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PATENT ABSTRACTS OF JAPAN, vol. 12, no. 164 (M-698)[3011], 18th May 1988; JP-A-62 280 084 (DAINIPPON PRINTING CO., LTD) 04-12-1987

PATENT ABSTRACTS OF JAPAN, vol. 6, no. 142 (M-146)[1020], 31st July 1982; JP-A-57 64 595 (FUJI XEROX K.K.) 19-04-1982

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Description

FIELD OF THE INVENTION AND RELATED ART

The present invention relates to a thermal transfer recording method of transferring multi-color images such as two-color images onto a recording medium.

The thermal or heat-sensitive transfer recording method has recently been widely used because it has general advantages of the thermal recording method such that the apparatus employed is light in weight, compact, free of noise, excellent in operability and adapted to easy maintenance, and also has other advantages such that it does not require a color-formation type converted paper but provides recorded images with excellent durability.

The thermal recording method generally employs a thermal transfer material comprising a heat-transferable ink containing a colorant dispersed in a heat-fusible binder coated on a support generally in the form of sheet. The recording is generally conducted by superposing the thermal transfer material on a recording medium such as paper so that the heat-transferable ink layer will contact the recording medium, supplying heat from the support side of the thermal transfer material by means of a thermal head etc. to transfer the melted ink layer to the recording medium, thereby forming a transferred ink image corresponding to the heat supplying pattern on the recording medium.

Further, there is also a commercial demand for a method of obtaining two-color images while retaining the advantages of the thermal transfer recording method as described above. Accordingly, there have been proposed several techniques for obtaining two-color images.

In order to obtain two-color images on plain paper by the thermal transfer recording method, Japanese Laid-Open Patent Application No. 148591/1981 discloses a two-color type thermal transfer recording element (transfer material) comprising a substrate and two heat-fusible ink layers including a high-melting point ink layer A and a low-melting point ink layer B containing mutually different colorants disposed in this order on the substrate. When a low thermal input energy is applied to the element, only the low-melting point layer B is transferred onto plain paper, while when a high thermal input energy is applied to the element, both the heat-fusible ink layers A and B are transferred onto the plain paper, so that two-color images can be obtained.

Further Japanese Laid-Open Patent Application No. 64389/1984 discloses a two-color thermal transfer ink sheet which comprises, on a substrate, an ink layer comprising an ink which melt-exudes at a lower temperature and another ink which is melt-peeled at a higher temperature than the melt-exudation temperature.

In the methods using the above mentioned thermal transfer material, two-color recording is effected by changing the energy applied to a thermal head at two levels so as to change the temperature of the ink layers. However, when a high energy is input to the ink layers to provide a high temperature, a lower temperature portion is formed at the periphery of a higher temperature portion due to heat diffusion, so that a bordering of a lower temperature color is formed around the higher temperature printed image. Further, when a high energy is supplied to a thermal head, it requires a relatively long time until the thermal head is cooled so that a higher-temperature printed image is liable to be accompanied with a trailing of a lower-temperature color. Further, in any of the above methods, there is a constraint that a relatively low melting material is required for providing an ink to be transferred at a lower temperature, whereby they give rise to problems such as ground soiling and low storability of the thermal transfer material.

As a technique for dissolving the above-mentioned problems, our search group has proposed a recording method as disclosed in Japanese Laid-Open Patent Application No. 137789/1986 (U.S. Patent Application Serial No. 819,497).

In this recording method, there is employed a thermal transfer material comprising a support and at least a first ink layer and a second ink layer disposed in this order on the support, and after heat is applied to the thermal transfer material, a length of time from the heat application until the separation between the transfer material and a recording medium is so controlled that the second ink layer selectively, or both the first and second ink layers are transferred to the recording medium.

Our research group has further proposed, as a thermal transfer material for use in such recording method, one as disclosed in Japanese Laid-Open Patent Application No. 295075/1986 and one as disclosed in Japanese Laid-Open Patent Application No. 295079/1986.

Japanese Laid-Open Patent Application No. 295075/1986 discloses a thermal transfer material wherein at least one of a first ink layer and a second ink layer is caused to contain a silicone oil or a fluorine containing surfactant thereby to easily cause separation between the first and second ink layers. Japanese Laid-Open Patent Application No. 295079/1986 discloses a thermal transfer material wherein a fine powder layer being not melted by a heat energy applied for recording is disposed between a first ink layer and a second ink layer thereby to easily cause separation therebetween.

The above-mentioned recording method, as disclosed in Japanese Laid-Open Patent Application No. 137789/1986 (U.S. Patent Application Serial No. 819,497), has solved the problems of bordering, trailing, etc., in the prior art. In this method, there may be a case where a material capable of having a relatively high adhesion to a recording medium for obtaining images of higher quality on the recording medium. In this case, when the second ink layer is selectively transferred to the recording medium, mixing of colors is liable to occur because the color of the first ink layer is liable to mix with images of the second ink layer. Accordingly, in such a case, it is not necessarily easy to selectively transfer the second ink layer to the recording medium stably and with excellent reproducibility.

SUMMARY OF THE INVENTION

A principal object of the present invention is to solve the above-mentioned problems accompanying the prior art and to provide a thermal transfer recording method which provides clear multi-color images showing good transferability to a recording medium and good color separation through a simple process, and which does not necessarily require a low-melting material having a tendency to decrease the storability of a thermal transfer material.

We have discovered that in order to transfer a second ink layer more selectively in the above recording medium disclosed in Japanese Laid-Open Patent Application No. 137789/1986 (U.S. Patent Application Serial No. 819,497), it is necessary to stably control the length of time from the energy application until the separation between a thermal transfer material and a recording medium, with precision at a level of 10^{-3} sec. and with high reproducibility.

As a result of our various experiments based on the above knowledge, it is further discovered that in order to realize such precise control of separation, there are never negligible the stability and reproducibility in an extremely little delay in the separation between the thermal transfer material and the recording medium, which is counted from the passage of the transfer material across the trailing end of a heat-applying means such as a thermal head. Such delay is at a level of 10^{-3} sec. or less, which has been neglected in the conventional thermal transfer recording methods for obtaining two-color images.

Further, we have discovered that in order to realize the stability and reproducibility at such level of time, a conventional thermal transfer apparatus has been useless and there has been required a special thermal transfer apparatus capable of applying a peeling force of above a prescribed magnitude in a direction of from a recording medium to a thermal transfer material at the time of separation therebetween.

