester resin having a melting

point of 64° C and a number-average molecular weight of 1784.

An ink having the same composition as that of Example 1 except that the polyester resin prepared in this example was used was prepared. An ink film was prepared therefrom and the printability thereof was examined in the same manner as that of Example 1. The density after the transfer was determined to reveal that the pulse duration of the applied voltage necessitated for forming a transferred image having a density of 1.2 was 0.67 sec.

Even when the ink film was crumpled up with hands, no ink came off to exhibit a high coating film strength.

Comparative Example 1

Paraffin wax	60 parts
carnauba wax	25 parts
carbon black	15 parts

A composition comprising the above-described components was treated with an attritor at 100° C for 4 h to prepare a dispersion to be used as the thermal transfer ink. The ink was applied to the same polyethylene terephthalate film as that used in Example 1 having a thickness of 6 μ by hot melt coating process to form a coating film having a thickness of 3.5 μ to form a thermal transfer ink film.

An attempt was made to conduct printing with the prepared thermal transfer ink film in the same manner as that of Example 1. When the pulse duration of the applied voltage was 0.65 sec, the transferred image had a density as low as 0.20. The pulse duration of the applied voltage necessary for forming the transferred image having a density of 1.2 was 0.85 sec.

When the ink film was crumpled up with hands, the ink layer was peeled off to indicate that the coating film strength was very low.

Comparative Example 2

A polyester having a melting point of 67° C and a number-average molecular weight of 1900 was prepared from 354 g of hexamethylene glycol and 606 g of sebacic acid in the same manner as that of Example 1. The NMR of the polyester resin thus obtained was determined to find no peak around a chemical shift δ of 6.8 (see Fig. 6). In the IR analysis, no peak was found at around 1660 cm^{-1} (see Fig. 7). Thus it was confirmed according to the NMR and IR analyses that the polyester had no ethylenically unsaturated bond.

An ink and an ink film having the same composition as that of Example 1 except that the polyester resin prepared in this comparative example was used were prepared. The printability of the film was examined in the same manner as that of Example 1. The density of the transferred image was determined to reveal that the pulse duration of the applied voltage necessitated for forming a transferred image having a density of 1.2 was 0.67 sec. This fact indicated that the film had a high sensitivity. However, the ink film had a defect that when it was crumpled up with hands, ink came off seriously.

Test Example 1

The solubilities (shown in terms of wt.% of the solid concentration in the solution) of the polyester resins prepared in Examples 1, 2 and 3 and Comparative Example 2 in toluene were determined to obtain the results shown in Fig. 1.

It is apparent from Fig. 1 that as compared with the saturated polyester resin prepared in Comparative Example 2, the polyester resins having ethylenically unsaturated bonds in the molecule prepared in Examples 1, 2 and 3 had a higher solubility in toluene and formed only a smaller amount of crystals even at a low temperature.

Test Example 2

The viscosities of the inks prepared in Examples 1 and 2 and Comparative Example 2 were determined at various temperatures to obtain the results shown in Fig. 2.

It is apparent from Fig. 2 that the increase in the viscosity of the inks prepared in Examples 1 and 2 at low temperatures was only slight. This will be understood well from the data of the solubilities shown in Fig.

5 1.

Example 4

10 A mixture of the following composition containing the polyester resin having a melting point of 61 ° C, a solidifying point of 53 ° C and a number-average molecular weight of 2500 which was prepared in Example 1 was kneaded with a ball mill for 12 h to prepare a thermal transfer ink:

15	Polyester resin	15 parts
	ethylene/vinyl acetate resin	3 parts
	carnauba wax	6 parts
	carbon black	6 parts
	toluene	70 parts

20

The ink was applied to a polyethylene terephthalate film having a thickness of 6 μ to form about 7 g/m² (on dry basis) of a coating film. The prepared thermal transfer ink film was used for printing with a commercially available thermal transfer printer (Bungo Mini 7E; a personal word processor of NEC). The printability was evaluated by continuous black solid printing. A part of the ribbon was used repeatedly and a change in the density of the print as determined with a Macbeth densitometer was examined. The results are shown in Fig. 3.

25

It is apparent from Fig. 3 that an optical density (OD) above 1.0 was kept until the printing was repeated three times to prove a high capacity of the ink for repeated printing. Even when the ink ribbon was crumpled up with hands, no ink came off to prove a high coating film strength.

30

Comparative Example 3

35 An ink having the same composition as that of Example 4 except that the polyester resin was replaced with Wax HNP-10 having a melting point of 75 ° C and a solidifying point of 75 ° C (a product of Nippon Seiro Co.) was prepared. An ink film was prepared from the ink and its printability was evaluated in the same manner as that of Example 4.

