

Thermal Recording Method, Thermal Recording Medium
Used in the Method and Method for Producing the
Thermal Recording Medium

5 This invention relates to thermal recording, and more specifically, to a thermal recording method using physical changes and enabling stable recording while causing only minimal changes with the passing of time, a thermal recording medium used in the method and a method for
10 producing the recording medium.

 This invention can be effectively applied to printing figures and the like corresponding to the contents of a magnetic recording in a prepaid magnetic card such as a telephone card to enable the magnetically recorded contents
15 to be macroscopically seen.

 Conventionally, there are two methods for recording information on a recording paper by heating the heating element of a thermal head at desired timing intervals according to predetermined recording signals while scanning
20 the thermal head over the recording paper. These methods consist firstly of a heat transcription method in which a desired pattern is transcribed on a normal recording paper by heating and melting the ink of a heat sensitive ink ribbon which is interposed between a thermal head and the
25 recording paper, and secondly, a thermal method in which a thermal recording paper is coloured in a desired pattern.

 Since ink is not applied to a recording paper and the heat sensitive layer of the recording paper itself is coloured in the thermal method, this method is advantageous
30 because the printed record is not affected even when external frictional force is applied to the recording paper after recording. The thermal method is also advantageous because no ink ribbons are necessary.

 However, in the conventional thermal method, since a
35 layer containing a heat sensitive colour former is used as the heat sensitive layer of the recording paper, the heat sensitive layer is coloured due to chemical changes of the

colour former during heating, and therefrom a sufficiently good quality and stability of the printed record is difficult to obtain because the degree of colouring may vary depending on environmental conditions.

5 According to a first aspect of this invention, a thermal recording medium comprises a metallic thin layer, a heat sensitive layer formed on the metallic thin layer and a contrast layer formed on either the heat sensitive layer or the metallic thin layer, the metallic thin layer
10 being made of a low melting point metal or a low melting point alloy having a thickness of 100 to 2000 Å, the heat sensitive layer being able to be melted on heating so that particles from the metallic thin layer can be dispersed therein, the contrast layer being a magnetic recording
15 layer and visually contrasting with the above metallic thin layer.

 According to a second aspect of this invention a method for producing a thermal recording medium according to the first aspect comprises the steps of:

20 forming a wear-resistant layer on a release surface of a transfer member;

 forming the thermal recording medium on the wear-resistant layer; and,

 removing the transfer member.

25 According to a third aspect of this invention, a method for producing a thermal recording medium is characterized in that materials containing minute particles are employed when forming the heat sensitive layer underlying the metallic thin layer so as to form a
30 roughened surface, and subsequently the metallic thin layer is formed on the roughened surface of the heat sensitive layer so as to obtain a roughened surface of the metallic thin layer.

35 According to a fourth aspect of this invention, a thermal recording method is characterized by heating in a desired pattern the heat sensitive layer and the metallic thin layer of the thermal recording medium so as to melt

the heated areas of the metallic thin layer and disperse the molten metallic thin layer as fine particles into the heat sensitive layer thereby destroying it in the desired pattern.

5 The invention will now be described with reference to the accompanying drawings; in which:-

Figs. 1, 4 and 5 are cross-sectional views of the main parts of the thermal recording media of this invention;

10 Figs. 2(a) - (e) and Figs 7(a) - (d) illustrate the production processes for the thermal recording media of this invention;

Fig. 3 is a cross-sectional view illustrating a method for recording in the thermal recording medium of this invention; and,

15 Figs. 6(a) and (b) are plan views illustrating the formation of indications produced by writing visible patterns in the thermal recording medium of this invention.

20 In Fig. 1, a contrast layer 4 is formed on the upper surface of a base 2, a first heat sensitive layer 6 is formed on the contrast layer 4, a metallic thin layer 8 is formed on the heat sensitive layer 6, a second heat sensitive layer 10 is formed on the metallic thin layer 8 and a wear-resistant layer 12 is formed on the heat sensitive layer 10.

25 For the base 2, synthetic paper, sheets of synthetic resins such as polyethylene terephthalates, epoxy resins, polyvinyl chlorides and polycarbonates and similar materials can be used. The base 2 can have a proper shape such as a card-like shape.