The thermal transfer recording method according to the present invention has been provided on the basis of the above discovery, and comprises: providing a thermal transfer material comprising a support and at least a first ink layer and a second ink layer disposed in this order on the support,

superposing the transfer material on a recording medium so that the ink layers contact the recording medium,

applying energy to the transfer material corresponding to information to be recorded, and

separating the transfer material from the recording medium in a length of time until separation counted from the energy application so that the second ink layer is selectively transferred to the recording medium in a shorter time until separation, and both the first and second ink layers are transferred to the recording medium in a longer time until separation;

wherein the thermal transfer material is separated under the action of a peeling force of not less than 0.196N (20 g.f) and less than 1.96N (200 g.f) in a direction perpendicular to and leaving from the surface of the recording medium toward the thermal transfer material, when the thermal transfer material is peeled off from the recording medium in the shorter time until separation.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings, wherein like arts are denoted by like reference numerals. In the description appearing hereinafter, "part(s)" and "%" used for describing quantities are by weight unless otherwise noted specifically.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 to 3 and Figures 5 to 7 are respectively schematic sectional views in the thickness direction of a thermal transfer material; wherein Figure 1 shows a thermal transfer apparatus for use in the thermal transfer recording method according to the present invention, Figure 2 shows an enlarged view of the heat-applying portion in Figure 1, and Figure 3 and Figures 5 to 7 respectively show an example of a thermal transfer material for use in the present invention.

Figure 4 is a graph showing a variation of adhesion strength between various layers with the elapse of time.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 is a schematic sectional view for illustrating an embodiment of the thermal transfer recording method according to the present invention.

Referring to Figure 1, a thermal transfer material 1 comprises a support and a first ink layer and second ink layer disposed in this order on the support. The thermal transfer material is wound off from a supplying core 2a and moved in a direction of an arrow A, and passes through a heat-applying position at which a thermal head 3 confronts a recording medium 5 such as plain paper disposed on a platen 4. Thereafter, the thermal transfer material is wound up about a winding core 2b.

At the heat-applying position, the thermal head 3 contacts or abuts on the support side of the thermal transfer material 1, while the recording medium 5 contacts or abuts on the second ink layer side of the thermal transfer material 1. Further, on the support side of the thermal transfer material 1, at an intermediate position between the thermal head 3 and the winding core 2b, a control member 6 for controlling the length of time until separation is disposed movably in a direction of an arrow B, perpendicular to the surface of the recording medium 5 to be recorded.

The above-mentioned thermal transfer material 1, the supplying core 2a, the winding core 2b, the thermal head 3, and the control member 6 are housed in a carriage 7 disposed movably in a direction of an arrow C.

By using such apparatus, when the control member 6 does not contact the thermal transfer material 1, heat energy corresponding to information to be recorded is supplied to the thermal transfer material 1 by means of the thermal head 3 contacting the support side of the transfer material 1 moving in the direction of the arrow A. Thereafter, if the transfer material 1 is immediately peeled off from the recording medium 5 (i.e., in a relatively short length of time after the heat application), the second ink layer of the transfer material 1 is selectively transferred to the recording medium 5 threby to form a recorded image in the color of the second ink layer (e.g., red) on the recording medium 5. The above-mentioned "relatively short length of time" may preferably be 0.5 to 10 msec.

On the other hand, the control member 6 is moved in the direction of the arrow B so as to be disposed as shown by a dotted line 6a in Figure 1, thereby to press the transfer material 1 on the recording medium 5, as shown by a dotted line 1a. In this state, after heat energy is similarly supplied to the transfer material 1, if the transfer material 1 is peeled off from the recording medium 5 as shown by the dotted line 1a (i.e., in a relatively long length of time after the heat application), both the first and second ink layers are transferred to the recording medium 5, thereby to form a recorded image ordinarily in the color of the first ink layer (e.g., black) on the recording medium 5. The above-mentioned "relatively long length of time" may preferably be 30 to 500 msec.

Incidentally, a pressing force based on the above control member 6 may be sufficient to make the transfer material 1 contact the recording medium 5, and is not necessarily a strong pressing force. If the pressing force is too strong, it rather decreases a running characteristic of the transfer material 1, or causes a problem such as ground soiling of the recording medium 5.

Hereinabove, the outline of the thermal transfer recording method according to the present invention has been described. Now, there will be explained a peeling force in the case of selectively transferring the second ink layer in the present invention.

Figure 2 is an enlarged view of the heat-applying portion in Figure 1.

Referring to Figure 2, the thermal head 3 presses the thermal transfer material 1 to the recording medium 5 by a pressing force F. The thermal transfer material 1, immediately after supplied with heat by means of a heater portion 3a of the thermal head 3, is peeled off at the trailing end 3b of the thermal head 3, at an angle θ with the recording medium 5 and under a tension T. The angle θ may preferably be 20° - 70°, more preferably 40° - 60°.

In this case, if a tension acting in the direction of movement of the thermal transfer material 1 is represented by T, a peeling force 8 acting in the direction perpendicular to the surface of the recording medium 5 to be recorded, and of from this surface to the thermal transfer material 1 (i.e., the component of the tension T along the above perpendicular direction) is represented by $T\sin\theta$. The magnitude of the peeling force 8 is required to be 0.196N (20 g.f (g-force)) or more, and less than 1.96N (200 g.f), and may be preferably 0.49 - 1.47N (50 to 150 g.f) more preferably 0.784 - 1.176N (80 to 120 g.f.). The width of the thermal transfer material 1 may preferably be about 3 to 50 mm. The peeling force per unit width of the transfer material may preferably be 0.004 - 0.686 N/mm (0.4 to 70 g.f/mm), more preferably 0.01 - 0.49 N/mm (1 to 50 g.f/mm), particularly preferably 0.016 - 0.392 N/mm (1.6 to 40 g.f/mm).

If the peeling force 8 is less than 20 g.f, it is difficult to precisely control the length of time from the heat application to the peeling at a level of 10^{-3} sec. Therefore, it is impossible to stably cause separation with high reproducibility, whereby a first ink constituting the first ink layer is liable to be mixed in a recorded image of the second ink layer (e.g., spots of the first ink is attached to the transferred second ink layer).

On the other hand, if the peeling force 8 is 1.96N (200 g.f) or more, the contact pressure of the thermal transfer material 1 on the thermal head 3 becomes too high thereby to cause sticking, or the thermal transfer material 1 cannot desirably contact the recording medium 5 thereby to deteriorate the image quality.

The magnitude of the peeling force 8 may be controlled or regulated by changing that of the above-mentioned tension T or the peeling angle θ (i.e., the angle formed by the thermal transfer material 1 with the surface of the recording medium 5 to be recorded, at the trailing end of the thermal head). In order to control the peeling force 8 more stably, it is preferable to regulate the tension T.

The magnitude of the tension T may be regulated, e.g., by a torque applied to the winding core 2b in Figure 1. Further, the tension T may be measured, e.g., by means of a spring scale. More specifically, it may be measured by disposing the spring scale and the winding core 2b in the same situation so that between the thermal transfer material 1 and the winding core 2b.