The results are shown in Fig. 3. Almost the whole of the ink was transferred in the first printing step so that the repeated use thereof was utterly impossible.

40

Claims

45 1. An ink composition for thermal transfer which comprises a coloring matter, a vehicle and a polyester having a melting point of 50 to 110 degree C, determined by the DSC method and a number-average molecular weight of 300 to 6,000 and containing 1 to 30 ethylenic unsaturations.

2. A composition as claimed in Claim 1, which comprises 40 to 80 percent by weight, based on the entire solid components, of the polyester and 10 to 30 percent by weight, based on the entire solid components, of the coloring matter.

50 3. An ink film for thermal transfer which comprises a substrate and an ink layer, coated on the substrate, comprising the ink composition as defined in Claim 1.

55

FIG. 1

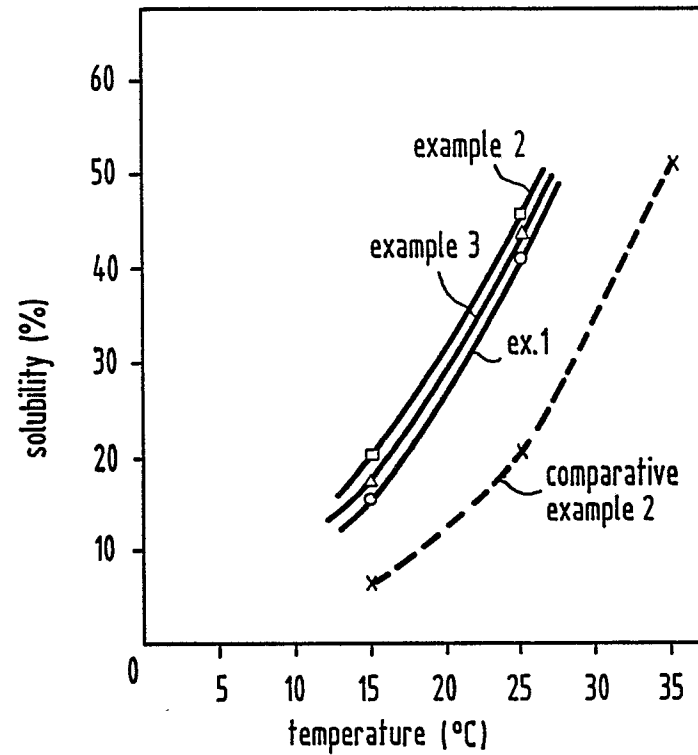
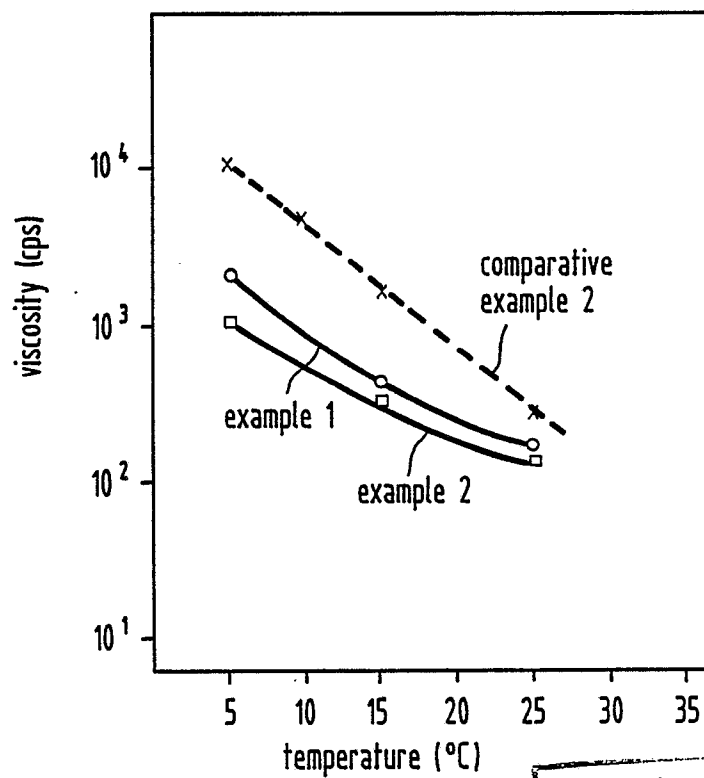