30 Any material visually contrasting with the above metallic thin layer 8 can be used as the contrast layer 4. It is preferable that the contrast layer 4 be a dark colour such as black because the metallic thin layer 8 generally has a whitish colour. For example, a material prepared by
35 mixing a pigment or a dye with desired colour into a binder such as a polyester resin, an alkyd resin, a vinyl resin, a polyurethane resin or a mixture of at least two of these

resins can be used to form the contrast layer 4. The thickness of the contrast layer 4 may be 20 μm or less but preferably about 2 - 15 μm .

5 The first and second heat sensitive layers 6 and 10
are provided to improve the writing and recording
characteristics of the metallic thin layer 8 (sensitization
effect) and to disperse and receive fine particles
resulting from melting the material of the metallic thin
layer during the writing process. A material prepared by
10 adding, according to necessity, a wax such as a paraffin
wax, a microcrystalline wax, a synthetic oxidized wax,
montan wax, Fischer-Tropsch wax, a low molecular weight
polyethylene wax, a paraffin wax derivative, a montan wax
derivative or a microcrystalline wax derivative, stearic
15 acid, a stearate or the like used as an additive to reduce
the viscosity of the material to a low melting point
natural resin such as shellac, a rosin or a terpene resin,
a synthetic resin such as a nitrocellulose resin, an
acrylic resin, a polyester resin, a polyvinylchloride
20 resin, a polyvinylidenechloride resin, a vinyl acetate
resin, a polystyrene resin, a polybutyral resin or a
polyolefin resin or a combination of at least two of these
resins used as the main component can be used as a heat
sensitive material for the heat sensitive layers 6 and 10.
25 When the additive used to reduce the viscosity of the heat
sensitive material is in a form of minute particles, the
additive is dispersed in the main component. When the
additive used to reduce the viscosity of the heat sensitive
material is solid, the additive is mixed with the main
30 component either by dissolving the additive in a solvent or
by melting the additive by heating. When the heat
sensitive material is applied as a coating to the metallic
thin layer 8, a solvent for the second heat sensitive layer
10 is chosen which will not damage the metallic thin layer
35 8 and first heat sensitive layer 6. Such a solvent for the
second heat sensitive layer 10 may be selected from among
solvents such as glycol ethers and alcohols. The

thicknesses of the heat sensitive layers 6 and 10 may be 10 μm or less and preferably about 0.5 - 5 μm .

The metallic thin layer 8 covers the contrast layer 4 and is used as a recording film. The metallic materials used to form the metallic thin layer 8 are generally low melting point metals such as Sn, Bi, Se, Te, Zn, Pb, In, and Tl as well as low melting point alloys containing these metals such as Pb-Sn and Bi-Sn. The thickness of the metallic thin layer 8 may be about 100 - 2,000 Å and preferably about 300 - 500 Å.

For the wear-resistant layer 12, heat-resistant materials such as cellulose resins, urethane resins, polyester resins, vinyl resins, epoxy resins and acrylic resins can be used. To such a resin, a phthalic acid ester, an ester of fatty acid, an orthophosphoric acid ester or a similar compound can be added as a plasticizer and a low molecular weight polyethylene, polyamide, stearylamine, a silicone or a similar compound can be added to give smoothness. In addition, when the resin is applied as a coating to the heat sensitive layer 10, a solvent which will not damage the heat sensitive layer 10 and metallic thin layer 8 must be used. The solvent may be selected from among solvents such as glycol ethers and alcohols. The amount of the solvent used can be reduced by employing an ultraviolet-ray-cured resin or an electron-ray-cured resin. An acrylic, epoxy, polyester or similar resin can be used as the ultraviolet-ray-cured resin. The thickness of the wear-resistant layer 12 may be 10 μm or less and preferably about 1 - 5 μm .

The production processes for such a thermal recording medium will now be described.