Hereinbelow, the thermal transfer material for use in the present invention will be described in further detail.

Figure 3 is a schematic sectional view in the thickness direction of a basic embodiment of the thermal transfer material used in the invention. Referring to Figure 3, the thermal transfer material 1 comprises a support 10 ordinarily in the form of a sheet, and a first ink layer 11 and a second ink layer 12 formed on and in this order from the support 1.

In the thermal transfer material 1 used in the present invention, the relation with respect to largeness of adhesion (strength) between the adhesion (F_2) between the first ink layer 11 and the second ink layer 12, and the adhesion (F_1) between the first ink layer 11 and the support 10, must be inverted between those at a high temperature and at a low temperature, e.g., in the course of cooling of the ink layers after application of heat thereto sufficient to cause thermal transfer of the ink layers. For example, when the transfer material 1 is heated, the ink layers 11 and 12 are so constituted that the separation between the first ink layer 11 and the second ink layer 12 is better than that between the first ink layer 11 and the support 10 immediately after heating, and the separation between the first ink layer 11 and the support 10 becomes relatively easier after a considerable time has passed from the heating until the separation of the support 10 from a recording medium, i.e., at the time when the transfer material 1 is cooled after the transfer material 1 and the recording medium has been superposed, heated and retained for a substantial time after heating and before peeling.

The above mentioned characteristics of the respective layers will be further explained with reference to Figure 4.

Incidentally, the adhesion (F_2) between the second and first ink layers and the adhesion (F_1) between the first ink layer and the support are evaluated according to relative easiness between the separation between the second and first ink layers, and the separation between the first ink layer and the support, when transfer recording is effected on a recording medium. Such evaluation of the adhesions is not affected by the form of separation between ink layers (e.g., whether or not the separation between the second and first ink layers has occurred strictly at the boundary between these layers, or whether or not some adhesive layer described hereinafter, if any, remains on the thermal transfer material).

Now, referring to Figure 4, the adhesion (F_2) between the first ink layer 11 and the second ink layer 12, and the adhesion (F_1) between the first ink lyaer 11 and the support 10, change on heating and cooling. If the second ink layer 12 in Figure 3 is composed of a material showing a large change in adhesion or cohesion and the first ink layer 11 is composed of a material showing a small change in adhesion or cohesion, the adhesion F_2 sharply decreases on temperature increase due to heating by a thermal head. As a result, the adhesion F_2 is weaker than the adhesion F_1 as shown in Figure 4, at a time immediately after heating (i.e., before the temperature being lowered). Accordingly, if the transfer material is peeled from the recording medium immediately after the transfer material is heated while the second ink layer 12 thereof being in contact with the recording medium, i.e., at a time t_1 in Figure 4, only the second ink layer 12 is transferred to the recording medium 5.

In contrast, if the transfer material is peeled from the recording medium at a time t_2 in Figure 4 when a little time has passed after heating (i.e., the temperature of the ink layer has been lowered) and the adhesion F_2 is recovered to exceed the adhesion F_1, the first ink layer 11 is transferred together with the second ink layer 12 to the recording medium.

Accordingly, if the color tones of the first ink layer 11 and the second ink layer 12 are composed to be different from each other in the thermal transfer material, clear two-color recorded images can be obtained according to the thermal transfer recording method of the present invention.

When the color of the first ink layer 11 and the second ink layer 12 are desired to be obtained substantially as they are, it is preferred to dispose a first ink layer 11 of a dark color such as black and a second ink layer 12 of a brighter color than that of the first ink layer such as red.

Further, the first and second ink layers can be made in the same hue but different in density from each other, whereby two-color images with dense and pale portions can be obtained in the same manner as described above. Further, the first ink layer can function as a correcting ink layer by incorporating, e.g., a white pigment having a strong hiding power therein.

In the above embodiments explained with reference to Figure 4, the relative adhesions between the layers after a substantial time after heating are essentially the same as those before heating. This is, however, not an essential requirement. For example, in a case where the ink layers are formed by emulsion-coating, the states of the ink layers after a little while after heating can be different from those of the ink layers before heating.

Further, the separation between the first ink layer 11 and the support 10 need not necessarily occur at the boundary between them but may occur within the first ink layer 11.

Figures 5 to 7 are respectively schematic sectional views in the thickness direction showing a laminar structure of another embodiment of the thermal transfer material used in the invention.

Figure 5 shows a thermal transfer material wherein a first adhesive layer 13a is disposed between the first ink layer 11 and the support 10, and Figure 6 shows a thermal transfer material wherein a second adhesive layer 13b is disposed between the second ink layer 12 and the first ink layer 11.

The above first adhesive layer 13a may preferably be composed of a material showing a relatively small change in adhesion on temperature change such as broadly (or gradually) meltable resins. On the other hand, the above second adhesive layer 13b may preferably be composed of a material showing a relatively large change in adhesion on temperature change such as sharply meltable waxes. Such first adhesive layer 13a shows a gradual change in its strength on temperature change and such second adhesive layer 13b shows a sharp change in its strength on temperature change. As a result, a variation in relative adhesions as shown in Figure 4 may be obtained, similarly as in the embodiment of Figure 3.

The above first adhesive layer 13a and second adhesive layer 13b may be disposed in combination, as shown in Figure 7.

In a case where an adhesive layer is disposed as shown in Figures 5 to 7, it is easier to select materials constituting the first and second ink layers for obtaining a desired change in adhesion, and to prevent these ink layers from mixing. Accordingly, such adhesive layer may preferably be used in order to improve clearness of two-color recorded images.

As the support 10 of the thermal transfer material, it is possible to use films of, e.g., polyester, aramide resin, nylon, polycarbonate, or capacitor paper, preferably having a thickness of about 3 to 12 μm. Too thick a support is not desirable becuase the heat conductivity becomes inferior. If a sufficient heat resistance and a strength are attained, a support may be thinner than 3 μm.

The structures and compositions of the embodiments shown in Figure 3 and Figures 5 to 7 will be described in more detail.

The first and second ink layers should preferably contain 1 to 50 % of a colorant and have a softening temperature within the range of 60 to 180 °C. A softening temperature of the second ink layer 12 below 60 °C results in a poor storability and is not preferred. A softening temperature above 180 °C provides a poor heat sensitivity and is not preferred.

On the other hand, the first ink layer 11 in the embodiments shown in Figure 3 and Figures 5 to 7 can contain up to about 90 %, preferably 1 to 80 %, of a colorant.

The embodiment shown in Figure 6 will specifically be described hereinbelow.

Referring to Figure 6, the first ink layer 11 should preferably be heat-fusible but can be adhesive or tacky at room temperature, can have a remarkably high softening temperature or can be one lacking a fusibility. On the other hand, the second adhesive layer 13b is generally preferred to have a softening temperature of 60 to 180 °C.

