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

(11) EP 0 820 875 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.01.1998 Bulletin 1998/05

(51) Int Cl.[6]: **B41M 5/40**

(21) Application number: **97305483.6**

(22) Date of filing: **22.07.1997**

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

(30) Priority: **24.07.1996 JP 212185/96**
24.07.1996 JP 212186/96

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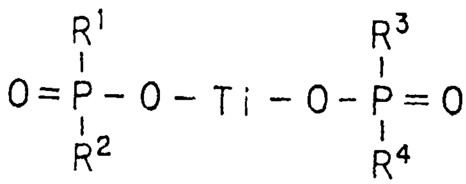
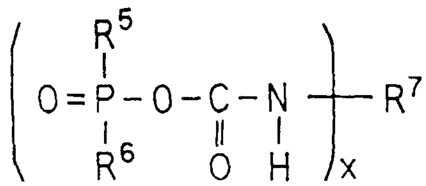
(54) Thermal transfer sheet having a specific lubricant slipping layer

(57) A thermal transfer sheet of the present invention has a heat resistant slip layer on its back surface. The heat resistant slip layer comprises organic phosphoric ester derivative represented by the following formula (1) or formula (2) as a lubricant



··· (1)

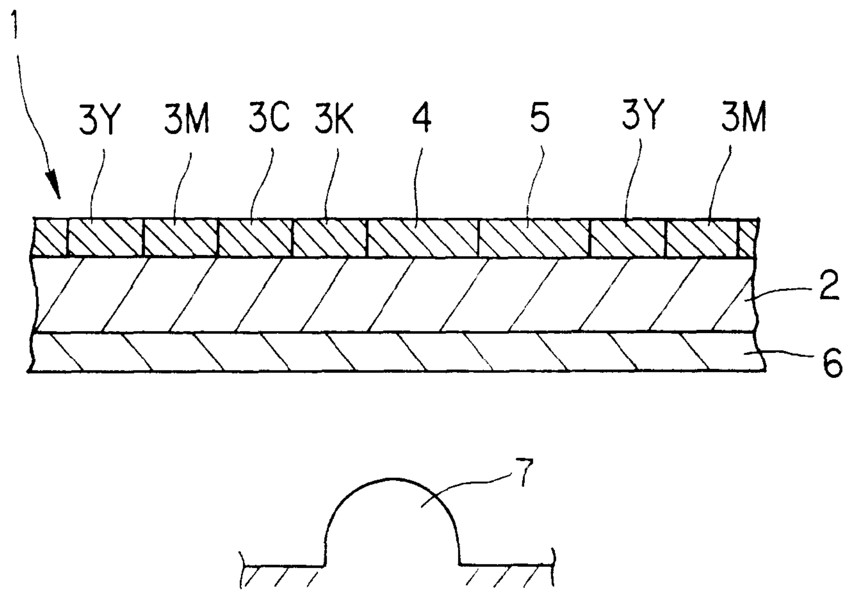


··· (2)

[in formulas (1) and (2), each of R^1 to R^6 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; R^7 denotes saturated aliphatic chain, unsaturated aliphatic chain or aromatic chain; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20; and "x" denotes integer of 1 or more]

EP 0 820 875 A1

FIG. 1



Description

BACKGROUND OF THE INVENTION

The present invention relates to a thermal transfer sheet, and particularly relates to a thermal transfer sheet provided with a heat resistant slip layer comprising a specific material, which can prevent dropping out or misregistration of print to be caused by crumples of the thermal transfer sheet or an image-receiving material in a printing process, sticking of a thermal head to the thermal transfer sheet, and formation of head grime to be caused by a heating operation with the use of the thermal head and a cooling process thereafter.

As conventional thermal transfer sheets, there have been known a sublimation type thermal transfer sheet and a heat fusion type thermal transfer sheet. A typical sublimation thermal transfer sheet is composed of a substrate film made of plastic such as polyester and a dye layer as a thermally transferable coloring material layer which is disposed on one surface of the substrate film and made of sublimation dye and binder resin. On the other hand, the heat fusion thermal transfer sheet has a heat fusible ink layer made of a heat fusible composition containing coloring material instead of the dye layer. Such a thermal transfer sheet is image-wise heated from its back surface side by a heating means such as the thermal head to transfer the dye of the dye layer or the heat fusible composition of the heat fusible ink layer to the image-receiving material, thus forming an image.

Use of the conventional thermal transfer sheet having a substrate film made of relatively heat fusible material such as plastic has caused problem in a process for formation of the image, such as deterioration of a peeling ability and a slipping ability against the thermal head and breakage of the substrate film. In order to solve that problem, a heat resistant slip layer has been formed on a surface of the substrate film opposite to the surface on which the coloring material layer is disposed by using modified resin such as thermosetting resin and silicone resin solely or in combination with cross linking agent. However, along with improvements in printing speed and printing quality of a printer, there has been a great demand for a more excellent heat resisting and slipping ability of the heat resistant slip layer. Accordingly, there has been made an attempt to add a lubricant such as surface active agent, oil, organometallic salt and wax any one of which has the good slipping ability and the good releasing (or peeling) ability in a heated condition into the heat resistant slip layer.

At the time of image formation, printing energy to be applied to the thermal transfer sheet by the thermal head is varied in a wide range according to respective printing densities, and the slipping ability and the releasing ability are desired to be stable within the whole range of the printing energy. However, the conventional lubricant has still caused problem.

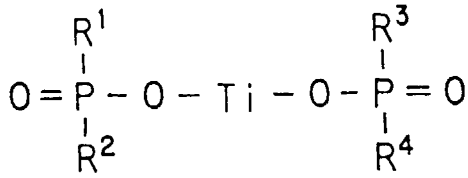
More specifically, in a case where the lubricant to be added is liquid, it may have a poor compatibility to the binder resin for the heat resistant slip layer. Furthermore, when the liquid lubricant has a low viscosity, the lubricant may transfer to the opposite surface of the substrate film or a surface of a conveying roll in the manufacturing or working process to cause a shortage of the lubricant in the heat resistant slip layer of the thermal transfer sheet as an end product. Accordingly, the use of the liquid lubricant may cause a deterioration of the slipping ability. Furthermore, when the thermal transfer sheet is rolled up, the use of the liquid lubricant may cause the transferring of the coloring material from the coloring material layer to the adjacent heat resistant slip layer, resulting in a contamination of the heat resistant slip layer.

On the other hand, in another case where the lubricant to be added is solid or wax, the slipping ability and the releasing ability may be insufficient because of its low responsiveness to a momentary heating, and further, the lubricant may be deposited on the surface of the thermal element such as the thermal head to become the head grime in a cooling process after the heating with the use of the thermal head, thus causing a bad influence to the printed surface. As shown in FIG. 2, when the thermal head 7 is sliding along the back surface 8 of the thermal transfer sheet, the head grime 10 is liable to be deposited on a surface of an advance direction (9) side of the thermal head 7.

SUMMARY OF THE INVENTION

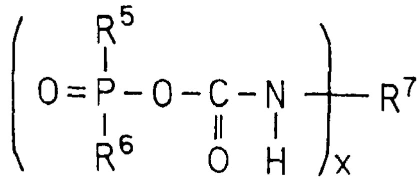
Accordingly, an object of the present invention is to provide a thermal transfer sheet in which properties of the heat resistant slip layer such as the slipping ability and the releasing ability are excellent in the heat responsiveness, and the formation of the head grim to be caused in the heating operation with the use of the thermal head and the cooling process thereafter is prevented.