FIG. 2



Neu eingereicht / Newly filed
Nouvellement déposé

FIG. 3

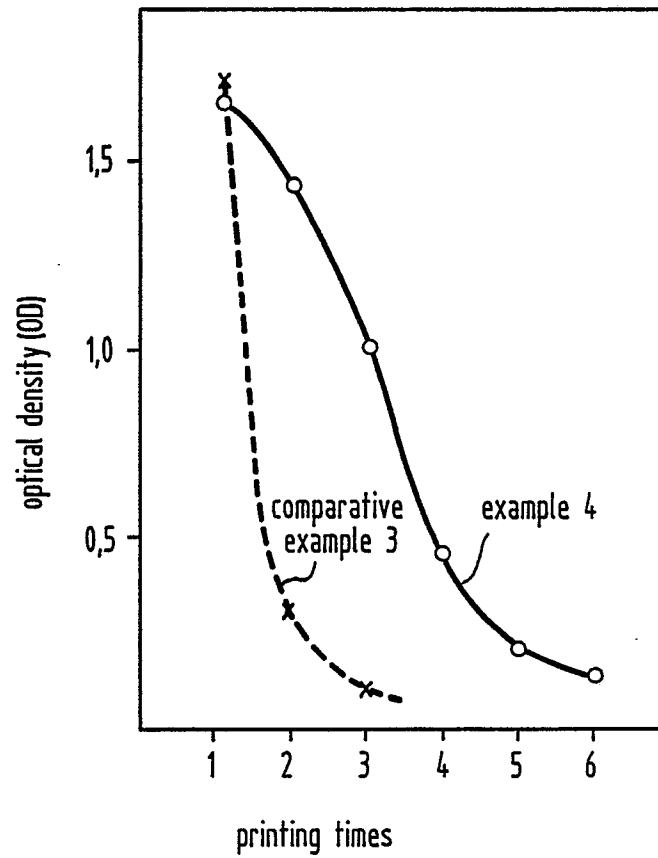


FIG. 4