The "softening temperature" used herein is a flow initiation temperature as obtained from an apparent viscosity-temperature curve of a sample ink based on a measurement by a flow tester (Model: CFT500, available from Shimazu Seisakusho K.K.) under the conditions of a load of 10 kg, and a temperature increasing rate of 2 °C/min.

It is preferred that the second adhesive layer 13b and the second ink layer 12 are so composed as to provide a melt viscosity (by a rotary viscometer) as an ink constituting each layer inclusive of various additives in the range of 10 cps to 1,000,000 cps at a temperature which is 30 ° C higher than the softening temperature of the respective layers. Particularly, the second ink layer 12 should preferably have a melt viscosity of 200 cps or higher at the above specified temperature in order to provide a good adhesion onto a recording medium such as paper. Further, the adhesive layer 13b should preferably have a melt viscosity lower than that of the second ink layer 12, respectively, at a temperature which is 30 ° C higher than the softening temperature of the second ink layer 12. By satisfying these conditions, when the transfer medium is peeled off at time t_1 as shown in Figure 4, a separation within the second ink layer 12 itself, is less liable to occur, whereby good images can be obtained.

In a case where the second ink layer 12 is selectively transferred when the thermal transfer material is peeled off from the recording medium at the time t_1 in Figure 4, the adhesive layer 13b should preferably be so composed as to provide a softening temperature which is equal to or lower than that of the second ink layer 12. When a recording is conducted by a thermal head, the trailing end portion of the image portion in the moving direction of the thermal head changes from a printing temperature to a non-printing temperature. However, during this course of cooling, if the second ink layer 12 is attached to the recording medium while the strength of the adhesive layer 13b is still relatively high, the first ink layer 11 can be transferred along with the second ink layer 12 to unintensionally provide the color of the first ink layer 11. This phenomenon can be prevented by setting the softening temperature of the adhesive layer 13b to be equal to or lower than that of the second ink layer 12 as descirbed above.

In the thermal transfer material used in the present invention, the total thickness of the ink layers on the support 10 (i.e., all the layers other than the support 10 inclusive of the adhesive layers) may desirably be 20 μm or less. Further, each of the first ink layer, the second ink layer and the first and second adhesive layers should have a thickness in the range of 0.5 to 10 μm.

It is desirable that the materials constituting the first ink layer 11 and the second ink layer 12 should be mutually incompatible with each other. This is because the adhesive layer 13b disposed between the first ink layer 11 and the second ink layer 12 can be crushed by pressing due to a thermal head so as to provide a partial contact between the first ink layer 11 and the second ink layer 12, and in such a case, the two-color separation is better retained by using mutually incompatible materials for the ink layers.

As a further modification, it is also effective to provide a heat-resistant layer on the back surface of the support 10 or between the support 10 and the first ink layer 11. It is also effective to provide a layer for increasing an adhesion onto a recording medium on the second ink layer 12. Further, a various functional layer may be disposed as desired between the respective layers or on the surface. The functional layer can contain a colorant.

As one effective example, such a functional layer containing a colorant may be provided as a layer showing a transferability when it is applied with a higher heat energy than the first and second ink layers so that it is transferred after the first and second ink layers to provide an additional color thereof onto the recording medium. Alternatively, a functional ink layer showing a transferability when applied with a pressure may be used so as to provide a similar effect.

As a heating means for the thermal transfer recording method of the present invention, ordinary heat sources such as infrared rays and laser beam may also be used in place of a thermal head. Further, in order to provide a conduction heating system, i.e., a system wherein a thermal transfer material itself generates a heat due to a current passing therethrough, a thin layer of a conductive material such as aluminum may be disposed as a return electrode between the support and the first ink layer, as desired.

The first ink layer 11, the second ink layer 12 and adhesive layers 13a and 13b may be formed by using one or more binders selected from the following class and adding thereto a colorant and other additives as desired. The binder may be selected from natural waxes such as whale wax, beeswax, lanolin, carnauba wax, candelilla wax, montan wax and ceresin wax; petroleum waxes such as paraffin wax and microcrystalline wax; synthetic waxes such as ester wax, low molecular weight polyethylene, Fischer-Tropsch wax and the like; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, and behenic acid; higher alcohols such as stearyl alcohol and behenyl alcohol; esters such as fatty acid esters of sucrose and fatty acid esters of sorbitane; amides such as oleic amide; thermoplastic resins including: homopolymers of styrene and substituted styrenes such as polystyrene, poly-p-chlorostyrene, and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymer, styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-α-chloromethyl methacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-acrylonitrile indene copolymer, styrene-maleic acid copolymer, and styrene-maleic acid ester copolymer; polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, polypropylene, polyester, polyurethane, polyamide, epoxy resin, polyvinyl butyral, polyacrylic acid resin, rosin, modified rosin, terpene resin, phenolic resin, aliphatic and alicyclic hydrocarbon resins, and aromatic petroleum resin; homopolymers and copolymers of olefin such as polyethylene, polypropylene, polyisobutylene, polyethylene wax, oxidized polyethylene, polytetrafluoroethylene, ethylene-acrylic acid copolymer, ethylene-ethyl acrylate copolymer and ethylene-vinyl acetate copolymer; and derivatives of these polymers.

The colorant may be selected from all of the known dyes and pigments including: carbon black, Nigrosin dyes, lamp black, Sudan Black SM, Alkali Blue, Fast Yellow G, Benzidine Yellow, Pigment Yellow, Indo Fast Orange, Irgadine Red, Paranitroaniline Red, Toluidine Red, Carmine FB, Permanent Bordeaux FRR, Pigment Orange R, Lithol Red 20, Lake Red C, Rhodamine FB, Rhodamine B Lake, Methyl Violet B Lake, Phthalocyanine Blue, Pigment Blue, Brilliant Green B, Phthalocyanine Green, Oil Yellow GG, Zapon Fast Yellow CGG, Kayaset Y963, Kayaset YG, Smiplast Yellow GG, Zapon Fast Orange RR, Oil Scarlet, Smiplast Orange G, Orasol Broan B, Zapon Fast Scarlet CG, Aizen Spiron Red BEH, Oil Pink OP, Victoria Blue F4R, Fastgen Blue 5007, Sudan Blue, and Oil Peacock Blue. Further, metal powder such as copper powder and aluminum powder or powder of mineral such as mica may also be used as a colorant. Further, other additives such as plasticizers, mineral oils, vegetable oils, etc., may also be added.

The ink layers and adhesive layers having the desired properties as described with reference to the relative adhesions as shown in Figure 4, may be obtained by appropriately controlling the properties such as molecular weights, crystallinities, etc., of the above mentioned materials or appropriately mixing a plurality of the above mentioned materials.