A thermal transfer sheet provided by the present invention comprises a substrate film, at least one transferable layer disposed on one surface side of said substrate film and a heat resistant slip layer disposed on another surface side of said substrate film, said heat resistant slip layer comprising organic phosphoric ester derivative represented by the following formula (1) or formula (2) as a lubricant;



··· (1)

[in the formula (1), each of R^1, R^2, R^3 and R^4 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; and "n" denotes integer of 1 to 20]



··· (2)

[in formula (2), each of R^5 and R^6 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; R^7 denotes saturated aliphatic chain, unsaturated aliphatic chain or aromatic chain; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20; and "x" denotes integer of 1 or more]

When the organic phosphoric ester derivative represented by the formula (1) or the formula (2) is used as the lubricant for the heat resistant slip layer of the thermal transfer sheet, the organic phosphoric ester derivative is compatible very well with the binder resin for the heat resistant slip layer and hardly transfers to another surface or object, and it becomes possible to prevent a contamination of the heat resistant slip layer to be caused by the transferring of the coloring material, to improve the slipping ability, the releasing ability and the like with respect to their responsiveness against the heating, and to prevent a formation of the head grime to be caused in the heating operation with the use of the heating element and the cooling process thereafter.

The heat resistant slip layer may contain: an organic or inorganic filler; a hardening agent such as isocyanate hardening agent, polyisocyanate, monomer containing unsaturated bond, polymer containing unsaturated bond, chelate compound and epoxy hardening agent; and another lubricant other than the organic phosphoric ester derivative described above.

The heat resistant slip layer usually comprises 100 weight parts of a binder resin and 1 to 100 weight parts of the organic phosphoric ester derivative. When the binder resin for the heat resistant slip layer contains the filler and/or the hardening agent, the heat resistant slip layer usually comprises 100 weight parts of the binder resin in a total amount including the filler and the hardening agent and 1 to 150 weight parts of the organic phosphoric ester derivative.

The heat resistant slip layer usually has an applied amount up to 3.0 g/m^2 in a solid component.

The transferable layer of the thermal transfer sheet may be a coloring material layer selected from the group consisting of a dye layer and a heat fusible ink layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of one example of a thermal transfer sheet according to the present invention.

FIG. 2 is an explanatory view indicating a formation process of a head grime.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will be described further in detail hereunder with reference to a preferred exemplary embodiment thereof. FIG. 1 shows a schematic sectional view of one example of the thermal transfer sheet according to the present invention. In FIG. 1, the thermal transfer sheet 1 has a substrate film 2, and plural kinds of transferable layers, i.e., coloring material layers of Yellow (3Y), Magenta (3M), Cyan (3C) and Black (3K), a transferable receptor layer 4 and a transferable protect layer 5 are formed on a front surface of the substrate film 2 side by side in this order. Furthermore, a heat resistant slip layer 6 is formed on a back surface of the substrate film 2.

A thermal element such as a thermal head 7 is brought into contact with the back surface of the thermal transfer sheet 1, and the thermal transfer sheet 1 is heated from its back surface side. Through such a heating operation, the transferable receptor layer 4 is first transferred onto an area to be printed of an image receiving material, and next, at least one color of the coloring material such as the dye or the heat fusible ink is transferred from any coloring material layer 3Y, 3M, 3C or 3K to the area provided with the receptor layer to form the image, and the transferable protect layer 5 is transferred onto the area having the formed image, thus obtaining a printed matter.

In the thermal transfer sheet of the present invention, one or more kinds of transferable layer optionally selected are disposed on the front surface side of the substrate film side by side, and the heat resistant slip layer containing the organic phosphoric ester derivative represented by the formula (1) or the formula (2) as a lubricant is disposed on the back surface side of the substrate film. The transferable layer to be disposed on the front surface side may be thermally transferable itself or contain a thermally transferable component. The transferable layer capable of transferring itself includes the heat fusible ink layer, the transferable receptor layer, the transferable protect layer and the like. The transferable layer enabling the component therein to transfer includes the sublimation dye layer.

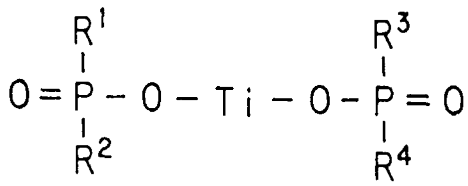
Detailed explanation for the substrate film and the layers to be often formed on the substrate film will be described hereunder.

[SUBSTRATE FILM]

In the present invention, the substrate film for the thermal transfer sheet is not limited to a specific one as far as the film has a desired heat resistance and strength, and a known substrate film conventionally used for a general thermal transfer sheet may be used. An example for the substrate film includes the following films which usually have a thickness of 0.5 to 50 μm, and preferably 3 to 10 μm: a resin film such as a polyethylene terephthalate film, a poly 1,4-cyclohexylenedimethylene terephthalate film, a polyethylene naphthalate film, polyphenylene sulfide film, a polystyrene film, a polypropylene film, a polysulfone film, an aramid film, a polycarbonate film, a polyvinyl alcohol film, cellophane, a film of cellulose acetate or another cellulose derivative, a polyethylene film, a polyvinyl chloride film, a nylon film, a polyimide film and an ionomer film; a paper such as condenser paper and paraffin paper; a non woven fabric; and a composite film composed of these films such as a film composed of the resin film and any one of the paper and the non woven fabric.

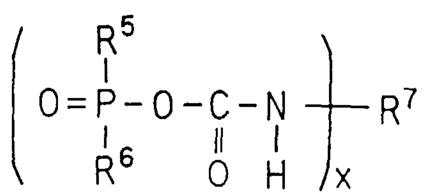
[HEAT RESISTANT SLIP LAYER]

The heat resistant slip layer on one surface of the substrate is formed of at least the binder resin and the organic phosphoric ester derivative represented by the following formula (1) or formula (2) as the lubricant, and it may contain various kind of additives as the occasion demands.



··· (1)

[in the formula (1), each of R^1, R^2, R^3 and R^4 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; and "n" denotes integer of 1 to 20; and R^1, R^2, R^3 and R^4 may be the same or different from each other]



··· (2)

[in formula (2), each of R^5 and R^6 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; R^7 denotes saturated aliphatic chain, unsaturated aliphatic chain or aromatic chain; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20; and "x" denotes integer of 1 or more; and R^5 and R^6 may be the same or different from each other; and the respective R^7 may be the same or different from each other]

The binder resin for the heat resistant slip layer is not limited to a specific one, and any one of thermoplastic resin and thermosetting resin may be used solely or in combination with each other as the binder resin. A reaction product obtained by reacting a resin having a reactive group with a hardening agent such as an isocyanate hardening agent, a monomer or oligomer or high polymer containing unsaturated bond, a chelate compound and an epoxy hardening agent may also be used as the binder resin having an improved heat resistance. A method for the hardening is not limited to a specific one, and the reaction product may be hardened by, for example, the heating or the ionizing radiation. Furthermore, each kind of modified resin obtained by modifying the binder resin with silicone, long chain alkyl or the like may be used as the binder resin for the heat resistant slip layer.