As shown in Fig. 2(a), a contrast layer 4 is formed on the surface of a white polyethylene terephthalate film 2 with 188 μm thickness. The contrast layer is formed by

Carbon black	4 pwt
Vinylchloride acetate resin	16 pwt
Methyl ethyl ketone	40 pwt

Toluene

40 pwt

mixing and dispersing the above components using a ball mill for six hours to prepare a black coating and then applying the coating to the white polyethylene terephthalate film 2 using a bar coater #20 prior to drying the applied coating. The dry thickness of the contrast layer 4 is 5 μm .

Next, as shown in Fig. 2(b), a heat sensitive layer 6 with 2 μm thickness is formed on the contrast layer 4. The heat sensitive layer 6 is formed by

Transparent dried white lac resin 20 pwt

Ethanol 80 pwt

preparing a coating of the above composition and then applying the coating to the contrast layer 4 using a bar coater #14 prior to air-drying the applied coating.

Next, as shown in Fig. 2(c), an Sn thin layer 8 with 400 $\text{\AA}$ thickness is formed on the heat sensitive layer 6 at a rate of 5 $\text{\AA}/\text{sec}$. by vacuum evaporation coating under a reduced pressure of 5×10^{-5} Torr.

Next, as shown in Fig. 2(d), a heat sensitive layer 10 with 2 μm thickness is formed on the Sn thin layer 8 in the same manner as in the above process of Fig. 2(b).

Next, as shown in Fig. 2(e), a wear-resistant layer 12 with 1 μm thickness is formed on the heat sensitive layer 10. The wear-resistant layer is formed by applying a thermosetting polyester resin coating containing a glycol ether as the solvent (1836T-N; manufactured by Fujikura Kasei Co., Ltd.) to the heat sensitive layer 10 using a bar coater #7 and then heating the applied coating at 80°C for 30 minutes.

The heat sensitive layer 6 may be formed by

Ethylene-vinyl acetate copolymer 8 pwt
(Content of vinyl acetate, 55 wt%)

Hydrogenated terpene resin 8 pwt
Fischer-Tropsch wax 4 pwt
Toluene 80 pwt

applying a coating prepared by mixing the above components to the contrast layer 4 using a bar coater #14 and then air-drying the applied coating.

5 In addition, the heat sensitive layer 6 may be formed by

Vinylidene chloride resin	20 pwt
Methyl ethyl ketone	20 pwt
Toluene	20 pwt
Cyclohexanone	40 pwt

10 using a coating prepared by mixing the above components and the above heat sensitive layer 10 may be formed by

Vinyl acetate resin	20 pwt
Methanol	80 pwt

using a coating prepared by mixing the above components.

15 The surface of the heat sensitive layer 6 can be roughened by mixing a low molecular weight polyethylene powder into the coating during the formation of the heat sensitive layer 6. That is to say, when the heat sensitive layer 6 has been roughened, a metallic thin layer 8 is also

20 easily roughened during its formation in the following process and as a result, diffuse reflection by the metallic thin layer is increased, homogeneous white is obtained, the contract between the metallic thin layer 8 and the contrast layer 4 is further improved and visible patterns can be

25 easily seen macroscopically. For this purpose, the surface roughness (R_a in JIS B 0601) of the metallic thin layer 8 may be $0.1 \sim 2.0 \mu\text{m}$ and preferably $0.3 \sim 1.0 \mu\text{m}$. A polyimide resin powder, a low molecular weight tetrafluorethylene resin powder, calcium stearate, tin

30 stearate, a polystyrene latex, bentonite, wollastonite, talc, aluminium silicate, sericite, kaolin, clay, white carbon, calcium carbonate, chalk, slaked lime, dolomite powder, magnesium carbonate, barium sulfate or a similar substance can also be used as minute particles for

35 roughening the heat sensitive layer 6. The mean particle size of the minute particles may be $0.3 \sim 10 \mu\text{m}$ for example and preferably $0.6 \sim 5.0 \mu\text{m}$. Fifty parts by weight or

less, but preferably 20 parts by weight or less of the minute particles are used for 100 parts by weight of the resin.