The thermal transfer material used in the invention may be obtained by forming the respective layers by mixing the materials constituting the respective layers and an organic solvent such as methyl ethyl ketone, xylene and tetrahydrofuran capable of dissolving the binders and applying the thus formed coating liquids successively on the support. Alternatively, the so-called hot-melt coating method may be adopted, including the steps of blending, hot-melting and applying the materials in a molten state for the respective layers. The materials for the respective layers may be formed into aqueous emulsions by the addition of a dispersant such as a surfactant, and the aqueous emulsions may be applied to form the respective layers. Further, the respective layers of the transfer material may also be formed by using the above mentioned coating methods in combination, i.e., by using different methods for the respective layers.

As described hereinabove, according to the present invention, there is provided a thermal transfer recording method wherein energy is applied to a thermal transfer material comprising a support and at least a first ink layer and a second ink layer disposed in this order on the support, thereafter the thermal transfer material is peeled off from a recording medium in a relatively short length of time until separation while applying a peeling force of above a prescribed magnitude to the thermal transfer material.

According to the thermal transfer recording method of the present invention, the second ink layer is stably transferred to the recording medium with excellent reproducibility by precisely controlling the above length of time until separation at a level of 10^{-3} sec., whereby beautiful two-color transferred images of good color separation are provided.

Hereinbelow, the present invention will be explained more specifically while referring to specific examples of practice. Incidentally, the number-average molecular weight Mn of a sample such as oxidized polyethylene was measured in the following manner.

[Molecular Weight Measurement]

The VPO method (Vapor Pressure Osmometry Method) is used. A sample of oxidized polyethylene is dissolved in a solvent such as benzene at various concentrations (C) in the range of 0.2 to 1.0 g/100 ml to prepare several solutions. The osmotic pressure (π/C) of each solution is measured and plotted versus the concentration to prepare a concentration (C)-osmotic pressure (π/C) curve, which is extrapolated to obtain the osmotic pressure at the infinite dilution $(\pi/C)_0$. From the equation of $(\pi/C)_0 = RT/Mn$, the number-average molecular weight Mn of the sample is derived.

<u>Example 1</u>

<Ink 1>

Oxidized polyethylene aqueous dispersion (Mn = 5000, softening temp. = 140 ° C, particle size = 1 µm)	60 parts
Ethylene-vinyl acetate copolymer resin aqueous dispersion (softening temp. = 105 ° C, particle size = 0.5 µm)	20 parts
Carbon black aqueous dispersion	20 parts
(The amounts of aqueous dispersions for providing an ink formulation in this example and the other examples are all expressed based on their solid contents.)	

The above components were sufficiently mixed to prepare an ink 1. The ink 1 was applied on a 6 µ-thick PET (polyethylene terephthalate) film and dried at 70 ° C to form a 2 µ-thick first ink layer.

<Ink 2>

Carnauba wax aqueous dispersion (particle size: 0.5 µm)	100 parts
Silicone surfactant	0.1 part

An ink 2 having the above composition was applied on the above prepared first ink layer and water was evaporated thereform to leave a 1 µm-thick adhesive layer of carnauba wax.

<Ink 3>

Hydrogenated rosin ester aqueous dispersion (softening temp. = 90 ° C, particle size = 1 µm)	80 parts
Cyanine blue aqueous dispersion	20 parts

The above components were sufficiently mixed to prepare an ink 3, which was applied on the above prepared adheisve layer and dried at 80 ° C to form a 2 µm-thick second ink layer, whereby a thermal transfer material (I) having a structure as shown in Figure 6 was obtained.

Example 2

<Ink 4>

Oxidized polyethylene aqueous dispersion (Mn = 4000, softening temp. = 138 ° C, average particle size = 1 µm)	80 parts
Ethylene-vinyl acetate copolymer resin aqueous dispersion (softening temp. = 95 ° C, particle size = 0.5 µm)	20 parts

<Ink 5>

Oxidized polyethylene aqueous dispersion (Mn = 5000, softening temp. = 140 ° C, particle size = 1 µm)	80 parts
Carbon black aqueous dispersion	20 parts

<Ink 6>

Carnauba wax aqueous dispersion Silicone surfactant	100 parts 0.1 part

<Ink 7>

Oxidized polyethylene aqueous dispersion (Mn = 1900, softening temp. = 110 °C)	60 parts
Ethylene-vinyl acetate copolymer resin aqueous dispersion (softening temp. = 105 °C, particle size = 0.5 µm)	40 parts
Cyanine blue aqueous dispersion	20 parts

The above components were respectively sufficiently mixed to prepare inks 4, 5, 6 and 7.

These inks 4, 5, 6 and 7 were successively applied and dried on a 6 µm-thick PET film to form a 1 µm-thick first adhesive layer, a 2 µm-thick first ink layer, a 1 µm-thick second adhesive layer, and a 2 µm-thick second ink layer, whereby a thermal transfer material (II) having a sturcture as shown in Figure 7 was obtained.

Example 3

<Ink 8>

Oxidized polyethylene aqueous dispersion (Mn = 4000, softening temp. = 138 °C, particle size = 1 µm)	80 parts
Ethylene-vinyl acetate copolymer resin aqueous dispersion (softening temp. = 95 °C, particle size = 0.5 µm)	20 parts

<Ink 9>

Oxidized polyethylene aqueous dispersion (Mn = 5000, softening temp. = 140 °C, particle size = 1 µm)	80 parts
Carbon black aqueous dispersion	20 parts
Fluorine-containing surfactant	0.1 part

<Ink 10>

Carnauba wax aqueous dispersion (softening temp. = 83 °C)	40 parts
Terpene-phenol copolymerization resin aqueous dispersion (softening temp. = 100 °C)	40 parts
Cyanine blue aqueous dispersion	20 parts

The above components were respectively sufficiently mixed to prepare inks 8, 9 and 10.

Separately, an addition type silicone resin for release paper was applied at a rate of 0.3 g/m^2 on the back side of a 3.5 µm-thick PET film support and dried at 70 °C to provide a heat-resistant protective layer.

On the reverse side from the protective layer of the thus prepared back-coated PET film, the above inks 8, 9 and 10 were successively applied and dried to form a 1 µm-thick first adhesive layer, a 2 µm-thick first ink layer and a 2 µm-thick second ink layer, whereby a thermal transfer material (III) having a structure as shown in Figure 5 was obtained.