As the binder resin for the heat resistant slip layer, there may preferably be used, for example, polyester resin, polyacrylic ester resin, polyvinyl acetate resin, styrene acrylate resin, polyurethane resin, polyolefine resin, polystyrene resin, polyvinyl chloride resin, polyether resin, polyamide resin, polycarbonate resin, polyethylene resin polypropylene resin, polyacrylate resin, polyacrylamide resin, polyvinyl butyral resin, polyvinyl acetoacetal resin, and oily polyol, and more preferably used polyvinyl acetal resin such as polyvinyl acetoacetal resin. As the modified resin, there may be used various kinds of the silicone modified resin supplied on the market, acrylic polyol, acetal resin and a reaction product obtained by reacting a resin having hydroxyl group with monohydric higher alcohol derivative modified with isocyanate.

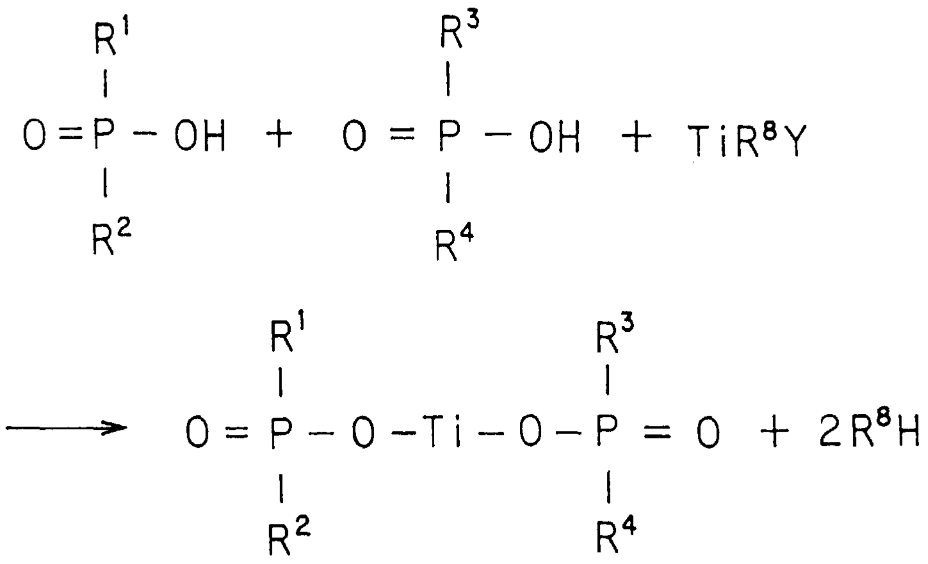
For the purpose of improving the heat resistant slip layer in its heat resistance, its coating workability and its adhesiveness to the substrate film, polyisocyanate which is to act as a cross linking agent may be added into the heat resistant slip layer. As the polyisocyanate, there may be any polyisocyanate compound conventionally used for paint, adhesive or bonding agent and synthesis of polyurethane. A concrete example of such a polyisocyanate includes the following manufactured products: TAKENATE (manufactured by TAKEDA YAKUHIN KOGYO Co. Ltd.), BARNOCK (manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.), COLONATE (manufactured by Nihon Polyurethane Kogyo Co. Ltd.), DURANATE (manufactured by Asahikasei Kogyo Co. Ltd.)and DESMODUR (manufactured by Bayer Co. Ltd.).

An amount of polyisocyanate is usually within a range of 5 to 280 weight parts to 100 weight parts of the binder resin for the heat resistant slip layer. A ratio of " -NCO/-OH " is preferably within a range of 0.6 to 2.0. An excessively small amount of polyisocyanate lowers a density of cross linkage to cause an insufficiency of the heat resistance. On the other hand, an excessively large amount of polyisocyanate causes difficulty in controlling shrinkage of a freshly-coated heat resistant slip layer and delay of the hardening time, and further, when an unreacted -NCO group still remains in the heat resistant slip layer, the remaining -NCO group reacts with moisture in the air and the binder resin or the dye in the coloring material layer, resulting in degradation of the property of the thermal transfer sheet.

The monomer or polymer (oligomer or high polymer) containing the unsaturated bond may also be used as the cross linking agent for the purpose of improving the heat resistant slip layer in its heat resistance, its coating workability and its adhesiveness to the substrate film. The monomer or polymer containing the unsaturated bond may be used solely in place of the isocyanate described above or in combination therewith. As a typical hardening method for those monomer and polymer, there may be used irradiation of an electron ray or an ultraviolet ray, and in a case of a large amount of the filler to be used, the irradiation of the electron ray is preferably carried out.

An example of the monomer or polymer containing the unsaturated bond includes the following compounds, and a wording "(metha)acrylate" described below means as acrylate and methacrylate: a bi-functional monomer such as tetraethyleneglycol di(metha)acrylate, divinylbenzene and diallyl phthalate; a ter-functional monomer such as triallyl isocyanate and trimethylolpropane tri(metha)acrylate; tetramethylolmethane tetra(metha)acrylate; trimethoxyethoxy vinylsilane; a quinque or more functional monomer; and an oligomer or high polymer made from the above described monomer.

The organic phosphoric ester derivative represented by the formula (1) which is used as the lubricant in the present invention is a reaction product obtained by reacting an organic phosphoric ester with a titanium chelate, and its reaction process can be expressed by the following reaction formula (3):

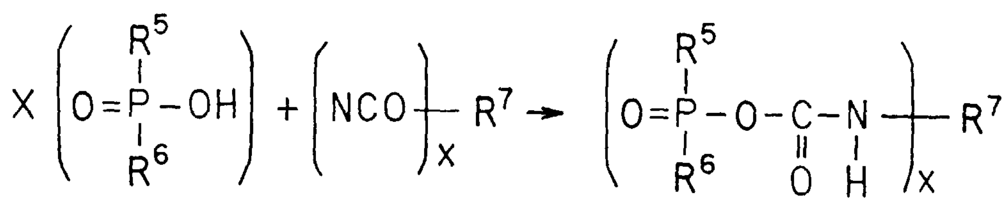


··· (3)

[in the formula (3), each of R^1, R^2, R^3 and R^4 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ 1 or OH; R^8 denotes OC_zH_{2z+1} or $NO_{z/2}C_zH_{2z+1}$; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20, "y" denotes integer of 2 to 4; and "z" denotes integer of 1 to 8; and R^1, R^2, R^3 and R^4 may be the same or different from each other; and the respective R^8 may be the same or different from each other]

For the reaction expressed by the above reaction formula (3), there may be used various kinds of the organic phosphoric ester, and a concrete example thereof includes: a series of PLYSURF (manufactured by Daiichi Kogyo Seiyaku Co. Ltd.); a series of JP (manufactured by Johoku Kagaku Kogyo Co. Ltd.); and a series of NIKKOL DDP (manufactured by Nikko Chemical Co. Ltd.). Besides, a concrete example of the titanium chelate agent includes: a series of ORGATIX TC (manufactured by Matsumoto Kosyo Co. Ltd.); TAA, TLA, TEAA, TEAT, TAT, TBSTA (manufactured by Nihon Soda Co. Ltd. or Mitsubishi Gas Chemical Co. Ltd.)