5 A method of recording in the thermal recording medium of this example will now be described.

As shown in Fig. 3, when a thermal head H is scanned over the wear-resistant layer 12 in the direction indicated by the arrow while making the thermal head H touch the layer 12 and the heating element of the head H is heated at the desired time intervals, the heat sensitive layers 6 and 10 and the metallic thin layer 8 are melted by the heating and fine particles resulting from the melting of metallic thin layer 8 are dispersed in the molten heat sensitive layers 6 and 10 due to the effect of surface tension. In the portion where the material of the metallic thin layer 8 has been dispersed as fine particles, the metallic thin layer 8 is destroyed and the heat sensitive layers 6 and 8 containing the dispersed fine particles solidify after the head H has passed over the portion thereby producing a fixed record. The portion not having been heated by the heating of the above head H exhibits a whitish colour because the metallic thin layer 8 remains intact, while the portion having been heated by the heating of the above head H exhibits the blackish colour of the contrast layer 4. Therefore, a visible pattern (information) is formed in a sufficient contrast. Although the dispersed fine particles exist in the heat sensitive layers 6 and 10 of the portion where the metallic thin layer 8 has been destroyed, macroscopic observation of the contrast layer 4 is not hindered because the amount of dispersed fine particles is small.

Although the thermal head H is used as a means of heating in the above example, any other suitable means for supplying heat equal to that supplied by the thermal head H and capable of similarly destroying the metallic thin layer 8 can be used in this invention.

Although, as is preferred, the metallic thin layer 8 is interposed between the two heat sensitive layers 6 and 10 in the above example because the material of the metallic thin layer 8 heated by the thermal head H is very favourably dispersed as fine particles, the effect is also obtained even when one of the heat sensitive layers 6 and 10 is omitted.

In this invention, a magnetic recording layer can be used as the contrast layer 4 and a card-like thermal recording medium with a given shape can be obtained by punching.

For the magnetic recording layer, those conventionally used as a magnetic recording layer in a magnetic recording medium can be used. For example, Ba-ferrite, Sr-ferrite, Co-coated γ -Fe₂O₃, γ -Fe₂O₃, needle-like iron powder or CrO₂ with particle size of 10 μ m or less, preferably 0.01 ~ 5 μ m, can be used as a magnetic material and a commonly used polyester, alkyd, vinyl or polyurethane resin or a mixture of at least two of these resins can be used as a binder resin. A suitable ratio of the binder resin to the magnetic material is set by considering adhesiveness to the base, paint film strength, voltage detected by a magnetic head, and the like. The ratio by weight of the binder resin to the magnetic material may be in the range of 1/1 ~ 1/10, preferably 1/2 ~ 1/8. A typical thickness of the magnetic recording layer is about 10 ~ 15 μ m.

Such a card-like thermal recording medium also functioning as a magnetic recording medium as mentioned above can be used as a prepaid card. In such cases, thermal recording is effectively applied to printing records of card usage (dates and charges) and the particulars of the remainder. Specifically, the remainder sum recorded in the magnetic recording layer of a prepaid card is revised every time it is used and the details are printed in the surface of the card by thermal recording which enables the user to know the remaining contents of the card.

It is preferably that the total thickness of the heat sensitive layer 6, the metallic thin layer 8, the heat sensitive layer 10 and the wear-resistant layer 12 be 10 μm or less in order to avoid a large distance between a magnetic head and the magnetic recording layer so that the thermal recording medium functions efficiently.

In addition, in this invention, it is also possible to use a heat sensitive layer formed between the metallic thin layer and the base as a contrast layer by making the colour of the heat sensitive layer in a visual contrast with the metallic thin layer. In such cases, the contrast layer can be omitted.

Figs. 4 and 5 are cross-sectional views of the main parts of examples of the thermal recording medium of this invention. In these drawings, the same members as those shown in Fig. 1 are represented by the same symbols.

In the example shown in Fig. 4, a desired design 14 is printed on the surface of the base 2 opposite to the contrast layer 4, and a desired design 16 is also printed on the wear-resistant layer 12. The design 16 and visible patterns produced by the thermal recording may synergistically form desired indications.