The thus prepared thermal transfer materials (I) - (III) were respectively cut into an 6 mm-wide tapes and used for recording by means of a thermal transfer recording apparatus for an English typewriter (Typestar 6, mfd. by Canon K.K.). Referring to Figure 1, as a thermal head 3, one prepared by Rohm K.K., having a length from the center of the heat generating part 3a to the trailing end 3b (as shown in Figure 2) of 350 µm was used. A carriage loading the thermal head 3 and a thermal transfer material ribbon 1 was moved in the direction of an arrow C, of which moving velocity was 50 mm/sec. Accordingly, the time (t_1 in Figure 4) from heating until the peeling-off of the ink ribbon from a recording medium was about 7 msec in the rapid peeling-off mode. In order to delay the time of the peeling-off, a control member 6 for controlling the peeling-off was disposed at about 5 mm (i.e., ℓ = 5 mm as shown in Figure 1) after the trailing end 3b of the thermal head (i.e., downstream side of the trailing end 3b with respect to the moving direction of the thermal transfer material 1).

As a result, when the control member 6 was moved toward the recording medium, the delayed time of peeling-off (t_2 in Figure 4) was about 100 msec after the heating. Incidentally, as a preliminary test, the position of the control member 6 was changed in different ways, whereby it was confirmed that the result of the recording was not substantially different from the case of ℓ = 5 mm, if it was disposed at a position from 2 mm to 20 mm (i.e., ℓ = 2 - 20 mm) after the trailing end of the thermal head.

Where the transfer recording was conducted on plain paper by the use of the thermal transfer materials (I), (II) and (III), while changing a peeling force 8 (shown in Figure 2) into various values such as 0.147, 0.196, 0.294, 0.98, 1.862, 1.96, and 2.156N (15, 20, 30, 100, 190, 200, and 220 g.f), blue images were obtained when the transfer material was peeled rapidly and black images were obtained when the transfer material was peeled at the delayed time.

However, in case where the peeling force 8 was 0.147N (15 g.f), black color was mixed with blue images, whereby clear blue images were not obtained. To the contrary, in a case where the peeling force 8 was 0.196, 0.294, 0.98 or 1.862N (20, 30, 100, or 190 g.f), clear blue images were obtained. Further, in a case where the peeling force 8 was 1.96 or 2.156N (200 or 220 g.f), sticking of the thermal transfer material to the thermal head became marked as the peeling force became larger, whereby only images of low quality were obtained. Incidentally, when the peeling force 8 was changed in such a manner, black images obtained were not substantially different from each other.

Claims

1. A thermal transfer recording method comprising:

providing a thermal transfer material comprising a support and at least a first ink layer and a second ink layer disposed in this order on the support,

superposing the transfer material on a recording medium so that the ink layers contact the recording medium,

applying energy to the transfer material corresponding to information to be recorded, and

separating the transfer material from the recording medium in a length of time until separation counted from the energy application so that the second ink layer is selectively transferred to the recording medium in a shorter time until separation, and both the first and second ink layers are transferred to the recording medium in a longer time until separation,

wherein the thermal transfer material is separated under the action of a peeling force of not less than 0.196N (20 g.f) and less than 1.96N (200 g.f) in a direction perpendicular to and leaving from the surface of the recording medium toward the thermal transfer material, when the thermal transfer material is peeled off from the recording medium in said shorter time until separation.

2. A method according to Claim 1, wherein said peeling force is 0.49 to 1.47N (50 to 150 g.f.).

3. A method according to Claim 2, wherein said peeling force is 0.784 to 1.176N (80 to 120 g.f.).

4. A method according to Claim 1, wherein said energy is applied by means of a thermal head.

5. A method according to Claim 1, wherein the thermal transfer material comprises a thin layer of conductive material between the first ink layer and the support, and said energy is applied as a heat due to a current passing through the thermal transfer material.

6. A method according to Claim 1, wherein the first ink layer has a black color and the second ink layer has a red color.

7. A method according to Claim 1, wherein the thermal transfer material comprises an adhesive layer between the first ink layer and the support.

8. A method according to Claim 1, wherein the thermal transfer material comprises an adhesive layer between the first and second ink layers.

9. A method according to Claim 1, wherein the thermal transfer material comprises adhesive layers between the first ink layer and the support, and between the first and second ink layers.

Patentansprüche

1. Aufzeichnungsverfahren durch thermischen Transfer, in dem man:

   ein thermisches Transfermaterial zur Verfügung stellt, das einen Träger und mindestens eine erste Tintenschicht und eine zweite Tintenschicht umfasst, die in dieser Reihenfolge auf dem Träger angeordnet sind,

   das Transfermaterial auf ein Aufzeichnungsmedium schichtet, so daß die Tintenschichten in Kontakt mit dem Aufzeichnungsmedium sind,

   Energie auf das Transfermaterial ausübt, was einer aufzuzeichnenden Information entspricht, und

   das Transfermaterial von dem Aufzeichnungsmedium in einem Zeitraum bis zur Trennung, gezählt ab der Energieausübung abtrennt, so daß die zweite Tintenschicht selektiv auf das Aufzeichnungsmedium in einer kürzeren Zeit bis zur Trennung übertragen wird und sowohl die erste als auch die zweite Tintenschicht auf das Aufzeichnungsmedium in einer längeren Zeit bis zur Trennung übertragen werden, **dadurch gekennzeichnet** daß das thermische Transfermaterial durch Einwirkung einer Ablösungskraft von nicht weniger als 0,169 N (20 g.f) und weniger als 1,96 N (200 g.f) in einer Richtung senkrecht zu und von der Oberfläche des Aufzeichnungsmediums weg auf das thermische Transfermaterial hin, abgetrennt wird, wenn das thermische Transfermaterial von dem Aufzeichnungsmedium in der kürzeren Zeit bis zur Trennung abgelöst wird.

2. Verfahren nach Anspruch 1 **dadurch gekennzeichnet**, daß die Ablösekraft 0,49 bis 1,47 N (50 bis 150 g.f) beträgt.

3. Verfahren nach Anspruch 2 **dadurch gekennzeichnet**, daß die Ablösekraft 0,784 bis 1,176 N (80 bis 120 g.f) beträgt.

4. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß Energie mit Hilfe eines thermischen Kopfes ausgeübt wird.

5. Verfahren nach Anspruch 1 **dadurch gekennzeichnet**, daß das thermische Transfermaterial eine dünne Schicht eines leitenden Materials zwischen der ersten Tintenschicht und dem Träger umfasst und die Energie als Hitze, bedingt durch einen Strom, der durch das thermische Transfermaterial fließt, ausgeübt wird.

6. Verfahren nach Anspruch 1 **dadurch gekennzeichnet**, daß die erste Tintenschicht eine schwarze Farbe und die zweite Tintenschicht eine rote Farbe hat.

7. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß das thermische Transfermaterial eine Klebeschicht zwischen der ersten Tintenschicht und dem Träger umfasst.

8. Verfahren nach Anspruch 1 **dadurch gekennzeichnet**, daß das thermische Transfermaterial eine Klebeschicht zwischen der ersten und zweiten Tintenschicht umfasst.