The organic phosphoric ester derivative represented by the formula (2) can be used as the lubricant in the present invention in place of the organic phosphoric ester derivative represented by the formula (1) or in combination with the same. The organic phosphoric ester derivative represented by the formula (2) is a reaction product obtained by reacting an organic phosphoric ester with a isocyanate, and its reaction process can be expressed by the following reaction formula (4):



··· (4)

[in the formula (4), each of R^5 and R^6 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; R_7 denotes saturated aliphatic chain, unsaturated aliphatic chain or aromatic chain; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20; and "x" denotes integer of 1 or more; and R^5 and R^6 may be the same or different from each other; and the respective R^7 may be the same or different from each other]

For the reaction expressed by the above reaction formula (4), there may be used various kinds of the organic phosphoric ester, and a concrete example thereof is similar to that used in the reaction formula (3). Besides, the isocyanate for the reaction formula (4) is not limited to a specific one as far as it contains isocyanate group, and there may be used: for example, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), 1,5-naphthalene diisocyanate (NDI), tolidine diisocyanate (TODI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), p-phenylene diisocyanate, xylylene diisocyanate (XDI), hydrogenated HDI (H_6 HDI), hydrogenated MDI (H_{12} HDI), lysine diisocyanate (LDI), tetramethylxylene diisocyanate (TMXDI), lysine ester triisocyanate, 1,6,11-undecane triisocyanate, 1,8-diisocyanate-4-isocyanate methyloctane, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, trimethylhexamethylene diisocyanate (TMDI) and the like.

It becomes possible to provide a sufficient slipping ability and a releasing ability for the heat resistant slip layer by the addition of one or more kinds of the organic phosphoric ester derivatives represented by the formula (1) or (2). An added amount of the organic phosphoric ester derivatives is usually within a range of 1 to 100 weight parts, and preferably 2 to 50 weight parts, with respect to 100 weight parts of the binder resin for the heat resistant slip layer. In a case where the binder resin contains the hardening agent, the filler and the like, an added amount of the organic phosphoric ester derivatives is usually within a range of 1 to 150 weight parts, and preferably 50 to 120 weight parts, with respect to 100 weight parts of the binder resin in a total amount including the hardening agent, the filler and the like.

An excessively small added amount of the organic phosphoric ester derivative causes an insufficient releasing ability of the heat resistant slip layer with respect to the thermal head or another heating element, thus resulting in the dropping out or the misregistration of the print to be caused by the crumples of the thermal transfer sheet or the image-receiving material in a printing process, and the sticking of a thermal head to the thermal transfer sheet. On the other hand, an excessively large added amount of the organic phosphoric ester derivatives causes the deposition of the head grime on the thermal head or another heating element during the heating operation and the cooling process thereafter, thus resulting in a bad influence on the surface to be printed.

A lubricant other than the organic phosphoric ester derivative represented by formulas (1) or (2) may be used in combination therewith in order to further improve and stabilize the property of the heat resistant slip layer. As the lubricant other than the organic phosphoric ester derivative, there may be used: for example, a phosphoric ester series surface active agent; polyethylene phenyl polysiloxane; fatty acid amide; fatty acid ester; long chain aliphatic compound; low molecular polypropylene; a block copolymer of ethylene oxide and propylene oxide; a condensation product of fatty acid salt and polyether compound; an addition product of perfluoro ethylene oxide; a nonionic surfactant such as a sorbitan acid ester series surface active agent; and sodium salt of long chain alkyl sulfonic acid. An amount for use of such an lubricant is usually 5 to 100 weight parts, and preferably 5 to 50 weight parts, with respect to 100 weight parts of the above organic phosphoric ester derivative.

For the purpose of providing a good workability, a conveyance stability and a capability to clean the thermal head for the thermal transfer sheet, it is preferable to use an organic or inorganic filler for the heat resistant slip layer. The filler should have a proper particle diameter and a proper particle shape for forming convexo-concave to the surface of the heat resistant slip layer, and not cause wear of the thermal head. As a proper filler, there may be used: for example, the inorganic filler such as talc, kaoline, clay, calcium carbonate, magnesium hydroxide, magnesium carbonate, magnesium oxide, precipitated barium sulfate, molybdenum disulfide, hydrotulcite silica; the organic filler such as acrylic resin, benzoguanamine resin, silicone resin, fluoro resin. It is preferable that the filler has a slipping ability, a low hardness and a capability to clean the thermal head.

The filler may directly be added and dispersed into the binder resin. Further, it is preferable that a mixture containing the filler is prepared by dispersing the filler in a dispersion medium such as resin and surface active agent any one of which has a good wetting to the filler and a relatively low viscosity, and the thus prepared mixture is added into the binder resin. An example of the dispersion medium includes polyether polyol such as UNIOL TG-1000, -2000 and -3000 (manufactured by Nihon Yushi Co. Ltd.), polyurethane resin such as OLESTER -C1000 and -C1066 (manufactured by Mitsuitoatsu Co. Ltd.), PEG and various kinds of surface active agent.

In one method, the heat resistant slip layer may be formed by: previously selecting proper solvent such as acetone, methyl ethyl ketone, toluene, xylene and another organic solvent or water in order to control the coating suitability; dissolving or dispersing the raw material as described above in the selected solvent to prepare a coating liquid; applying the coating liquid on the back surface side of the substrate film through the known coating method or means such as a gravure coater, a roll coater and a wire coater; and then drying it to solidify. An applied amount of the coating liquid, i.e., a thickness of the heat resistant slip layer is usually up to 3.0 g/m^2, and preferably in a range of 0.1 to 1.0 g/m^2 based on a content of a solid component, and the heat resistant slip layer having a sufficient property can be formed within such an amount. In a case where the polyisocyanate is used together, because the unreacted polyisocyanate group is liable to be left in the coated layer even after the drying process, it is preferable to carry out a heating and aging treatment so as to run out of the unreacted polyisocyanate group.

It is effective to form a primer layer previous to the formation of the heat resistant slip layer. The primer layer is desired to have a sufficient adhesiveness to the substrate film and the heat resistant slip layer, and a sufficient heat resistance and a sufficient dimensional stability so as to prevent a thermal deformation of the substrate film. The primer layer may be formed of any one of thermoplastic resin, thermosetting resin, a mixture of a hardening agent and a resin having reaction group which is reactive with the hardening agent, and a coating composition capable of the cross linking reaction by the irradiation of the light or the ionizing radiation. A coating amount of the primer layer is usually up to 1.0 g/m^2, and preferably in a range of 0.1 to 0.5 g/m^2, based on the content of the solid component.

[COLORING MATERIAL LAYER]

A thermal transferable coloring material layer may be formed on the front surface of the substrate film. In a case of the sublimation thermal transfer sheet, a dye layer containing sublimation dye is formed on the substrate film, and in a case of the heat fusion type thermal transfer sheet, a heat fusible ink layer colored with pigment or the like is formed thereon. The sublimation thermal transfer sheet will intensively be described hereunder. Though detail of another coloring material layer is omitted, the coloring material layer is not limited to only the sublimation type dye layer.