In the example shown in Fig. 5, a desired design 14 is printed on the surface of the base 2 opposite the contrast layer 4 and the design 14 is covered by an over coat layer 18. A desired design 20 is printed on the metallic thin layer 8 and the heat sensitive layer 10 is formed over the design 20. In addition, a desired design 22 is printed on the heat sensitive layer 10 and the wear-resistant layer 12 is formed over the design 22. The designs 20 and 22 have the same effect as the above design 16.

Figs. 6(a) and (b) are plan views illustrating how indications are formed by writing visible patterns in a magnetic card wherein a magnetic recording layer is used as the contrast layer which is an example of the thermal recording medium of this invention.

Fig. 6(a) is an unused magnetic card on the surface of which "DATE" 16a, "CHARGE" 16b, "REMAINDER" 16c and lines 16d are previously formed as the above printed design 16.

5 Fig. 6(b) indicates a used magnetic card wherein the date of use 30a, the charge 30b and the remainder sum 30c are recorded in given positions corresponding to the above printed designs 16a, 16b and 16c by such visible pattern writing as described with reference to Fig. 3.

10 Figs. 7(a) - (d) indicate another example of the production processes for the thermal recording medium of this invention.

As shown in Fig. 7(a), a transfer sheet 24 one surface (lower surface) of which is a release surface is prepared.

15 Next, as shown in Fig. 7(b), a wear-resistant layer 12, a heat sensitive layer 10, metallic thin layer 8, a heat sensitive layer 6 and a contrast layer 4 are formed in this order on the release surface of said transfer sheet.

20 Next, as shown in Fig. 7(c), a base 2 is bonded to the contrast layer 4 by using an adhesive. The symbol 26 represents an adhesive layer.

Next, as shown in Fig. 7(d), the transfer sheet 24 is removed to obtain a thermal recording medium of the same structure shown in Fig. 1.

25 According to the thermal recording of this invention mentioned above, since visible information can be recorded as a contrast between the metallic thin layer and the contrast layer by partially physically destroying the metallic thin layer according to a desired recording pattern, a good quality printed record can be realized and
30 the stability of recording is also excellent.

CLAIMS

1. A thermal recording medium comprising a metallic thin layer, a heat sensitive layer formed on the metallic thin layer and a contrast layer formed on either the heat sensitive layer or the metallic thin layer, the metallic thin layer being made of a low melting point metal or a low melting point alloy having a thickness of 100 to 2000 Å, the heat sensitive layer being able to be melted on heating so that particles from the metallic thin layer can be dispersed therein, and the contrast layer being a magnetic recording layer and visually contrasting with the above metallic thin layer.
2. A thermal recording medium according to claim 1, wherein the contrast layer is formed on a base.
3. A thermal recording medium according to claims 1 or 2, wherein heat sensitive layers are formed on both surfaces of the metallic thin layer.
4. A thermal recording medium according to any preceding claim when dependent on claim 2, wherein a wear-resistant layer is formed on the surface of the thermal recording medium remote from the base.
5. A thermal recording medium according to any preceding claim, wherein the heat sensitive layer contains particles for forming a roughened surface on which the metallic thin layer is deposited.
6. A method for producing a thermal recording medium according to claim 4, comprising the steps of:
- forming the wear-resistant layer on a release surface of a transfer member;
 - forming the thermal recording medium on the wear-resistant layer; and,
 - removing the transfer member.
7. A method for producing a thermal recording medium according to claim 1, wherein materials containing particles are employed when forming the heat sensitive layer underlying the metallic thin layer so as to form a



roughened surface, and subsequently the metallic thin layer is formed on the roughened surface of the heat sensitive layer so as to obtain a roughened surface of the metallic thin layer.

5 8. A thermal recording method which is characterized by heating in a desired pattern the heat sensitive layer and the metallic thin layer of the thermal recording medium according to claim 1, so as to melt the heated areas of the metallic thin layer and disperse the molten metallic thin
10 layer as fine particles into the heat sensitive layer thereby destroying it in the desired pattern.

9. A thermal recording method according to claim 8, wherein the heat sensitive layer and the metallic thin layer are heated by a thermal head touching the thermal
15 recording medium.