9. Verfahren nach Anspruch 1 **dadurch gekennzeichnet**, daß das thermische Transfermaterial Klebeschichten zwischen der ersten Tintenschicht und dem Träger und zwischen der ersten und zweiten Tintenschicht umfasst.

Revendications

1. Procédé d'enregistrement par transfert thermique, qui consiste :

à prendre un matériel de transfert thermique comprenant un support et au moins une première couche d'encre et une seconde couche d'encre disposées dans cet ordre sur le support,

à superposer le matériel de transfert à un milieu d'enregistrement de manière que les couches d'encre entrent en contact avec ce milieu,

à appliquer de l'énergie au matériel de transfert correspondant à l'information devant être enregistrée, et

à séparer le matériel de transfert du milieu d'enregistrement en un intervalle de temps jusqu'à la séparation compté à partir de l'application d'énergie de manière que la seconde couche d'encre soit transférée sélectivement au milieu d'enregistrement en un temps plus court jusqu'à la séparation, et que les première et seconde couches d'encre soient transférées au milieu d'enregistrement en un temps plus long jusqu'à la séparation,

le matériel de transfert thermique étant séparé sous l'action d'une force de décollement non inférieure à 0,196 N (20 g.f) et ne dépassant pas 1,96 N (200 g.f) dans une direction perpendiculaire à, et partant de, la surface du milieu d'enregistrement vers le matériel de transfert thermique, lorsque ce matériel est décollé du milieu d'enregistrement dans ledit intervalle de temps plus court jusqu'à la séparation.

2. Procédé suivant la revendication 1, dans lequel la force de décollement va de 0,49 à 1,47 N (50 à 150 g.f).

3. Procédé suivant la revendication 2, dans lequel la force de décollement va de 0,784 à 1,176 N (80 à 120 g.f).

4. Procédé suivant la revendication 1, dans lequel l'énergie est appliquée au moyen d'une tête thermique.

5. Procédé suivant la revendication 1, dans lequel le matériel de transfert thermique comprend une mince couche de matière conductrice entre la première couche d'encre et le support, et ladite énergie est appliquée sous forme de chaleur dégagée par le passage d'un courant à travers le matériel de transfert thermique.

6. Procédé suivant la revendication 1, dans lequel la première couche d'encre a une couleur noire et la seconde couche d'encre a une couleur rouge.

7. Procédé suivant la revendication 1, dans lequel le matériel de transfert thermique comprend une couche d'adhésif entre la première couche d'encre et le support.

8. Procédé suivant la revendication 1, dans lequel le matériel de transfert thermique comprend une couche d'adhésif entre les première et seconde couches d'encre.

9. Procédé suivant la revendication 1, dans lequel le matériel de transfert thermique comprend des couches d'adhésif entre la première couche d'encre et le support, et entre les première et seconde couches d'encre.