A dye for the sublimation type dye layer is not limited to a specific one, and a dye conventionally used for the known thermal transfer sheet may be used in the present invention. For example: a preferable red dye includes MS Red G, Macro Red Violet R, Ceres Red 7B, Samaron Red HBSL and Resolin Red F3BS; and a yellow dye includes Phorone Brilliant Yellow 6GL, PTY-52 and Macrolex Yellow 6G; and a preferable blue dyes includes Kayaset Blue 714, Waxoline Blue AP-FW, Phorone Brilliant Blue S-R and MS Blue 100.

For a binder resin to carry and sustain the dye, any kind of known binder resin can be used. A preferable binder resin includes: for example, cellulose resin such as ethyl cellulose, hydroxyethyl cellulose, ethyl hydroxycellulose, hydroxypropyl cellulose, methyl cellulose, cellulose acetate and cellulose acetate butyrate; vinyl resin such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, polyvinyl acetoacetal and polyvinyl pyrrolidone; acrylic resin such as poly (metha)acrylate and poly(metha)acrylamide; polyurethane resin; polyamide resin; and polyester resin. Of these binder resins, there may preferably be used the cellulose series, vinyl series, acrylic series, polyurethane series and polyester series resins in view of heat resistance, transability of the dye and the like.

The dye layer may be formed on one surface of the substrate film by the following manner. More specifically, a mixture of the dye, the resin binder and an optionally added additive such as release agent, organic or inorganic particle are dispersed in a proper organic solvent such as toluene, methyl ethyl ketone, ethanol, isopropyl alcohol, cyclohexanone and DMF, or dissolved in the above organic solvent or water to prepare a coating liquid, and the thus prepared coating liquid is applied on the substrate film and dried through any coating method such as the gravure printing, the screen printing and the reverse roll coating with the use of a gravure plate.

An applied amount of the dye layer is usually in a range of 0.2 to 5.0 g/m^2, and preferably 0.4 to 2.0 g/m^2, based on a content of a solid component. Besides, an amount ratio of the sublimation dye in the dye layer is usually in a range of 5 to 90 weight %, and preferably 10 to 70 weight %, with respect to a weight of the dye layer.

In a case where a monochromatic image is to be printed, one kind of the dye layer may be formed by selecting only one proper dye. On the other hand, in a case where an image is to be printed in various colors, at least two kinds of the dye layers should be formed in a combination of, for example, Yellow, Magenta and Cyan, or further with Black by selecting respective proper dyes.

The image receiving material to be used together with the thermal transfer sheet of the present invention is not limited to a specific one. In a case of the sublimation transfer, there may be used any image receiving material as far as its record surface has receptiveness to the above dye, and furthermore, though the receiving material is formed of non-receptive material such as paper, metal, glass and synthetic resin, such a non-receptive receiving material can also be used by forming a dye receptor layer on its one surface. On the other hand, in a case of the heat fusion transfer, the surface of the receiving material has no need of the receptiveness to the dye, and a normal paper, a plastic film or the like can be used with no receptor layer.

When the thermal transfer sheet of the present invention is subjected to the thermal transfer printing, any known thermal transfer printer is applicable.

According to the above-mentioned present invention, because the lubricant having a good compatibility to the binder resin for the heat resistant slip layer and a low transferring ability is added into the heat resistant slip layer, it is possible to provide a thermal transfer sheet which has the excellent heat responsiveness in the slipping ability and the releasing ability, prevents the formation of the head grim in the heating operation with use of the thermal head and the cooling process thereafter, prevents the formation of the crumple at the time of printing, and provides the printed image having high quality with no dropping out and misregistration.

The present invention will be described hereunder more in detail by way of experiment examples, in which a term "part(s)" or "%" generally denotes weight part(s) or weight %, though not mentioned specifically.

SERIES OF EXAMPLE A

[Preparation Example A-1]

100 weight parts of PLYSURF A208S (manufactured by Daiichi Kogyo Seiyaku Co. Ltd.) was reacted with 42 weight parts of ORGATIX TC-400 (manufactured by Matsumoto Kosyo Co. Ltd.) to obtain a solution of compound having 94 % of solid component.

[Preparation Example A-2]

100 weight parts of JP-510 (manufactured by Johoku Kagaku Co. Ltd.) was reacted with 44 weight parts of OR-

GATIX TC-400 (manufactured by Matsumoto Kosyo Co. Ltd.) to obtain a solution of compound having 92 % of solid component.

[Preparation Example A-3]

100 weight parts of NIKKOL (manufactured by Nikko Chemical Co. Ltd.) was reacted with 44 weight parts of TAA (manufactured by Nihon Soda Co. Ltd.) to obtain a solution of compound having 92 % of solid component.

[Preparation Example A-4]

42 weight parts of TEAT (manufactured by Mitsubishi Gas Kagaku Co. Ltd.) was added into a mixture of 50 weight parts of PLYSURF A208S (manufactured by Daiichi Kogyo Seiyaku Co. Ltd.) and 50 weight parts of JP-518-O (manufactured by Johoku Kagaku Co. Ltd.), and reaction was carried out to obtain a solution of compound having 94 % of solid component.

[Example A-1]

First, the coating material A for the heat resistant slip layer having the following composition was applied onto one surface of the substrate film of the polyester film having a thickness of 4.5 μm in an applied amount of about 1.0 g/m^2 (in dried state), and then dried to form the heat resistant slip layer.

<Material For Heat resistant slip layer A>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	3.6 parts
Solution obtained in Preparation Example A-1	3.0 parts
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	0.2 parts
Toluene	11.0 parts
Ethyl Acetate	11.0 parts

Next, the ink for the dye layer having the following composition was applied onto another surface of the above-mentioned substrate film, on which the heat resistant slip layer was not formed, in an applied amount of 1.0 g/m^2 (in dried state) with the gravure coater, and then dried to form the dye layer. Thus the thermal transfer sheet of Example A-1 according to the present invention was obtained.

<Ink For Formation Of Dye Layer>	
C.I. SOLVENT BLUE 22	5.5 parts
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	3.0 parts
Methyl ethyl ketone	22.0 parts
Toluene	68.0 parts

[Example A-2]

The thermal transfer sheet of Example A-2 according to the present invention was obtained in the same manner as that in Example A-1, except that the coating material B for the heat resistant slip layer having the following composition was used instead of the coating material A, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer B>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Solution obtained in Preparation Example A-1	6.5 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Example A-3]

The thermal transfer sheet of Example A-3 according to the present invention was obtained in the same manner as that in Example A-1, except that the coating material C for the heat resistant slip layer having the following composition was used instead of the coating material A, and the electron ray irradiation step at 175 KeV of an accelerating voltage and 3 Mrad for the cross linking and hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer C>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyfunctional monomer (KAYARAD DPHA, manufactured by Nihon Kayaku Co. Ltd.)	0.7 parts
Solution obtained in Preparation Example A-2	5.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Toluene	12.0 parts
Ethyl acetate	12.0 parts

[Example A-4]

The thermal transfer sheet of Example A-4 according to the present invention was obtained in the same manner as that in Example A-1, except that the coating material D for the heat resistant slip layer having the following composition was used instead of the coating material A.

<Material For Heat resistant slip layer D>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Solution obtained in Preparation Example A-3	4.0 parts
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	3.2 parts
Toluene	10.0 parts
Ethyl acetate	10.0 parts

[Example A-5]

The thermal transfer sheet of Example A-5 according to the present invention was obtained in the same manner as that in Example A-1, except that the coating material E for the heat resistant slip layer having the following composition was used instead of the coating material A.