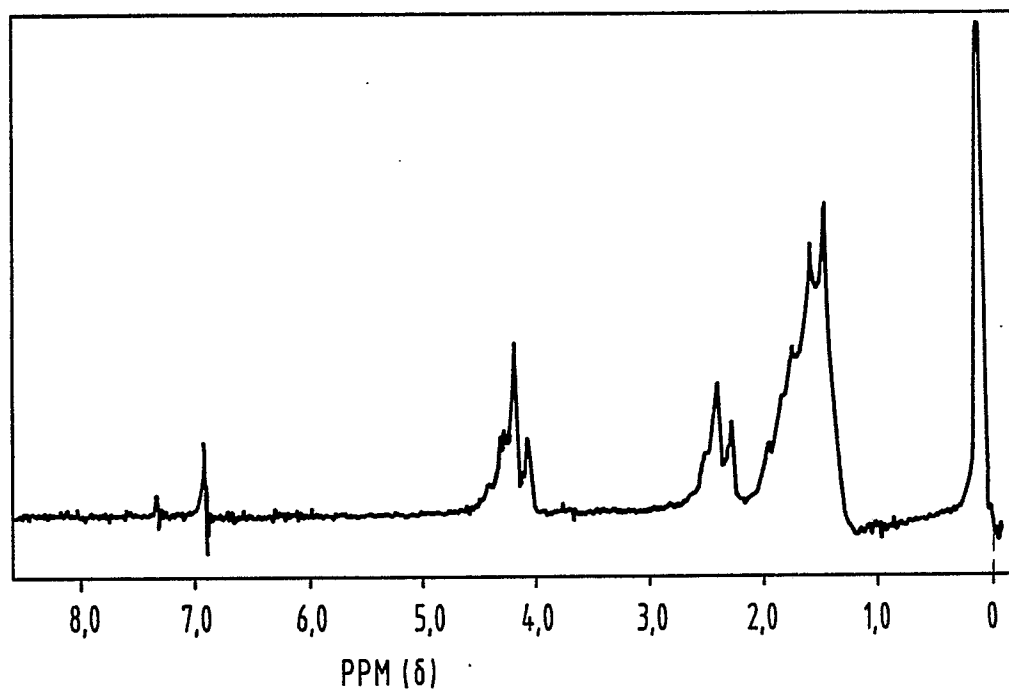


FIG. 5

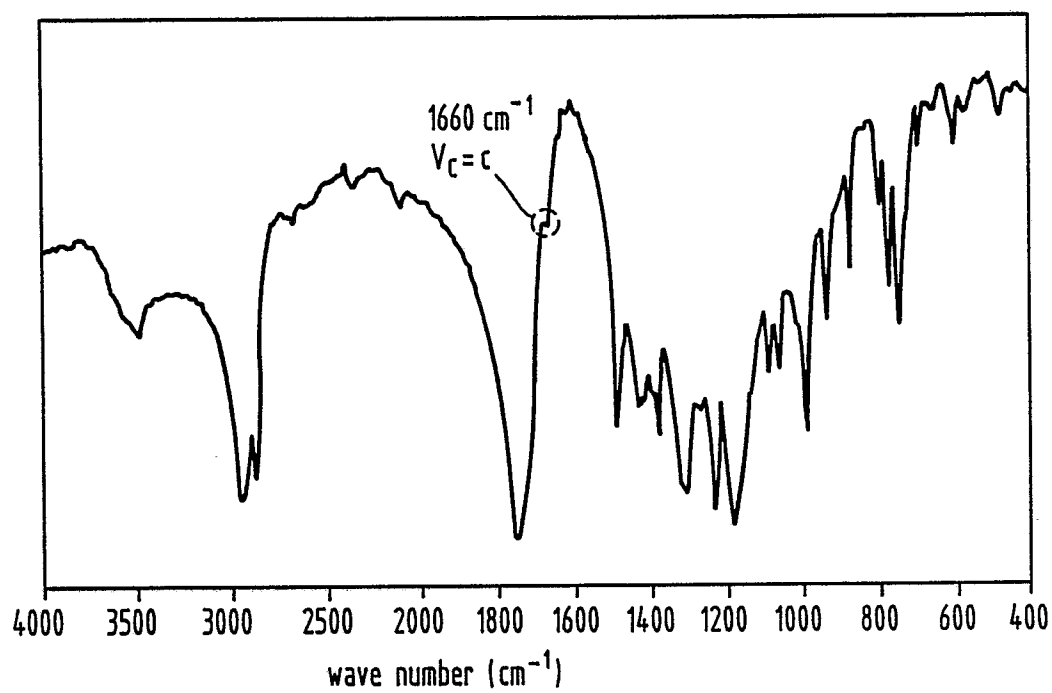


FIG. 6

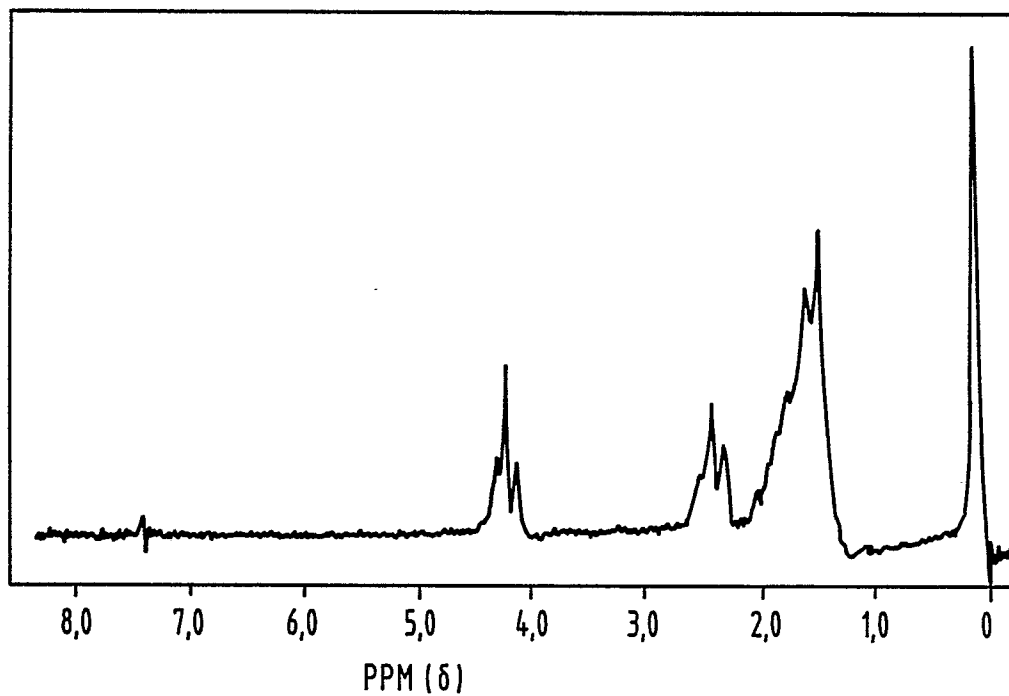


FIG. 7