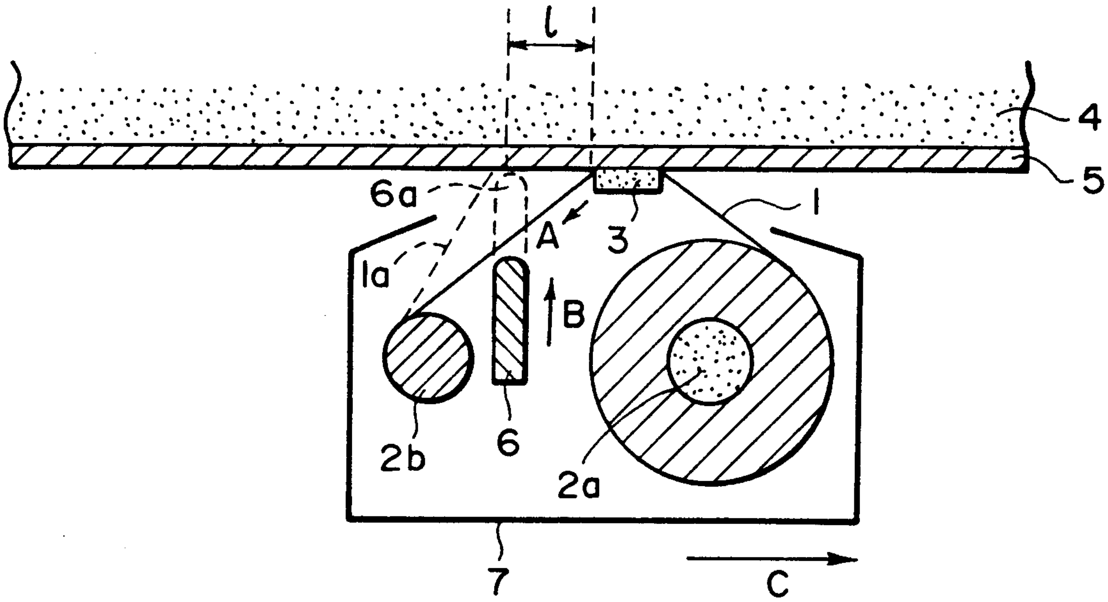

FIG. 1

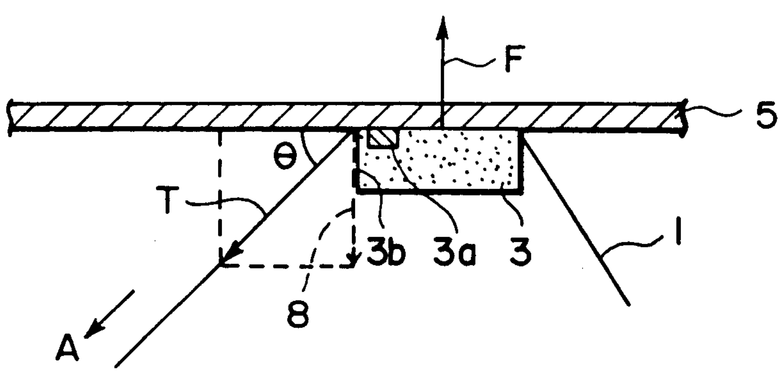

FIG. 2

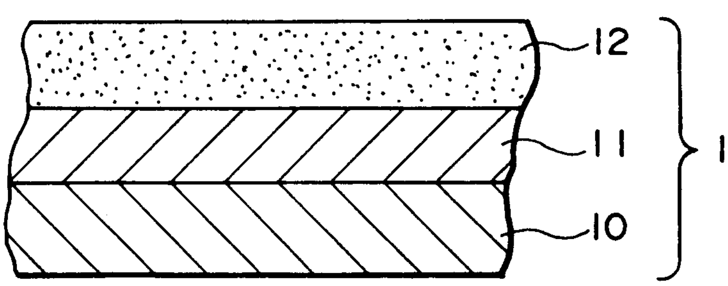

FIG. 3

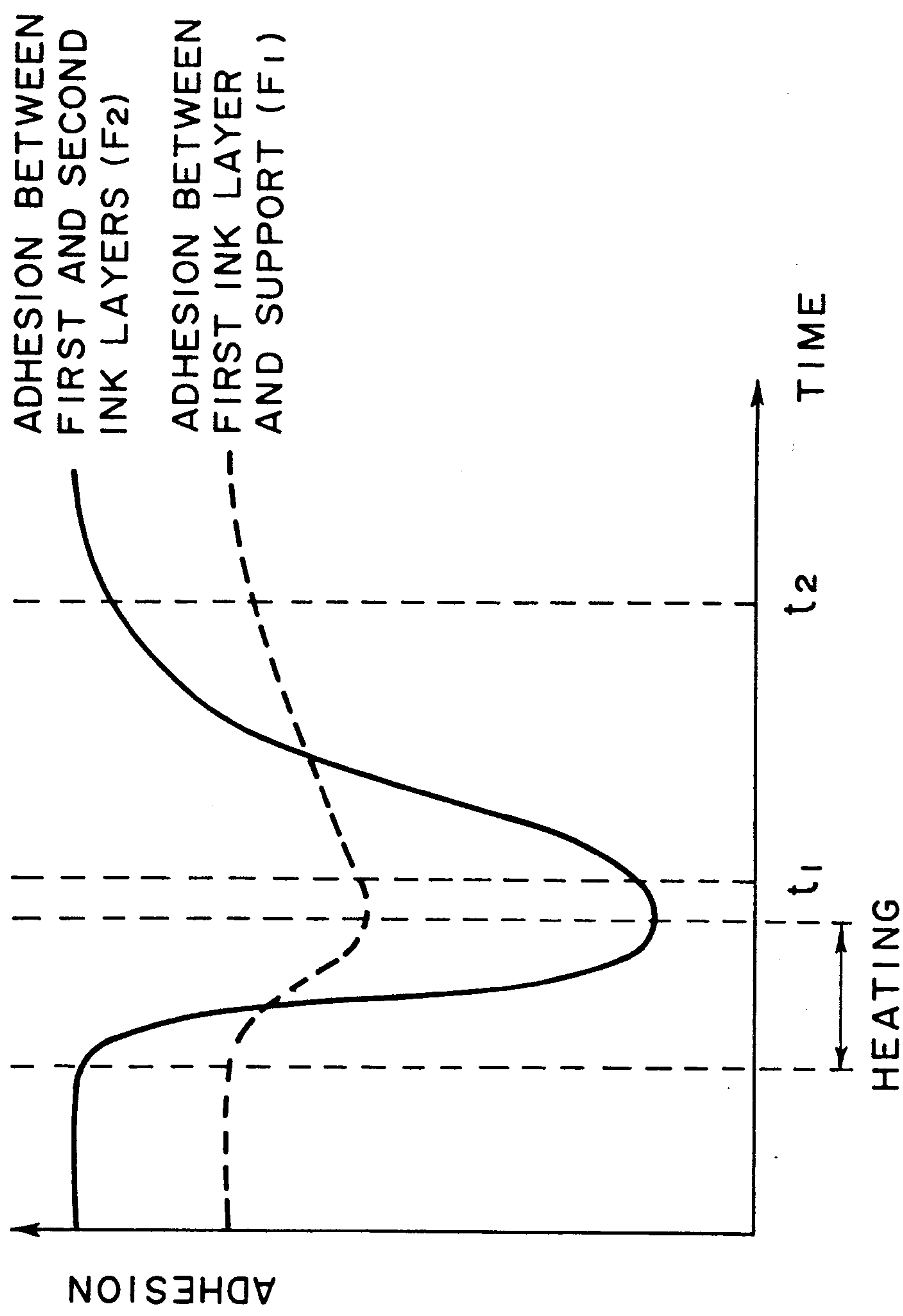
ADHESION BETWEEN FIRST AND SECOND INK LAYERS (F2)
ADHESION BETWEEN FIRST INK LAYER AND SUPPORT (F1)
ADHESION
TIME
t2
t1
HEATING

FIG. 4

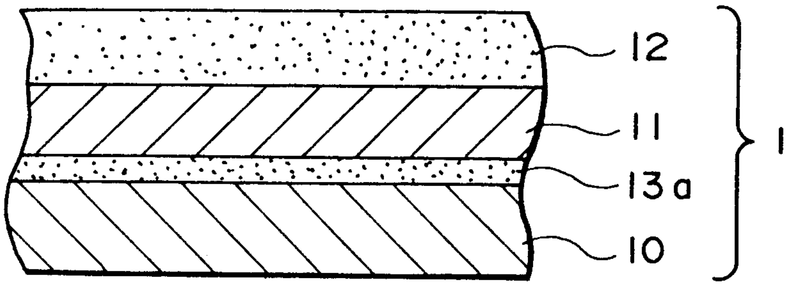

FIG. 5

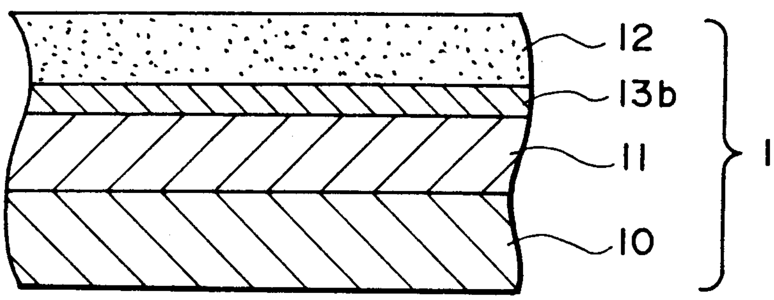

FIG. 6

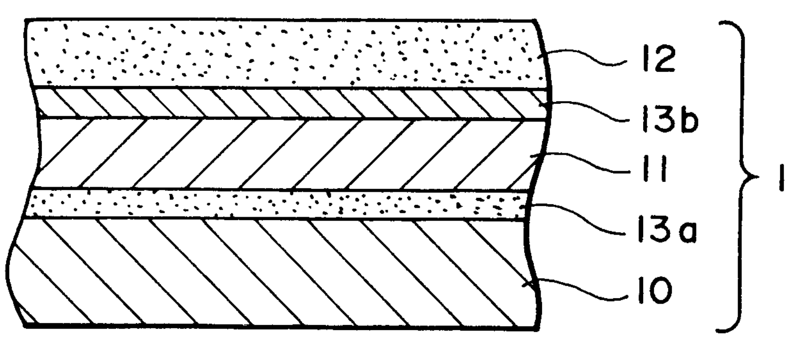

FIG. 7