<Material For Heat resistant slip layer E>	
Acrylic polyol resin (SU-100A, manufactured by Soken Kagaku Co., Ltd.)	4.6 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	56.3 parts
Solution obtained in Preparation Example A-4	13.0 parts
Polyether polyol (UNIOL TG4000, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Example A-6]

The thermal transfer sheet of Example A-6 according to the present invention was obtained in the same manner as that in Example A-1, except that the coating material F for the heat resistant slip layer having the following composition was used instead of the coating material A.

<Material For Heat resistant slip layer F>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts

(continued)

<Material For Heat resistant slip layer F>	
Solution obtained in Preparation Example A-3	6.5 parts
Solution obtained in Preparation Example A-4	6.5 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Comparative Example A-1]

The thermal transfer sheet of Comparative Example A-1 was obtained in the same manner as that in Example A-1, except that the coating material G for the heat resistant slip layer having the following composition was used instead of the coating material A, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer G>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (PLYSURF A208B, manufactured by Daiichi Kogyo Seiyaku Co. Ltd.)	13.0 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Comparative Example A-2]

The thermal transfer sheet of Comparative Example A-2 was obtained in the same manner as that in Example A-1, except that the coating material H for the heat resistant slip layer having the following composition was used instead of the coating material A, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer H>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (JP-510, manufactured by Johoku Kagaku Co. Ltd.)	13.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	33.0 parts
Toluene	33.0 parts

[Comparative Example A-3]

The thermal transfer sheet of Comparative Example A-3 was obtained in the same manner as that in Example A-1, except that the coating material I for the heat resistant slip layer having the following composition was used instead of the coating material A, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer I>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (NIKKOL, manufactured by Nikko Chemical Co. Ltd.)	13.0 parts

(continued)

<Material For Heat resistant slip layer I>	
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	0.2 parts
Methyl ethyl ketone	33.0 parts
Toluene	33.0 parts

[Comparative Example A-4]

The thermal transfer sheet of Comparative Example A-4 was obtained in the same manner as that in Example A-1, except that the coating material J for the heat resistant slip layer having the following composition was used instead of the coating material A, and the electron ray irradiation step at 175 KeV of an accelerating voltage and 3 Mrad for the cross linking and hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer J>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyfunctional monomer (KAYARAD DPHA, manufactured by Nihon Kayaku Co. Ltd.)	0.7 parts
Phosphoric ester lubricant (NIKKOL, manufactured by Nikko Chemical Co. Ltd.)	5.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Toluene	12.0 parts
Ethyl acetate	12.0 parts

[Test And Results]

The thermal transfer sheets obtained in the above mentioned Examples and Comparative Examples were subjected to the thermal transfer printing to evaluate an uneveness of output color caused by an irregular conveyance, a dropping out or a misregistration of print caused by crumples of the thermal transfer sheet or an image-receiving material in a printing process, a formation of the head grime, and a contamination of the heat resistant slip layer caused by the dye. The method and criterion for each evaluation are as follows. Further, the results are shown in TABLE 1.

<Output Color Uneveness By Irregular Conveyance>

The thermal transfer sheet made into a merchantable form by rolling up in a short diameter was stored at 40 °C for 48 hours, and then it was subjected to the thermal transfer printing with the use of a commercially available video printer having a low precision in a control of drive and a pattern generator (CG-931, manufactured by Kenwood Co., Ltd.) to print out a hypochromatic solid printed pattern which was overprinted with three colors. The above thermal transfer printing was carried out at an ordinary temperature and an ordinary humidity. Thereafter the uneveness of the out put color caused by the irregular conveyance and movement of the thermal transfer sheet was evaluated by visual observation on the basis of the following criterion.

<u>Criterion</u>

○: There was almost no occurrence of the out put color uneveness.
×: There was a remarkable occurrence of the out put color uneveness.

<Dropping Out Or Misregistration Of Print By Crumples>

The thermal transfer sheet made into a merchantable form by rolling up in a short diameter was stored at 40 °C for 48 hours, and then it was subjected to the thermal transfer printing with the use of a printer, in which a pressure of the thermal head was made imbalanced so as to easily cause the dropping out or the misregistration, and the pattern generator (CG-931, manufactured by Kenwood Co., Ltd.), to print out a hypochromatic solid printed pattern at 30 °C and 80 % RH. Thereafter, the dropping out or the misregistration of the print caused by the crumples of the thermal transfer sheet or the image-receiving material was evaluated by visual observation on the basis of the following criterion.

Criterion

○: There was no occurrence of the dropping out or misregistration.
Δ: There was an occurrence of the fine dropping out or misregistration in an end portion of the printed matter.
× : There was an occurrence of the large dropping out or misregistration extending in a horizontal direction of the printed matter.

<Formation Of Head Grime>

The thermal transfer sheet was subjected to the thermal transfer printing with the use of the commercially available printer and the pattern generator (CG-931, manufactured by Kenwood Co., Ltd.), to repeatedly print out fifty sheets of step pattern having an eight steps gradation. Thereafter, the surface of the heating portion of the thermal head was visually observed to evaluate the deposition of the head grim.

Criterion

○: There was no occurrence of the head grim deposition.
Δ: There was a little occurrence of the head grim deposition.
×: There was an occurrence of the head grim deposition.

<Dye Transferring Contamination>

The thermal transfer sheet made into a merchantable form by rolling up in a short diameter was stored at 60 °C for 48 hours, and thereafter the dye transferring contamination was evaluated by visually observing the extent of the dye transferred to the heat resistant slip layer.

Criterion

O: There was almost no occurrence of the dye transferring.
×: There was a remarkable occurrence of the dye transferring.

TABLE 1

Number of Example	Output Color Uneveness by Irregular Conveyance	Dropping Out Or Misregistration Of Print By Crumples	Formation of Head Grime	Dye Transferring Contamination
Example A-1	○	○	○	○
Example A-2	○	○	○	○
Example A-3	○	○	○	○
Example A-4	○	○	○	○
Example A-5	○	○	○	○
Example A-6	○	○	○	○
Comparative Example A-1	×	×	Δ	○
Comparative Example A-2	×	×	Δ	○
Comparative Example A-3	×	Δ	Δ	○
Comparative Example A-4	×	×	×	×

SERIES OF EXAMPLE B

[Preparation Example B-1]

44 weight parts of ethyl acetate was added into a mixture of 100 weight parts of PLYSURF A208S (manufactured by Daiichi Kogyo Seiyaku Co. Ltd.) and 52 weight parts of COLONATE L (manufactured by Nihon Polyurethane Kogyo Co. Ltd.), and reaction was carried out to obtain a solution of compound having 75 % of solid component.

[Preparation Example B-2]

100 weight parts of JP-510 (manufactured by Johoku Kagaku Co. Ltd.) was reacted with 100 weight parts of TAKENATE D218 (manufactured by Takeda Yakuhin Kogyo Co. Ltd.) to obtain a solution of compound having 75 % of solid component.

[Preparation Example B-3]

43 weight parts of ethyl acetate was added into a mixture of 100 weight parts of NIKKOL (manufactured by Nikko Chemical Co. Ltd.) and 30 weight parts of SUMIDUR T-80 (manufactured by Sumitomo Bayer Co. Ltd.), and reaction was carried out to obtain a solution of compound having 75 % of solid component.

[Preparation Example B-4]

85 weight parts of BARNOCK D750 (manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.) and 33 weight parts of ethyl acetate were added into a mixture of 50 weight parts of PLYSURF A208S (manufactured by Daiichi Kogyo Seiyaku Co. Ltd.) and 50 weight parts of JP-518-O (manufactured by Johoku Kagaku Co. Ltd.), and reaction was carried out to obtain a solution of compound having 75 % of solid component.

[Example B-1]

First, the coating material K for the heat resistant slip layer having the following composition was applied onto one surface of the substrate film of the polyester film having a thickness of 4.5 μm in an applied amount of about 1.0 g/m^2 (in dried state), and then dried to form the heat resistant slip layer.

<Material For Heat resistant slip layer K>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	3.6 parts
Solution obtained in Preparation Example B-1	3.6 parts
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	0.2 parts
Toluene	11.0 parts
Ethyl Acetate	11.0 parts

Next, the ink for the dye layer having the following composition was applied onto another surface of the above-mentioned substrate film, on which the heat resistant slip layer was not formed, in an applied amount of 1.0 g/m^2 (in dried state) with the gravure coater, and then dried to form the dye layer. Thus the thermal transfer sheet of Example B-1 according to the present invention was obtained.

<Ink For Formation Of Dye Layer>	
C.I. SOLVENT BLUE 22	5.5 parts
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	3.0 parts
Methyl ethyl ketone	22.0 parts
Toluene	68.0 parts

[Example B-2]

The thermal transfer sheet of Example B-2 according to the present invention was obtained in the same manner as that in Example B-1, except that the coating material L for the heat resistant slip layer having the following composition was used instead of the coating material K, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer L>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Solution obtained in Preparation Example B-1	16.0 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Example B-3]

The thermal transfer sheet of Example B-3 according to the present invention was obtained in the same manner as that in Example B-1, except that the coating material M for the heat resistant slip layer having the following composition was used instead of the coating material K, and the electron ray irradiation step at 175 KeV of an accelerating voltage and 3 Mrad for the cross linking and hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer M>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyfunctional monomer (KAYARAD DPHA, manufactured by Nihon Kayaku Co. Ltd.)	0.7 parts
Solution obtained in Preparation Example B-2	6.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Toluene	12.0 parts
Ethyl acetate	12.0 parts

[Example B-4]

The thermal transfer sheet of Example B-4 according to the present invention was obtained in the same manner as that in Example B-1, except that the coating material N for the heat resistant slip layer having the following composition was used instead of the coating material K.

<Material For Heat resistant slip layer N>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Solution obtained in Preparation Example B-3	4.8 parts
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	0.2 parts
Toluene	10.0 parts
Ethyl acetate	10.0 parts

[Example B-5]

The thermal transfer sheet of Example B-5 according to the present invention was obtained in the same manner as that in Example B-1, except that the coating material O for the heat resistant slip layer having the following composition was used instead of the coating material K.

<Material For Heat resistant slip layer O>	
Acrylic polyol resin (SU-100A, manufactured by Soken Kagaku Co., Ltd.)	4.6 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	18.0 parts
Solution obtained in Preparation Example B-4	15.6 parts
Polyether polyol (UNIOL TG4000, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts

(continued)

<Material For Heat resistant slip layer O>	
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Example B-6]

The thermal transfer sheet of Example B-6 according to the present invention was obtained in the same manner as that in Example B-1, except that the coating material P for the heat resistant slip layer having the following composition was used instead of the coating material K.

<Material For Heat resistant slip layer P>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Solution obtained in Preparation Example B-3	7.8 parts
Solution obtained in Preparation Example B-4	7.8 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Comparative Example B-1]

The thermal transfer sheet of Comparative Example B-1 was obtained in the same manner as that in Example B-1, except that the coating material Q for the heat resistant slip layer having the following composition was used instead of the coating material K, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer Q>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (PLYSURF A208B, manufactured by Daiichi Kogyo Seiyaku Co. Ltd.)	13.0 parts
Oily polyol (OLESTER C1066, manufactured by Mitsuitoatsu Kagaku Co. Ltd.)	0.3 parts
Kaolin (KAOLINITE ASP-072, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	28.0 parts
Toluene	28.0 parts

[Comparative Example B-2]

The thermal transfer sheet of Comparative Example B-2 was obtained in the same manner as that in Example B-1, except that the coating material R for the heat resistant slip layer having the following composition was used instead of the coating material K, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer R>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (JP-510, manufactured by Johoku Kagaku Co. Ltd.)	13.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Methyl ethyl ketone	33.0 parts

(continued)

<Material For Heat resistant slip layer R>	
Toluene	33.0 parts

[Comparative Example B-3]

The thermal transfer sheet of Comparative Example B-3 was obtained in the same manner as that in Example B-1, except that the coating material S for the heat resistant slip layer having the following composition was used instead of the coating material K, and the heating and aging step for the hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer S>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyisocyanate (BARNOCK D750-45, manufactured by Dainippon Ink Kagaku Kogyo Co. Ltd.)	19.2 parts
Phosphoric ester lubricant (NIKKOL, manufactured by Nikko Chemical Co. Ltd.)	13.0 parts
Talc (MICRO ACE P-3, manufactured by Nihon Talc Co., Ltd.)	0.2 parts
Methyl ethyl ketone	33.0 parts
Toluene	33.0 parts

[Comparative Example B-4]

The thermal transfer sheet of Comparative Example B-4 was obtained in the same manner as that in Example B-1, except that the coating material T for the heat resistant slip layer having the following composition was used instead of the coating material K, and the electron ray irradiation step at 175 KeV of an accelerating voltage and 3 Mrad for the cross linking and hardening treatment was carried out after the coating and drying step.

<Material For Heat resistant slip layer T>	
Polyvinyl acetoacetal resin (ETHLEC KS-5, manufactured by Sekisui Kagaku Kogyo Co., Ltd.)	4.3 parts
Polyfunctional monomer (KAYARAD DPHA, manufactured by Nihon Kayaku Co. Ltd.)	0.7 parts
Phosphoric ester lubricant (NIKKOL, manufactured by Nikko Chemical Co. Ltd.)	5.0 parts
Nonionic surfactant (NONION-OP85R, manufactured by Nihon Yushi Co. Ltd.)	0.3 parts
Clay (ASP-200, manufactured by Tsuchiya Kaolin Co., Ltd.)	0.2 parts
Toluene	12.0 parts
Ethyl acetate	12.0 parts

[Test And Results]

The thermal transfer sheets obtained in the series of Example B were tested in the same manner as that in the series of Example A to evaluate the uneveness of output color caused by the irregular conveyance, the dropping out or misregistration of print caused by crumples of the thermal transfer sheet or the image-receiving material in the printing process, the formation of the head grime, and the contamination of the heat resistant slip layer caused by the dye. The results of the series of Example B are shown in TABLE 2.

TABLE 2

Number of Example	Output Color Uneveness by Irregular Conveyance	Dropping Out Or Misregistration Of Print By Crumples	Formation of Head Grime	Dye Transferring Contamination
Example B-1	○	○	○	○
Example B-2	○	○	○	○
Example B-3	○	○	○	○

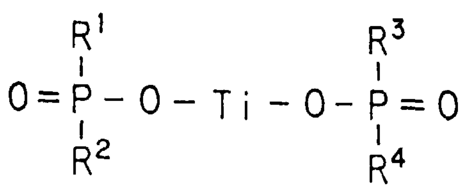
TABLE 2 (continued)

Number of Example	Output Color Uneveness by Irregular Conveyance	Dropping Out Or Misregistration Of Print By Crumples	Formation of Head Grime	Dye Transferring Contamination
Example B-4	○	○	○	○
Example B-5	○	○	○	○
Example B-6	○	○	○	○
Comparative Example B-1	×	×	Δ	○
Comparative Example B-2	×	×	Δ	○
Comparative Example B-3	×	Δ	Δ	○
Comparative Example B-4	×	×	×	×

Claims

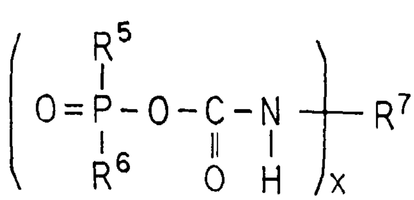
1. A thermal transfer sheet comprising:

a substrate film, at least one transferable layer disposed on one surface side of said substrate film and a heat resistant slip layer disposed on another surface side of said substrate film, said heat resistant slip layer comprising organic phosphoric ester derivative represented by the following formula (1) or formula (2) as a lubricant;



··· (1)

[in the formula (1), each of R^1, R^2, R^3 and R^4 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; and "n" denotes integer of 1 to 20]



··· (2)

[in formula (2), each of R^5 and R^6 denotes OC_kH_{2k+1}, $(OCH_2CH_2)_mOC_nH_{2n+1}$, $(OCH_2CH_2)_mOCOC_nH_{2n+1}$ or OH; R^7 denotes saturated aliphatic chain, unsaturated aliphatic chain or aromatic chain; "k" denotes integer of 8 to 20; "m" denotes integer of 1 to 10; "n" denotes integer of 1 to 20; and "x" denotes integer of 1 or more]

2. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer further comprises an organic filler or an inorganic filler.

3. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer further comprises at least one hardening agent selected from the group consisting of isocyanate hardening agent, polyisocyanate, monomer containing unsaturated bond, polymer containing unsaturated bond, chelate compound and epoxy hardening agent.

4. A thermal transfer sheet according to claim 3, wherein said hardening agent is the polyisocyanate.

5. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer further comprises another lubricant other than said organic phosphoric ester derivative.

6. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer comprises 100 weight parts of a binder resin and 1 to 100 weight parts of said organic phosphoric ester derivative.

7. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer comprises a binder resin including filler and hardening agent in an amount of 100 weight parts and said organic phosphoric ester derivative in an amount of 1 to 150 weight parts.

8. A thermal transfer sheet according to claim 1, wherein said heat resistant slip layer has an applied amount up to 3.0 g/m^2 in a solid component.

9. A thermal transfer sheet according to claim 1, wherein said transferable layer is a coloring material layer selected from the group consisting of a dye layer and a heat fusible ink layer.

FIG. 1

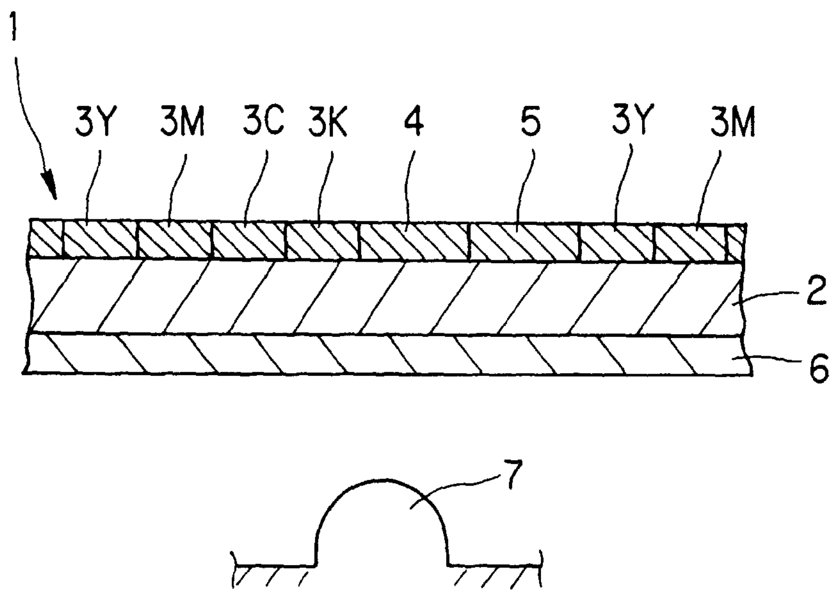
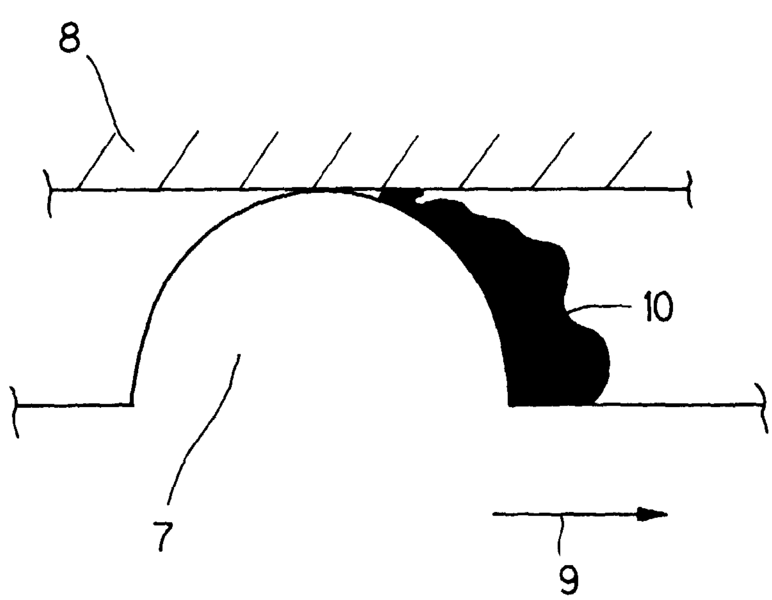


FIG. 2

PRIOR ART



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 5483

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	EP 0 458 538 A (IMPERIAL CHEMICAL INDUSTRIES PLC) * page 2, line 51 - page 3, line 7 * * page 3, line 58 - page 4, line 27 * * claims 1-6; examples 1-14 * ---	1-9	B41M5/40
A	EP 0 513 630 A (EASTMAN KODAK COMPANY) * page 3, line 29 - page 5, line 55 * * claims 1-10; example 1 * ---	1-9	
A	EP 0 523 623 A (SONY CORPORATION) * page 3, line 10 - page 5, line 20 * * claims 1-7; examples 1-8 * ---	1-9	
A	EP 0 577 051 A (DAI NIPPON PRINTING COMPANY LIMITED) * page 4, line 1 - page 5, line 1 * * claims 1,3,7-9; examples A,B,D * * figure 1 * -----	1-9	
			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	19 September 1997	Bacon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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